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Laboratory Measurements of Contaminant Attenuation of Uranium Mill Tailings Leachates by Sediments and Clay Liners

Prepared by R. J. Serne, S. R. Peterson, G. W. Gee

Pacific Northwest Laboratory
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Prepared by
R. J. Serne, S. R. Peterson, G. W. Gee

Pacific Northwest Laboratory
Richland, WA 99352

Prepared for
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Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555
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PREVIOUS DOCUMENTS IN SERIES

This progress report is the sixth NUREG document prepared for this project, Assessment of Leachate Movement from Uranium Mill Tailings (FIN B2292). The project has two thrust areas, laboratory determination of contaminant retardation in sediments and clay liners and computer model development/simulation of water movement and contaminant migration. The project was initiated in April 1979. Other NUREG reports from this project are:

NUREG/CR-1494, "Interaction of Uranium Mill Tailings Leachate with Soils and Clay Liners: Laboratory Analysis/Progress Report," G. W. Gee, A. C. Campbell, D. R. Sherwood, R. G. Strickert and S. J. Phillips, June 1980.

NUREG/CR-1495, "Model Assessment of Alternatives for Reducing Seepage from Buried Uranium Mill Tailings at the Morton Ranch Site in Central Wyoming," R. W. Nelson, A. E. Reisenauer and G. W. Gee, June 1980.

NUREG/CR-2360, "TRUST: A Computer Program for Variably Saturated Flow in Multidimensional Deformable Media," A. E. Reisenauer, K. T. Key, T. N. Narasimhan and R. W. Nelson, January 1982.

NUREG/CR-2845, "DIGRD: An Interactive Grid Generating Program," H. P. Foote, W. A. Rice and C. T. Kincaid, October 1982.

NUREG/CR-2946, "The Long Term Stability of Earthen Materials in Contact with Acidic Tailings Solutions," S. R. Peterson, R. L. Erikson and G. W. Gee, November 1982.

ABSTRACT

We discuss FY82 progress on the development of laboratory tools to aid in the prediction of migration potential of contaminants present in acidic uranium mill tailings leachate. Further, empirical data on trace metal and radio-nuclide migration through a clay liner are presented.

Acidic uranium mill tailings solution from a Wyoming mill was percolated through a composite sediment called Morton Ranch Clay liner. These laboratory columns and subsequent sediment extraction data show: 1) As, Cr, Pb, Ag, Th and V migrate very slowly; 2) U, Cd, Ni, Zn, Fe, Mn and similar transition metals are initially immobilized during acid neutralization but later are remobilized as the tailings solution exhausts the clay liner's acid buffering capacity. Such metals remain immobilized as long as the effluent pH remains above a pH value of 4 to 4.5 but they become mobile once the effluent pH drops below this range; and 3) fractions of the Se and Mo present in the influent tailings solution are very mobile.

Possible controlling mechanisms for the pH dependent immobilization-mobilization of the trace metals are discussed. More study is required to understand the controlling mechanisms for Se and Mo and Ra for which data were not successfully collected.

Using several column lengths (from 4.5 to 65 cm) and pore volume residence times (from 0.8 to 40 days) we found no significant differences in contaminant migration rates or types and extent of controlling processes. Thus, we conclude that the laboratory results may be capable of extrapolation to actual disposal site conditions.

CONTENTS

PREVIOUS DOCUMENTS IN SERIES.....	ii
ABSTRACT.....	iii
CONTENTS.....	v
ACKNOWLEDGMENTS.....	xi
EXECUTIVE SUMMARY AND CONCLUSIONS.....	1
INTRODUCTION.....	6
METHODS AND MATERIALS.....	8
SOLUTIONS.....	8
SEDIMENT ANALYSES.....	10
PERMEABILITY COLUMN EXPERIMENTS.....	11
VACUUM (MECHANICAL) EXTRACTOR EXPERIMENTS.....	11
RADIOTRACING OF ACIDIC MILL TAILINGS SOLUTION.....	15
DISSECTION OF COLUMNS.....	21
SEMI-SELECTIVE EXTRACTION PROCEDURE.....	23
RESULTS AND DISCUSSION.....	27
SOLUTION ANALYSES.....	27
SEDIMENT ANALYSES.....	28
PERMEABILITY COLUMN CELLS.....	28
pH AND CONTAMINANT BREAKTHROUGHS FROM PERMEABILITY AND VACUUM EXTRACTION.....	30
Aluminum.....	34
Iron.....	37
Uranium.....	40
Calcium.....	40
Sulfate.....	41

Other Elements.....	43
RADIOTRACER RESULTS IN VACUUM EXTRACTOR COLUMN EXPERIMENTS.....	49
RADIOTRACER DISTRIBUTIONS RETAINED IN THE VACUUM EXTRACTOR SEDIMENTS.....	52
SELECTIVE EXTRACTION RESULTS - STABLE ELEMENTS.....	60
SELECTIVE EXTRACTION RESULTS - RADIONUCLIDES.....	66
SUMMARY.....	69
FUTURE STUDIES.....	76
REFERENCES.....	77
APPENDIX A - COMPARISON OF ICP AND AA/GF RESULTS ON ACIDIC URANIUM TAILINGS SOLUTIONS AND COLUMN EFFLUENTS.....	A.1
APPENDIX B - CHEMICAL COMPOSITION OF COLUMN EFFLUENTS.....	B.1
APPENDIX C - RADIONUCLIDE DISTRIBUTION RETAINED ON THE SEDIMENTS.....	C.1
APPENDIX D - SEMI-SELECTIVE EXTRACTION DATA.....	D.1
DISTRIBUTION LIST.....	Distr-1

FIGURES

1	Schematic of Syringe System	14
2	Diagram of System 1 Column Effluents Which Became the Influent for Succeeding Columns.....	16
3	Diagram of System 2 Column Effluents Which Became the Influent for Succeeding Columns for Columns Leached with Radiotracer Solution 2.....	17
4	pH Versus Pore Volume for Permeability Cell.....	31
5	pH Versus Pore Volume for Vacuum Extractor Columns.....	32
6	Relative Concentration (C/Co) of Al Versus Cumulative Pore Volume of Effluent for Columns 1-6 and Permeability Cell 5.....	35
7	Concentration (mg/l) of Al Versus pH for Columns 1-6 and Permeability Cell 5.....	36
8	Relative Concentration (C/Co) of Fe Versus Cumulative Pore Volumes for Columns 1-6 and Permeability Cell.....	38
9	Concentration (mg/l) of Fe Versus pH for Columns 1-6 and Permeability Cell 5.....	39
10	Relative Concentration (C/Co) of U Versus Cumulative Pore Volumes for Columns 1-6 and Permeability Cell 5.....	41
11	Concentration (mg/l) of U Versus pH for Columns 1-6 and Permeability Cell 5.....	42
12	Relative Concentrations of Ca (C/Co) Versus Cumulative pore Volumes for Column 1-6, 8-12, 15-18, 19-21, 22-23, 24 and Permeability Cell 5.....	43
13	Concentrations of Ca (mg/l) Versus pH for Columns 1-6, 8-12, 15-18, 19-21, 22-23, 24 and Permeability Cell 5.....	44
14	Relative Concentrations of SO ₄ (C/Co) Versus Cumulative Pore Volumes for Columns 1-6 and Permeability Cell 5.....	45
15	Concentrations of SO ₄ (mg/l) Versus pH for Columns 1-6 and Permeability Cell 5.....	46
16	Relative Concentrations of Cd (C/Co) Versus Cumulative Pore Volume for Selected Vacuum Extractor Columns.....	47

17	Concentration of Cd (mg/l) Versus pH for Selected Vacuum Extractor Columns.....	48
18	Distribution of ⁷³ As, ⁵¹ Cr, ⁵⁹ Fe and ⁵⁴ Mn Retained in Morton Ranch Clay Liner.....	54
19	Distribution of ^{110m} Ag, ⁷⁹ Se, ¹⁰⁹ Cd and ²²⁸ Ra Retained in Morton Ranch Clay Liner.....	55
20	Distribution of ²¹⁰ Pb Retained in Morton Ranch Clay Liner.....	56

TABLES

1	Details on Radioisotope Counting.....	10
2	Composition of Various Highland Mill Tailing Solutions Used in Laboratory Experiments, mg/l.....	12
3	Physical and Chemical Characteristics of the Morton Ranch Clay Liner Material.....	13
4	Details on Highland Mills Tailings Solution #2-1.....	18
5	Solution Changes Due to Spiking H.M. #2-1.....	19
6	Details on Highland Mills Tailings Solution #2 (H.M. #2-2).....	20
7	Dissolution Scheme for Each Column.....	22
8	Samples on Which Semi-Selective Extraction of the Geochemical Phases were Performed (Vacuum Extractor System 1).....	24
9	Samples on Which Semi-Selective Extraction of the Geochemical Phases were Performed (Vacuum Extractor System 2).....	25
10	Extractants, Conditions Under which the Extractions were Performed and Geochemical Phases Extracted.....	26
11	Preferred Analytical Techniques for Selected Constituents for Acid Uranium Mill Tailings Related Solutions.....	29
12	Sample Volume Requirements to Perform Chemical Analysis (ml).....	30
13	Relative Concentration (C/Co) Data for Ratiotracers Compared with the Total Elemental Concentration Ratios.....	50

14	Percent Radionuclide Retained Versus Depth for Composite Vacuum Extractor Columns.....	53
15	R and K_d Values for Radiotracers Used in the Vacuum Extractor Experiments.....	59
16	Summary of Migration Potential.....	75
A.1	Comparison of ICP Versus AA/GF Analyses for Selected Solutions; Concentrations are in mg/l.....	A.1
B.1	Chemical Analyses of Effluent Solutions from Permeability Column 5 (mg/l).....	B.1
B.2	Chemical Composition of Vacuum Extractor Columns 1-6 Effluents (mg/l) at Selected Pore Volumes.....	B.2
B.3	Chemical Composition of Vacuum Extractor Columns 8-12 Effluent (mg/l) at Selected Cumulative Pore Volumes.....	B.3
B.4	Chemical Composition of Vacuum Extractor Columns 15-18 Effluent (mg/l) at Selected Cumulative Pore Volumes.....	B.4
B.5	Chemical Composition of Vacuum Extractor Columns 19-21 Effluent (mg/l) at Selected Cumulative Pore Volumes.....	B.5
B.6	Chemical Composition of Vacuum Extractor Columns 22-23 Effluent (mg/l) at Selected Cumulative Pore Volumes.....	B.6
B.7	Chemical Composition of Vacuum Extractor Column 24 Effluent (mg/l) at Selected Cumulative Pore Volumes.....	B.7
B.8	Chemical Composition of Vacuum Extractor Columns 7, 13 and 14 Effluent at Selected Cumulative Pore Volumes.....	B.8
C.1	Radionuclide Distribution in Vacuum Extractor Column Sediments at End of Experiment.....	C.1
C.2	Radionuclide Distribution in Vacuum Extractor Column Sediments at End of Experiment.....	C.2
D.1	Volume of Extractant and Weight Data Actually Used in Semi-Selective Extraction Scheme.....	D.1
D.2	ICP Analyses of Extract Solutions from Vacuum Extractor Columns Shown in Figure 2.....	D.2
D.3	ICP Analyses of Extract Solutions from Vacuum Extractor Columns Shown in Figure 3.....	D.3

D.4	ICP Analyses of Extract Solutions from Original Morton Ranch Clay Liner.....	D.4
D.5	XRF Analyses of Vacuum Extractor System 1 Sediments Before and After Selective Extraction.....	D.5
D.6	XRF Analyses of Vacuum Extractor System 2 and Original Morton Ranch Clay Liner Sediments Before and After Selective Extraction.....	D.6
D.7	Student's t-Statistics on Difference Between Original and Residual Sediment Content Vacuum Extractor System 1.....	D.9
D.8	Student's t-Statistics on Difference Between Original and Residual Sediment Content of Vacuum Extractor System 2.....	D.11
D.9	Radiocounting Data for Extract Solutions from Vacuum Extractor System 1.....	D.13
D.10	Radionuclide Data for Extract Solutions from Vacuum Extractor System 2.....	D.14
D.11	Radiocounting Data for Sediments from Vacuum Extractor System 1 and 2.....	D.15

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EXECUTIVE SUMMARY AND CONCLUSIONS

Acidic uranium mill tailings leachate or seepage is potentially hazardous especially at sites where wastes are disposed in impoundments with high permeability, low acid-buffering capacities or with short pathlengths to the water table. To develop experimental and modeling tools to predict the long-term environmental impact of leachate movement this project was initiated by the Nuclear Regulatory Commission in 1979. This report is the sixth NUREG document from the project and presents FY82 progress on laboratory experimentation to understand contaminant attenuation processes.

Our main goal in the work reported was to gain qualitative or semi-quantitative data on the migration rates of potentially hazardous trace metals and radionuclides such as arsenic, cadmium, chromium, molybdenum, lead, radium, selenium, silver, thorium and vanadium.

Several types of experiments and numerous analyses of solutions and sediments were performed to increase our understanding of contaminant migration. We performed two types of column experiments wherein acidic uranium mill tailings solution (from Exxon Highland Mill in Wyoming) was percolated through Morton Ranch clay liner material (a composite sandstone, siltstone, mudstone and shale from Morton Ranch uranium mine in Wyoming).

In one experiment the clay liner was packed in columns 5 cm diameter by 4.5 cm length and acidic tailings solution was slowly percolated at constant head for up to 3 years (average pore volume residence time was 40-60 days). The second column method consisted of forcing acidic mill tailings through a suite of columns 2.6 cm in diameter by 10.8 cm long at a rate of 1 pore volume per 18 hours. The effluents were then subsampled for analysis and the bulk of the volume passed through additional columns. This serial operation was continued for six tiers in one experiment (65 cm total length) and three tiers (32.5 cm) in a second. The second column experiments had numerous radiotracers added to the acidic tailings solution to increase analysis sensitivity and to allow the tailings seepage borne contaminants to be distinguished from the total present (tailings solution plus original clay liner). Column effluent subsamples were collected and completely analyzed for chemical composition. The clay liner prior to use and after contact with up to 16 pore volumes of acidic tailings solution was characterized for total chemical content versus depth in the column. Finally, the sediments were extracted with various chemical reagents that provide insight into the relative strength that binds the contaminants and with what geochemical phases the contaminants are associated.

These three data types (column effluent, nuclide distributions bound to sediment versus depth and selective extraction) from slightly different approaches were combined to allow us a comprehensive tool to judge the relative migration rates of the contaminants and to provide insight into the processes that bind the contaminants. Such knowledge is a necessary first step in our long range objective, to develop quantitative (mathematical) relationships to be used in computer codes (transport models) to predict contaminant migration.

Further, the use of the two column methods allows us to address whether kinetic effects (a concern with any short lived laboratory experiment) or pathlength scaling effects are significantly affecting results and thus minimizing the applicability to actual field conditions. The results of the various laboratory experiments described in the main text allow us to make the following conclusions for the particular clay liner sediment and the particular acidic uranium mill tailings solution used.

Arsenic and chromium present in the acid tailings solution (between 0.5 and 3.5 mg/l well above EPA drinking water standards of 0.05 mg/l) readily becomes bound to the clay liner. Both radiotracer and total arsenic analyses support the finding that arsenic does not seem to remobilize after the neutralizing capacity of the clay liner is exhausted. Arsenic extraction data suggest that sediment bound arsenic like chromium and selenium is bound to amorphous and crystalline iron and perhaps aluminum oxides. We speculate that the controlling process is anion attraction/exchange of the arsenic, chromium and selenium partially present as anions in the solution. At low pH values the hydrous oxides are protonated $(Al, Fe)-(OH)_2^{4-x}$ such that a net positive surface charge is present to which anions are attracted. A second immobilization process could be precipitation of ferric arsenates and selenites both very insoluble compounds.

Relatively speaking arsenic is bound more firmly than chromium and selenium. The residual sediments after chemical extraction with five progressively harsher reagents contained 22% by weight of the originally bound arsenic and <15% of the chromium. Although the residual sediments contained 50% by weight of the originally bound selenium there is a very mobile form present as evidenced by high selenium concentrations in the first samples of column effluent and detectable Se radiotracer throughout the contacted clay liner at all depths even though the majority of selenium tracer is bound in the top of the column. The selenium data suggest that perhaps several species may be present with at least one being mobile and apparently slow to interconvert to more easily attenuated forms. Computer speciation modeling shows selenate (SeO_4^{2-}) will predominate in these solutions and perhaps is the mobile form of selenium. We suggest that the data show arsenic and chromium do not readily remobilize after the acid tailings exhausts the clay liner's neutralizing capacity and that a relatively mobile and somewhat pH independent selenium species exists.

Total molybdenum results show high molybdenum effluent concentrations occur in the first solution emanating from the columns but little molybdenum in subsequent effluents. More work is needed to identify the forms and processes by which molybdenum and selenium migrate and we expect the next document in this series on geochemical modeling (due June 1983) to provide additional insight. Neutralization studies of acidic tailings solutions with various reagents such as calcium carbonate (limestone), hydrated lime $[Ca(OH)_2]$, sodium hydroxide and sodium carbonate also show that molybdenum and selenium are not readily removed from solution and thus warrant further attention (see Sherwood and Serne 1982).

Silver is present in the acidic tailings solution at less than detectable concentrations (<0.05 mg/l) but by using the radiotracer ^{110m}Ag we found that silver is rapidly retained in the upper 10% of the clay liner when acidic solution is percolated through the liner. The radiosilver that is bound in the sediments appears to be either bound strongly (on a weight basis 50% of the bound silver is not extractable) or associated with cation exchange sites. It appears that the silver migrates very slowly through the clay liner even after the neutralization capacity has been exhausted. Detectable silver (tracer or stable element) was not observed in any column effluent solutions.

Although little data are available on vanadium it does not appear to be very mobile. We saw no measureable vanadium in column effluents and the total vanadium concentration bound in the column after solution percolation shows elevated concentrations in only the top half. Although we have no selective extraction data by chemical analogy we speculate that anionic vanadium VO_4^{3-} may be bound in a similar fashion as arsenic and chromium or that the low solubility uranium-vanadium mineral tyuymunite may be controlling the solution concentration of vanadium. Again the upcoming modeling report should provide insight.

The data available in this work for transition metals such as cadmium, cobalt, nickel, zinc and copper allow us to conclude that they are immobilized by the sediment during the neutralization process and remobilized as the acid front travels through the column upon exhaustion of the sediment's buffering capacity. The bound transition metals are associated with amorphous and crystalline hydrous oxides especially under neutral pH conditions and partly with cation exchange sites [especially under more acidic pH (3-4.5) conditions]. All these trace metals show very low column effluent concentrations while the pH is near neutral and relatively high concentrations as the pH front (pH ~4) arrives at the column effluent. Concentration of these metals at this point typically exceed the acid tailings solution concentration suggesting redissolution of previously bound metals is occurring. The pH front redissolution process is thus similar to a snow plow that collects large quantities of snow in front of its blade. The data further suggest that a quantitative description of the chemical interactions will require not only expressions for the pH dependent immobilization on hydrous oxides (perhaps via thermodynamic solubility relationships) but also retardation by retention on ion exchange sites. Uranium data do not show the snow plow effect but are pH sensitive in that increased solution uranium values occur once the pH front breaks through. Further the total uranium distribution bound in the sediment at the end of the experiment shows a peak concentration just on the acidic side of the pH front. A similar uranium peak was observed in the field under a tailings solution evaporation pond (Peterson et al. 1982 and Erikson and Sherwood 1982).

Lead data show that it is retained by sediments more strongly than the other transition metals and associates much less with cation exchange sites. No detectable total lead nor ^{210}Pb was found in column effluents. Again chemical extraction results show that much of the bound lead is associated with hydrous oxides of iron and aluminum. Although data were not obtained on ^{230}Th

we speculate that it will behave very similarly to lead and not migrate very far into the sediment. Sherwood and Serne (1982) found thorium readily removed by all neutralizing agents used.

Manganese, iron and aluminum column effluent data support the importance of hydrous oxide formation upon acid tailings solution neutralization as a major process lowering their solution concentration. Based on selective extraction results cation exchange may play an even greater role than pH neutralization for manganese. Cation exchange especially in the more acidic top portions of the columns is also important for aluminum and iron. Maximum manganese concentrations in the sediment occur just at the leading edge of the pH front breakthrough. Again, these data point out the need to combine the precipitation/dissolution of pH sensitive hydrous oxides with cation exchange relationships to best describe mass transport of the metals. Ongoing computer modeling work that considers only the former process will be reported soon at which point we should be able to assess better the importance of including cation-exchange in predicting the migration of metals in acidic U mill tailings solutions percolating through sediments.

Other data are presented that corroborate the cause of the residual buffering capacity discussed by Peterson et al. (1982) and Relyea and Martin (1982) and the importance of gypsum formation on the fate of calcium and sulfate. Unfortunately data for radium were not reliable and do not allow us to speculate on its fate. Future laboratory studies will give special attention to determining radium migration potentials.

A comparison of the data from the different column sizes (4.5 cm versus up to 65 cm) and different residence times per pore volume (40 days versus 0.75 days) shows favorable agreement. We thus feel that the laboratory data and tools are applicable and useful for predicting the fate of contaminants at actual uranium mill disposal sites.

High-acid high-salt tailings solutions present significant analytical problems for metals analysis so we directed our preliminary efforts towards determination of recommended techniques and practical detection limits. For metals analysis we determined that dilution of the tailings and column effluent solutions was required to reduce spectral, physical and non-specific absorption interferences to acceptable ranges to allow accurate results. The dilution procedure directly increased detection limits for most trace metals to the range 10-50 parts per billion. Thus, for routine analysis of large numbers of samples practical detection limits for most trace metals are at or slightly exceed recommended drinking water maximum concentration levels. In general, the trace metals concentrations of the acidic U mill tailings solutions are present in the low parts per million range and thus readily measured. Notable exceptions include Ba and Pb which are present at <50 part per billion. In general, the neutralized effluents emanating from the sediment columns show trace metal concentrations at or below the practical detection limits (10-50 ppb). Notable exceptions in the initial effluents include Se and Mo and perhaps Zn.

Ion chromatography is capable of detecting sulfate, chloride, fluoride, nitrate and bromide down to the low parts per million in the acid tailings solution and sediment contacted effluents. Sulfate predominates (2,000 to 20,000 ppm) in the solutions and chloride is present at 100-300 ppm concentrations. Nitrate varies from the low ppm's to 500 ppm, fluoride from less than detectable to 10 ppm and Br is usually not detectable (<0.5 ppm). Recommended analytical techniques, practical detection limits for macro cations, metals and anions and trace metals are given in Table 11 to guide future solution analysis.

In summary, the empirical trace contaminant data suggest that:

- arsenic, chromium, lead, silver, thorium and vanadium are readily immobilized by the clay liner and not released after acid conditions prevail
- cadmium, iron, manganese, nickel, zinc, similar trace metals and uranium are immobilized by the clay liner as long as the solution pH is not driven below pH 4.5 by continual acid solution attack
- portions of selenium and molybdenum are very mobile and travel with the same velocity as the water
- laboratory results are capable of being extrapolated to actual field disposal conditions.

Further probable controlling mechanisms such as hydrous oxide precipitation, element-specific low-solubility compound formation, anion exchange on protonated hydrous oxide surfaces and cation exchange on the clay liner surfaces are identified.

Recommendations for additional investigation include:

- geochemical modeling exercises to further refine the importance of the probable controlling mechanisms
- additional laboratory work on a lower valued cation exchange capacity material
- additional experimentation to successfully determine radium migration potential
- refinement of the selective extraction methods to allow adequate mass balance determinations.

INTRODUCTION

The acid milling process to extract and purify uranium produces two wastes for disposal: solid tailings and process wastewater. In the United States (U.S.), disposal of the wastes varies substantially from site to site. Below-grade or pit disposal of uranium mill tailings is the "prime option" for long-term management of tailings recommended by the U.S. Nuclear Regulatory Commission (U.S. NRC 1980). To contain the liquid waste in below-grade disposal systems, methods which include liner systems are recommended in order to reduce, to the "maximum extent reasonably achievable," the seepage of toxic materials into the ground water. However, the seepage must not result in deterioration of the quality of existing, unaffected ground water. In order to maintain the desired seepage control, the waste disposal system, whether a liner system or compacted sediments, must be capable of physically limiting water migration and/or capable of retarding the migration of soluble constituents [such as radionuclides, heavy metals and selected anions (e.g., SO_4^{2-} , F^- , NO_3^-)] via chemical reactions such as precipitation and adsorption.

Acidic leachate or seepage from disposed tailings is potentially hazardous at sites where wastes are disposed in tailings impoundments with high permeability, low-acid neutralizing capacities or with small distances to the existing water table. In Canada, the Elliot Lake and Bancroft areas have had the water quality adversely affected (Brown et al. 1981) and in the U.S., contamination of surface and/or ground water has also occurred, e.g., Canon City, CO (Cotter), Ford, WA (Dawn Mining), Gas Hills, WY (Union Carbide). Details may be found in Mineral Resources Waste Management Team Report 1 (1980).

To better understand such water quality degradation and to develop experimental and computer hydrologic and transport modeling tools to predict the long-term environmental impact of leachate movement from uranium mill tailings pits the Nuclear Regulatory Commission initiated this project, Assessment of Leachate Movement from Uranium Mill Tailings, in April 1979.

It is common knowledge that most soluble constituents in waste waters do not move at the same speed as the water flow because of several physicochemical interactions with the soils and sediments encountered. Chemical reactions that attenuate contaminant migration include precipitation and surface adsorption. The former is likely the primary attenuation mechanism for pH dependent contaminants (Mn, Fe, Al and most heavy metals and radionuclides) present in relatively high concentrations in acid uranium mill tailings liquors ($\sim 0.01 \text{ M H}_2\text{SO}_4$). Most of the contaminants dissolved from the ore and gangue minerals during acid U extraction are significantly less soluble at higher pH values typical of most soil/sediment regimes. Thus, sediment buffering (especially alkaline carbonate-rich sediments common in the Western U.S. where most of the U mills occur) can cause precipitation reactions to occur and reduce solution transport of contaminants.

The second mechanism involved in contaminant attenuation is surface adsorption. Surface/solution interactions can vary greatly from sediment to sediment. One of the main factors that influences surface interactions is ion-exchange.

This project via laboratory experimentation, field observation and geochemical thermodynamic modeling is focused on developing an understanding of the precipitation and adsorption reactions that attenuate contaminant migration from uranium mill tailings seepage upon percolation through soils, sediments and clay liners. Further we are attempting to transform this knowledge into mathematical (quantitative) relationships to be used in transport models to predict contaminant migration.

Computer codes are being developed to model uranium mill tailings drainage and concurrent contaminant transport. These codes will be sufficiently detailed to describe variable saturated flow and mass transport in multi-dimensions within deformable geologic media, i.e., media which can consolidate under pressure. Finally, the models will be used to evaluate several pit disposal schemes and to predict the amount of contaminant seepage from buried mine tailings. The results of the experimental and modeling efforts can then be used by the Nuclear Regulatory Commission to formulate technically based criteria for tailings disposal.

The data presented herein describe recent (FY82) progress in laboratory experimentation to understand contaminant attenuation processes. Progress and topical reports on other portions of the project are listed in the Previous Documents in Series section. Future reports will assimilate data within the various progress reports and will present a complete picture of our knowledge and predictive ability to assess the long-term effects of leachate and seepage on the environment.

METHODS AND MATERIALS

SOLUTIONS

Acidic tailings solution and the resultant effluent from tailings solution percolated through clay sediments were chemically analyzed to determine major cations, anions, trace metals, radionuclide content, pH and Eh. The various chemical extractant solutions used to determine the forms of retention were analyzed for major cations and selected trace metals.

The pH and Eh of the original tailings solution and column effluents from the vacuum extractor experiments (to be described) were measured at 25°C on filtered samples (0.45 μ m membrane filters). A combination glass electrode was used to measure pH. Standard buffer solutions at pH values of 4, 7 and 10 were used to calibrate the meter [Corning Model 130] prior to each suite of samples and about every 30 minutes if sample analysis was still being performed. The Eh of the solution was measured using a combination platinum-reference electrode. The meter [Markson Electromark Analyzer Model 4404] was standardized prior to each suite of analyses with quinhydrone saturated pH 4 and 7 buffers. The quinhydrone saturated buffers were prepared frequently (every few days) by adding an excess of solid quinhydrone to small aliquots of pH buffers. The millivolt readings on the meter directly measured Eh, using an automatic internal correction for the reference electrode. The Eh of the quinhydrone solutions at pH 7 and 4 are respectively +285 and +462 mv at 25°C. For meters which read only the difference between the solution and the reference electrode potential $Eh = E_{\text{measured}} + E_{\text{reference}}$. Values for $E_{\text{reference}}$ can be found in Langmuir 1971.

The acidic tailings solutions and vacuum extractor effluents, after filtration and pH/Eh measurement, were split into four aliquots for analysis of 1) major cations, 2) anions, 3) trace metals, and 4) radionuclides. Samples 1 and 3, each containing ten milliliters of the solution, were separately diluted to 20 mls with deionized water to which 1 drop of 6 N nitric acid was added to preserve the major cation sample and trace metals sample. The desired storage pH is 2 and one drop of 6 N nitric acid resulted in a pH of ~2. The second 10 mls aliquot was diluted to a total of 20 mls with deionized water for anion analyses. No nitric acid was added to this sample. The fourth sample was prepared by placing 14 mls of the solution in a 20 mls polyethylene liquid scintillation vial and adding 1 ml of 6 N nitric acid. This sample was used to count radionuclide contents.

The first three aliquots were diluted in half because we knew from past experience that precipitates might form during the wait until all analyses could be performed. Even with the dilution several of the anion samples developed reddish precipitates (presumably ferric iron) during storage after about two weeks. We assumed that the precipitates were ferric hydroxides and that the anions of interest remained in solution such that results were not changed by the precipitation.

A Jarrell-Ash 925 inductively coupled argon plasma emission spectrometer (ICP) was used to measure major cation and selected trace metal contents of the solutions. The instrument simultaneously measures thirty-three elements at fixed emission lines. Three seven-second emissions of the solution are performed and stored in a PDP 8 computer. Software programs automatically average the three runs for each element and the computer prints out the results. Standards for selected elements are run after about each set of 10 to 15 samples and the instrument recalibrated automatically. The high salt content of the acidic tailings solution and several of the extractor effluents necessitated sample dilutions of between 5 to 100 to get spectral and physical interferences within acceptable limits.

Trace metals were determined on acidified samples using graphite furnace atomic absorption [Perkin Elmer Model 5000 and HGA-500 Furnace with an AS-40 auto sampler]. Sample dilution was used until known-addition spikes showed recoveries of at least 80% of those found in deionized water. A maximum sample volume of 20 μ l was used. The dilution and known-addition techniques reduced chemical and physical interferences to acceptable levels and compensated for matrix effects, respectively. For As and Se a nickel based matrix modification technique was used (Ediger 1975 and Martin et al. 1975). For lead analyses the platform method was used (Slavin and Manning 1979).

Anions were measured on diluted samples using ion chromatography [Dionex Auto Ion Model 12S]. Chloride and sulfate were determined after 200-fold dilution while fluoride, bromide and nitrate were determined on 20-fold dilutions of the tailings and vacuum extractor effluent solutions. [Note: it is now possible to state that 100 and 10-fold dilutions, respectively, would have been adequate and would have lowered resultant detection limits by a factor of two.] The eluant used in the ion chromatograph is (0.0028M Na_2CO_3 -0.003M NaHCO_3) and thus precludes the analysis of solution alkalinity. Because the tailings solutions used were originally at a pH of 2.2 or below there was no alkalinity present, whereas vacuum extractor effluents with pH values above 4.5 would contain bicarbonates but we did not have enough solution left to perform an alkalinity titration.

The uranium content of the samples was determined on the acidified trace metal aliquot using pulsed laser fluorimetry. Dilutions of the aliquot were placed in a phosphoric acid buffered complexing agent, Fluran®, and the long-lived fluorescence of the U complex measured. Known addition was used to correct for any matrix interferences. As the technique is very sensitive for U (detection limit 0.05 $\mu\text{g/l}$) large dilutions of the tailings solution and extractor effluents were possible, thus minimizing matrix problems.

The radiotracer content of the vacuum extractor columns' effluents and selective extraction solutions were measured using intrinsic germanium, Ge(Li) and NaI X-ray and γ -ray detectors. The effluent count rates were compared to original tailings solution traced with various nuclides. All count rates were corrected for decay to the time of counting of the radiotraced influent. (The radiotracing methods will be discussed later.)

The radiotracers used, ^{51}Cr , ^{54}Mn , ^{59}Fe , ^{73}As , ^{75}Se , ^{109}Cd , $^{110\text{m}}\text{Ag}$, ^{210}Pb and ^{228}Ra , were high specific activity gamma or X-ray emitters.

The energy levels and abundances and detectors used are listed in Table 1.

TABLE 1. Details on Radioisotope Counting

Isotope	Energy Level (kev)	Type	Abundance	Detector
^{51}Cr	320	γ	9%	Intrinsic Ge
^{54}Mn	835	γ	100%	Ge(Li)
^{59}Fe	1095	γ	56%	Ge(Li)
^{73}As	54	γ	9%	Intrinsic Ge
^{75}Se	136	γ	57%	Intrinsic Ge
^{109}Cd	88	$^{109}\text{Ag}-\gamma$	3.7%	Intrinsic Ge
$^{110\text{m}}\text{Ag}$	658	γ	94%	Ge(Li)
^{210}Pb	46.5	γ	4%	Intrinsic Ge
^{228}Ra	904-988	$^{228}\text{Ac}-\gamma$	41%	NaI

SEDIMENT ANALYSES

The Morton Ranch Clay liner sediment was analyzed by X-ray fluorescence to determine total concentration of selected elements. Three excitation sources [Zr, Ag, and Am] were used to generate data as each source allows detection of some additional elements. The clay liner sediment was also analyzed after contact with the radiotraced tailings solutions within the vacuum extractors. The extractor columns were dissected into discrete depth zones and each depth zone treated as a separate sample. Further, these sediment samples (discrete depth zones after contact with radiotraced tailings solution) were extracted with five reagents. At the completion of the selective extraction steps the residual sediments were dried and analyzed by X-ray fluorescence again. All X-ray fluorescence analyses were performed on finely ground (mortar and pestle) aliquots.

Separate aliquots of the radiotraced tailings solution discrete depth zone sediments were dried and radiocounted to determine the relative distribution of nuclides versus depth. The counting techniques used for solutions were used on the sediments (see Table 1). Counts were determined on aliquots up to 10 g of sediment or of X grams of sediment and 10-X grams of beach sand mixture placed in 20 ml polyethylene liquid scintillation vials. Later known weights (0.1 to 2.0 g) of the sediments were mixed with cellulose binder and pressed into thin discs and counted. Samples (0.1 to 2.0 g dependent on activity) of the residual sediments after selective extraction were also pressed into discs and counted.

PERMEABILITY COLUMN EXPERIMENTS

The permeability column experiments involved contacting the Morton Ranch Clay liner material, with acid tailings solution from the Exxon Highland Mill (H.M.) in Wyoming. The Highland Mill (H.M.) tailings solution used in the permeability column experiments will be designated as H.M. tailings solution 1 (H.M. #1) while the H.M. tailings solution used in the vacuum extractor columns will be referred to as H.M. tailings solution 2 (H.M. #2).

The two H.M. tailings solutions were sampled at different times ~14 months apart. All analyzed constituents, except for iron, in H.M. tailings solutions 1 and 2 were approximately equivalent in concentration. Total Fe concentration in the H.M. tailings solution 1 was 2215 ppm while H.M. tailings solution 2 had a total iron concentration on the order of 560 ppm. The differences in total iron concentration can be explained, in large part, by changes in mill processing procedures, and by changes in the sampling location and shipping containers. Highland Mill tailings solution 1 was shipped in an iron drum while H.M. 2 was transported in plastic carboys. The characterization of the two Highland Mill tailings solutions (H.M. 1 and H.M. 2) is presented in Table 2.

The soil used in this study originated from a composite sample taken from exposed side walls of the partially-mined 1704 pit at the Morton Ranch Uranium Mine and Mill site located in Converse County, Wyoming. This material has been termed the Morton Ranch Clay liner and is a composite of sandstone, siltstone, mudstone and shale. A brief description of the site from which the Morton Ranch clay material was taken is given in Gee et al. (1980). Results of the physical and chemical analyses of the Morton Ranch Clay liner are presented in Table 3.

The set-up of the permeability column experiments and permeability cell effluent chemical composition are described in detail in Peterson et al. (1982). The column effluent concentrations from permeability cell #5 contacted with H.M. #1 have been extracted from Peterson et al. (1982) to compare with vacuum extractor effluent concentrations (contacted with H.M. #2) reported in this document.

VACUUM (MECHANICAL) EXTRACTOR EXPERIMENTS

The Morton Ranch Clay liner material was leached in a once-through configuration using a mechanical vacuum extractor (Concept Engineering, Inc., Lincoln, Nebraska). The vacuum (mechanical) extractor consists, essentially, of three slotted disks. The top two disks move as a unit while the bottom disk remains stationary. There are twenty-four slots on each disk to enable the vacuum extractor to hold twenty-four syringe systems. A syringe system is comprised of an upper, middle, and lower syringe (see Figure 1). A syringe system will hereafter be referred to as a column. The upper syringe was filled with a radiotraced tailings solution which was allowed to flow through an aperture, in the bottom of this syringe, into the middle syringe containing the soil or geologic material to be contacted. When the extractor is turned on, the upper two disks move as a unit, carrying the columns upward and away from the lower fixed

TABLE 2. Composition of Various Highland Mill Tailings Solutions Used in Laboratory Experiments, mg/l

Constituent	H. M. Tailings Solution #1 (used in permeability cells)	H. M. Tailings Solution #2 (used in vacuum extractors (measured))	H. M. Tailings Solution #2 Radiotraced #1 for vacuum extractors (calculated)	H. M. Tailings Solution #2 Radiotraced #1 (incorrect 5:1 dilution (measured))	H. M. Tailings Solution #2 Radiotraced #2 for vacuum extractor col. 7, 13, 14 (calculated)
Li	0.9	0.48	0.48	0.11	0.48
B	0.19	0.19	0.19	0.05	0.19
HCO ₃ /CO ₃	0.0	0.0	0.0	0.0	0.0
NO ₃	16.5	8.5	27.7	19.4	194
F	4.0	4.0	4.0	<0.5	4.0
Na	343	364	364	71	364
Mg	690	440	440	88	440
Al	600	396	396	79	396
Si	234	255	255	52	255
P	30	6.8	6.8	1.0	6.8
SO ₄	12,850	9,100	9,100	1,820	9,100
Cl	97	330	330	78	330
K	40	<3	<3	<3	<3
Ca	537	483	483	97	483
V	10.6	10.6	10.6	0.8	10.6
Cr	2.7	1.5	1.5	0.3	1.5
Mn	64	43	43	8.5	43
Fe	2,215	560	560	126	560
Co	<1	1	1	0.2	1
Ni	3.0	1.7	1.7	0.38	1.7
Cu	2.3	1.3	1.3	0.27	1.3
Zn	8.4	3.9	3.9	0.89	3.9
As	3.50	0.45	0.45	0.10	0.45
Se	0.6	1.18	1.18	0.24	1.18
Sr	15.7	6.6	6.6	1.4	6.6
Mo	0.35	<0.05	<0.05	<0.05	<0.05
Cd	0.04	0.04	0.04	<0.01	0.04
Sb	<1	<1	<1	<1	<1
Ba	<0.05	<0.05	<0.05	<0.05	<0.05
La	ND(a)	5.0	5.0	0.93	5.0
Pb	<0.05	<0.04	<0.04	<0.04	<0.05
U	40.0	7.2	7.2	1.54	7.2
pH	1.8	2.19	2.15(b)	ND	ND
Eh(mv)	910	750	ND	ND	ND
<u>Radionuclides (cps/ml)</u>					
⁵¹ Cr			6.6(b)	ND	0
⁵⁴ Mn			43.1(b)	ND	0
⁵⁹ Fe			2.25(b)	ND	0
⁷³ As			17.0(b)	ND	0
⁷⁵ Se			8.16(b)	ND	0
^{110m} Ag			2.85(b)	ND	0
¹⁰⁹ Cd			4.01(b)	ND	0
²¹⁰ Pb			35.5(b)	ND	466.5(b)
²²⁸ Ra			0	0	7.4(b)

(a) ND - not determined.
(b) Values were actually measured.

TABLE 3. Physical and Chemical Characteristics of the Morton Ranch Clay Liner Material

	<u>Morton Ranch Clay Liner</u>
Water Content (g/g) (%) (after air drying)	4.10
Particle Density (g/cm ³)	2.72
Particle Size Distribution (wt%)	
Sand (50-2000 μ m)	12.0
Silt (2-50 μ m)	54.0
Clay (<2 μ m)	34.0
pH of Saturated Paste	8.2
Eh of Saturated Phase (volts)	+0.406
EC of Saturated Extract (mmhos/cm)	0.70
Organic Matter (g/g) (%)	1.44
CaCO ₃ (g/g) (%)	0.04
Cation Exchange Capacity (CEC) (meq/100 g)	31.6

disk. This extracts the plunger from the lower syringe, creating a vacuum which is responsible for sucking the tailing solution from the upper syringe through the soil in the middle syringe. Adjustments can be made so that the plunger moves different distances and thus causes variable volumes of influent solution to move through the soil sample. The extractor also has a speed control to enable one to vary the time taken to complete each plunger stroke or cycle.

Before packing the clay liner in the middle syringe, a small wad ($\approx$ 2 cm diameter) of ashless filter pulp was placed in the bottom of the syringe and compressed with a packing plunger. This filter pulp was approximately 1 cm thick when packed. The Morton Ranch Clay liner material was subsequently packed on top of this ashless filter pulp. Soil columns (middle syringes) were packed to a density of 1.3 g/cm³, or 78 grams of soil in 60 cm³ of column, based on an air dry weight. The moisture content of the air-dry soil was 4.1% (see Table 3) resulting in a bulk density of 1.25 g/cm³ based on an oven-dry weight. Packing to the desired bulk density was achieved by tapping the syringe against the laboratory bench. Silicone lubricant was applied to the

FIGURE 1. Schematic of Syringe System (Vacuum Extractor Column)

rubber on the plunger and to the rubber on the bottom of the upper syringe to facilitate movement and sealing, respectively. Each column (syringe system) was appropriately labeled and placed in slots on the three disks of the vacuum extractor. Twenty-four columns were labeled, packed, and emplaced.

Two different radiotraced acid tailings solutions were used with each solution being confined to its own separate columns (syringe systems). Both radiotraced solutions were composed of acidic H.M. tailings liquor 2 (see Table 2). The radiotraced solutions differed in regard to the radioactive tracers that were added as spikes. Radiotraced solution 1 (H.M. #2-1) was the H.M. tailings solution 2 to which known amounts of radioactive ^{109}Cd , ^{73}As , ^{110m}Ag , ^{59}Fe , ^{75}Se , ^{51}Cr , and ^{210}Pb were added. Radiotraced solution 2 (H.M. #2-2) was the H.M. tailings solution 2 spiked with ^{210}Pb and ^{228}Ra (see the next section). The activities of the radioactive spikes are given in Tables 4 and 6. These solutions were then placed in the upper reservoir (syringe) of their corresponding column. The upper syringes were covered with parafilm to prevent evaporative losses; however, a pin hole in each cover allowed atmospheric equilibrium. Figures 2 and 3 show the columns to which the two solutions were added and how the effluent from one group of columns became the influent to the next group of columns. Through the use of sequential columns, such as these, one is able not only to simulate any length flow path containing intermittent sampling ports but is also able to obtain the most desirable sampling volume. The residence time of the solutions in the individual syringe columns was approximately 16 hours per pore volume of effluent.

Samples were collected as indicated by Figures 2 and 3 and correspond roughly to one sample per individual column pore volume of effluent. The pH and Eh of each sample was determined and then the solution sample was prepared for subsequent analysis as described previously. The elemental and radio-nuclide composition of the Morton Ranch Clay liner before and after contact with the tailings solution was determined by X-ray fluorescence and radio-counting as previously described.

RADIOTRACING OF ACIDIC MILL TAILINGS SOLUTION

Four liters of Exxon Highland Mill acid tailings solution #2 collected on December 15, 1981 were removed from the large storage carboy and filtered through a $0.45\ \mu\text{m}$ membrane filter. Between 100 and 1000 microliters (μl) of ^{51}Cr , ^{54}Mn , ^{59}Fe , ^{73}As , ^{75}Se , ^{109}Cd , ^{110m}Ag , and ^{210}Pb were added to an aliquot of the filtered tailings solution and the total volume brought to 2.0 liters with untraced filtered tailings solution. This solution was named Highland Mills traced stock.

A 15 ml aliquot was then counted on intrinsic germanium and lithium drifted germanium detectors. The resultant count rates showed that it was possible to obtain reasonable counting statistics on more dilute solutions thus we decided to dilute 400 ml of the original radiotraced solution, after filtration through a $0.45\ \mu\text{m}$ membrane filter, to 2.0 liters with filtered untraced tailings solution. The resultant solution was used in the vacuum extractor experiments just described and was called H.M. #2 radiotracer solution 1

FIGURE 2. Diagram of Those Column Effluents Which Became the Influent for Succeeding Columns for Columns Leached with Radiotracer Solution 1 (Highland Mill tailings solution 2 spiked with ^{109}Cd , ^{73}As , $^{110\text{m}}\text{Ag}$, ^{59}Fe , ^{73}Se , ^{51}Cr , and ^{210}Pb).

FIGURE 3. Diagram of Those Column Effluents Which Became the Influent for for Succeeding Columns for Columns Leached with Radiotraced Solution 2 (Highland Mill Tailings solution 2 spiked with ^{210}Pb and ^{228}Ra)

(H.M. #2-1). Details of the amount of spike added, and approximate carrier and matrix constituents added with the spikes are presented in Tables 4 and 5. In Table 4 we calculate that the spike addition adds 2 parts per billion Ag, 1 part per billion Se and Pb, and infinitesimal amounts of other trace metals to the tailings solution. Thus, the tracer additions should have little impact on the total concentration of the elements being studied and as detection limits for the elements range from 10 to 50 parts per billion we could not detect any increases due to using the radionuclides. Table 5 lists the individual tracer contributions and total contribution of matrix species to the tailings solution. As the pH of the acidic tailings solution was 2.19, addition of $3.185 \times 10^{-4}\text{M}$ additional acid does not appreciably affect the acidity. Similarly the fractional parts per million additions of Na and Cl cannot be distinguished. On the other hand, the addition of 19.2 parts per million nitrate significantly increases its concentration above the original value of about 8.5 parts per million.

TABLE 4. Details on Highland Mills Tailings Solution #2 - Radiotracer Solution #1

Nuclide	Form	Matrix	Approximate Specific Activity, mCi/mg	Tracer Added to Solution 1, ml/l	Activity of Tracer, mCi/ml	Stable Carrier Added, mg/l
^{51}Cr	Na_2CrO_4	0.08 M NaCl	350	0.050	0.03	4×10^{-6}
^{54}Mn	MnCl_2	0.09 M HCl	8000	0.010	10.00	1×10^{-5}
^{59}Fe	FeCl_3	0.09 M HCl	3	0.040	0.04	5×10^{-4}
^{73}As	H_3AsO_4	0.065 M HCl	22000	0.040	0.08	1×10^{-7}
^{75}Se	H_2SeO_3	0.12 M HNO_3	10	0.040	0.31	1×10^{-3}
^{109}Cd	CdCl_2	0.09 M HCl	2600	0.020	0.07	5×10^{-7}
$^{110\text{m}}\text{Ag}$	AgNO_3	0.12 M HNO_3	3	0.040	0.14	2×10^{-3}
^{210}Pb	$\text{Pb}(\text{NO}_3)_2$	3.0 M HNO_3	20	0.100	0.2	1×10^{-3}

TABLE 5. Solution Changes Due to Spiking H.M. #2-1

Nuclide	Effect on Tailings Solution
^{51}Cr	Adds 9.2×10^{-2} mg/l Na 1.4×10^{-1} mg/l Cl
^{54}Mn	Adds 9×10^{-7} M H^+ 3.2×10^{-2} mg/l Cl
^{59}Fe	Adds 3.6×10^{-6} M H^+ 1.28×10^{-1} mg/l Cl
^{73}As	Adds 2.6×10^{-6} M H^+ 9.23×10^{-2} mg/l Cl
^{75}Se	Adds 4.8×10^{-6} M H^+ 2.98×10^{-1} mg/l NO_3
^{109}Cd	Adds 1.8×10^{-6} M H^+ 6.39×10^{-2} mg/l Cl
^{110}mAg	Adds 4.8×10^{-6} M H^+ 2.98×10^{-1} mg/l NO_3
^{210}Pb	Adds 3.0×10^{-4} M H^+ 18.6 mg/l NO_3
Total Effect	Adds 9.2×10^{-2} mg/l Na 4.6×10^{-1} mg/l Cl 19.2 mg/l NO_3 3.185×10^{-4} M H^+

In subsequent preparation of radiotracer solution 1 the technician in charge of preparing the solution misinterpreted the directions for the 5 to 1 dilution of the Highland Mill radiotraced stock. Instead of dilution with filtered Highlands Mill tailings solution he used deionized water. The net result was that the tracer concentrations remained the same but the original solution composition was diluted to one-fifth strength. The break point for using full strength Highland Mill solution and one-fifth strength occurred after between 7.66 and 9.21 pore volumes of solution had been collected from the vacuum extractor first tier of clay liner columns (1-6). More discussion will be presented in the Results section.

A second traced Highland Mill solution #2 called radiotracer solution 2 (H.M. #2-2) was prepared and contained ^{210}Pb and ^{228}Ra . Again Highland Mill tailings #2 solution was filtered through 0.45 μm membrane filters and the tracers added. Details are given in Table 6.

TABLE 6. Details on Highland Mill Tailings Solution #2 (H.M. #2-2)

Nuclide	Form	Matrix	Approx Specific Activity, mCi/mg	Tracer Added to Solution 2, ml/l	Activity of Tracer, mCi/ml	Stable Carrier Added, mg/l	Matrix Species Added
^{210}Pb	$\text{Pb}(\text{NO}_3)_2$	3.0 M HNO_3	20	1	0.2	1×10^{-2}	3×10^{-3} M H^+ 186 mg/l NO_3
^{228}Ra	RaCl_2	0.1 M HCl	not known	0.2	0.001	unknown	2×10^{-5} M H^+ 7.1×10^{-1} mg/l Cl

The radiotracer solution 2 upon adding radiotracer changes the Highland Mill tailings solution 2 composition by adding 186 parts per million nitrate and 10 parts per billion stable lead carrier. The minor additions of acid and chloride cannot be distinguished. Further preparations of radiotracer solution 2 were correctly performed such that the vacuum extractor experiments using radiotracer solution 2 were continually contacted with full strength acid mill tailings solution.

Lead-210 was added to radiotracer solution 2 because it was determined that Compton effects of all the other higher energy radiotracers were seriously interfering with quantifying the lead activity in radiotracer solution #1 using the 46.5 kev peak. Radium-228 was used in a separate solution from the tracers in radiotracer solution 1 because we had such a small quantity that we were forced to use the more efficient NaI detector. The NaI detector has much poorer resolution than the intrinsic germanium and Ge(Li) detectors thus addition of numerous isotopes would have caused serious peak separation problems.

DISSECTION OF COLUMNS

Subsequent to contacting the columns with the spiked solutions (radio-traced solutions 1 and 2; see Table 2) the portion of the columns containing the Morton Ranch Clay liner (middle syringe) was dissected with a Buehler Isomet® low-speed saw. This saw was equipped with a sample holder that had been specially designed to hold the syringes while the cutting was in progress. Cuts were made with a diamond wafering blade. Each sample was rotated as soon as the saw blade cut through the syringe to maintain the cutting blade on the syringe surface and avoid smearing the sample. The saw blade was washed following each cut. Table 7 shows the dissected portions of each column. The numbers correspond to numbering on the side of the syringe with each number or unit being equivalent to one cubic centimeter (1 cm^3) of material. The larger numbers reside nearer the influent end of the leaching columns. For example, the 55-65 designation under columns 1-6 indicates that 10 cm^3 of material was cut from each of the six columns (1-6) and that this material was nearest the contacting solution. Consequently, the numbers represent profiles of the columns as we move from the top to the bottom of the columns.

The equivalent sections from each group of columns were combined, dried in a microwave oven, and bagged as a single composite sample for the selective extraction work that is explained in the following subsection. Again, the numbers 55-65, 45-55, etc. constitute different sections within a column while groups of columns are designated by 1-6, 8-12, etc.

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TABLE 7. Dissection Scheme for Each Column

Columns 1-6		Columns 8-12		Columns 15-18		Columns 19-21	
Syringe Reading	Actual Depth mm	Syringe Reading	Actual Depth mm	Syringe Reading	Actual Depth mm	Syringe Reading	Actual Depth mm
55-65	0-18.1	52-62	0-18.1	42-62	0-36.2	42-62	0-36.2
45-55	18.1-36.2	42-52	18.1-36.2	22-42	36.2-72.3	22-42	36.2-72.3
35-45	36.2-54.2	32-42	36.2-54.2	0-22	72.3-108.5	0-22	72.3-108.5
25-35	54.2-72.3	22-32	54.2-72.3				
15-25	72.3-90.4	12-22	72.3-90.4				
0-15	90.4-108.5	0-12	90.4-108.5				

Columns 22-23		Column 24		Column 7		Column 13		Column 14	
Syringe Reading	Actual Depth mm	Syringe Reading	Actual Depth mm	Syringe Reading	Actual Depth mm	Syringe Reading	Actual Depth mm	Syringe Reading	Actual Depth mm
42-62	0-36.2	32-62	0-54.2	51-61	0-18.1	41-61	0-36.2	42-62	0-36.2
22-42	36.2-72.3	0-32	54.2-108.5	41-51	18.2-36.2	21-41	36.2-72.3	22-42	36.2-72.3
0-22	72.3-108.5			31-41	36.2-54.2	0-21	72.3-108.5	0-22	72.3-108.5
				21-31	54.2-72.3				
				11-31	72.3-90.4				
				0-11	90.4-108.5				

SEMI-SELECTIVE EXTRACTION PROCEDURE

The dissected column samples identified in Table 7 were either taken as is or combined with other sections to form samples for the selective extraction (stripping) procedures. The samples on which the stripping techniques were performed are shown in Tables 8 and 9 along with identification as to which samples were combined. A sample of the original clay liner material was also included as a sample on which the stripping techniques were performed. The sections were either taken as they were or combined with other sections on the basis of radiocounting data.

The extractants, conditions under which the extractants were used, and geochemical phases expected to be extracted are presented in Table 10 along with a step designation.

TABLE 8. Samples on Which Semi-Selective Extraction of the Geochemical Phases were Performed (Vacuum Extractor System 1)

Columns	Sections	Samples (Stripping)	Comments
1-6 (contacted with H.M. #2-1)	55-65	55-65	No composite sample were made on Columns 1-6. All samples taken as they were.
	45-55	45-55	
	35-45	35-45	
	25-35	25-35	
	15-25	15-25	
	0-15	0-15	
8-12 (contacted with effluent solution from Columns 1-6)	52-62		Composite sample made of top 3 dissected sections. Ignored Sections 12-22.
	42-52		
	32-42	32-62	
	22-32	22-32	
	12-22	Ignored	
	0-12	0-12	
15-18 (contacted with effluent from Columns 8-12)	42-62		Composite made of 3 dissected sections
	22-42	0-62	
	0-22		
19-21 (contacted with effluent from Columns 15-18)	42-62	0-62	Composite made of these sections and Columns 22-23.
	22-42	+ Columns	
	0-22	22-23	
22-23 (contacted with effluent from Columns 19-21)	42-62	0-62	Composite made of these sections and Columns 19-21.
	22-42	+ Columns	
	0-22	19-21	
24 (contacted with effluent from Columns 22-23)	32-62	Ignored	Ignored Column 24
	0-32		

After each of Steps 1 and 2 were completed aliquots of solution were taken and prepared for analysis by ICP, AA, sulfate, and radiocounting. Following each of steps 3-5 the same samples were collected except that no sample was taken for sulfate analysis. All solutions resulting from the contact of the extractants with the dissected soil columns were centrifuged and the supernatant filtered through 0.45 μ m membrane filters before collecting the above mentioned samples for analysis. A small subsample of soil was also taken to determine moisture content after steps 2, 3, and 4. The remaining moist soil sample was weighed after extraction steps 2-4. The samples remaining after

TABLE 9. Samples on Which Semi-Selective Extraction of the Geochemical Phases Were Performed (Vacuum Extractor System 2)

Columns	Sections	Samples (Stripping)	Comments
7 (contacted with H.M. #2-2)	51-61 41-51 31-41 21-31 11-21 0-11	51-61 Ignored 31-41 0-31	Ignored Section 41-51. Composite made of bottom 3 sections.
13 (contacted with effluent from Column 7)	41-61 21-41 0-21	0-61 + Column 14	Composite sample made of this column and Column 14
14 (contacted with effluent from Column 13)	42-62 22-42 0-22	0-62 + Column 13	Composite sample made of this column and Column 13

the step 5 extraction was completed were dried, weighed and divided into two approximately equal portions for radiocounting and elemental determination by X-ray fluorescence. These residual sediments were called step 6.

TABLE 10. Extractants, Conditions Under Which the Extractions Were Performed, and Geochemical Phases Extracted

Extractant	Step	Solution	Soil:Solution Ratio	Time	Conditions	Geochemical Phases Extracted	References
Magnesium Chloride	1	1 M $MgCl_2$ pH = 7	1:20	30 min	Reciprocating Shaker	Exchangeable phase	This experiment
Magnesium Chloride Acidified	2	1 M $MgCl_2$ pH = 2.5 w/HCl	1:20	30 min	Reciprocating Shaker	Weak acid soluble	This experiment
Hydroxylamine Hydrochloride	3	0.1 M $NH_2OH \cdot HCl$ in 0.01 M HNO_3 pH = 2	1:50	30 min	Reciprocating Shaker	Manganese oxides	Chester and Hughes 1967 Chao 1972 Luoma 1981 Shuman 1982
Oxalate	4	0.2 M $(NH_4)_2C_2O_4$ in 0.2 M $H_2C_2O_4$ pH = 3	1:50	4 hr	Reciprocating, Shaker and in Dark	Amorphous Fe and Al	McKeage and Day 1966 Luoma 1981 Shuman 1982
Ascorbic Acid and Oxalate	5	Oxalate above + 0.1 M ascorbic acid	1:50	30 min	97°C, Stir Intermittently	Crystalline Fe and Al	Shuman 1982
	6	Residual Sediment	---	---	Oven Dry	Crystalline Al-Si-O and Residuals	

RESULTS AND DISCUSSION

SOLUTION ANALYSES

Preliminary work was performed to establish acceptable techniques for measuring solution concentrations of elements in the high-acid high-salt tailings solutions and permeability and vacuum extractor column effluents. The solutions represented potentially significant matrix problems. For the ICP work we determined that the high salt content caused several problems. Spectral interferences of one element on other elements' emission lines were evident and the interferences appeared to be nonlinear in that dilutions did not always result in corresponding drops in interference. Further, physical interferences were found to occur upon aspiration of sample into the plasma. As calcium and sulfate activities were in equilibrium with gypsum, precipitation could occur within the nebulizer used to aspirate sample. We guess that the change in pressure and temperature that occurs as sample is aspirated into the plasma could cause evaporative losses of the sample allowing precipitation to occur. The net result is sporadic plugging and variable sample flow rates that make quantitative analysis impossible. Therefore, sample dilution into deionized water was necessary to effectively run these samples.

The dilution typically was 5 to 100 fold with 10X being the optimum compromise to still allow low detection limits. Dilution directly affects possible detection limits thus high dilution factors preclude quantification of trace concentrations. The dilution process still results in some spectral interferences which are hand corrected. Uranium and iron at concentrations of >5 mg/l and >100 mg/l, respectively, cause significant positive biases on As, Ca, Cr, K, Mg, Mo, Na, and Pb. Calcium, magnesium and aluminum above 300 mg/l also cause significant spectral interferences. Thus, if any of the analyses showed that one or more of these five elements exceeded the stated limits, the analyses were repeated on a more dilute sample that brought all concentrations below the values found to cause significant spectral interferences or brought concentrations into a region where only a few hand corrections were necessary. The United States Geologic Survey has also adopted dilution at the expense of increasing detection limits as their method to use ICP as a quantitative analytical tool [see Fishman and Bradford 1982].

A similar decision, to use dilution, was made for trace metal analyses on the atomic absorption graphite furnace. The high salt content created too much non-specific absorption ("smoke peaks") upon atomization to allow quantitative analyses even when using aids such as deuterium background correction and nickel salt addition for matrix modification. Our procedure is to dilute samples until a known addition spike yields at least 80 percent recovery when compared to the signal determined by known-addition spikes in deionized water.

Finally, a comparison of ICP versus AA/GF was performed to determine which method was preferable for elements that both techniques were capable of measuring. Criteria considered included: 1) detection limit of the method versus sample expected concentrations, 2) precision of results and, 3) cost/time

estimates per analyses. For the acidic U mill tailings and related sediment-contacted effluents the techniques chosen for each element are shown in Table 11. In general, ICP is preferred whenever its performance is adequate because of its simultaneous analysis capabilities. Our Jarrell Ash Model 925 can analyze simultaneously 33 elements (23 of which are of interest to this project) whereas AA/GF gathers information on only one element at a time. Only when AA/GF offered significantly lower detection limits for important elements found at low concentrations within typical samples or when ICP results appeared to give suspiciously inflated values was AA/GF chosen. The ICP available was incapable of measuring several elements and AA/GF was chosen by default. Using the procedures described in the Methods and Materials section, sample throughput on the AA/GF and ICP, on acidic uranium mill tailings related solutions, is 5/hour and 15/hour, respectively. The results of selected direct comparisons of ICP versus graphite furnace atomic absorption on metals analysis in acid uranium mill tailings solutions and resultant effluent solutions upon contact with sediments are shown in Appendix A.

The amount of sample volume needed to perform all the chemical analyses of interest are presented in Table 12.

SEDIMENT ANALYSES

The X-ray fluorescence data on total elemental composition of the Morton Ranch Clay liner are given in Appendix D will be discussed later in this section along with the vacuum extractor and semi-selective extraction results.

PERMEABILITY COLUMN CELLS

Details on the effects of percolating acidic, high salt tailings solutions through Morton Ranch Clay liner material on permeability are discussed in Peterson et al. (1982). Briefly, chemical precipitation reactions caused by the clay liner's innate acid neutralizing capacity (buffering capacity) plug existing pores with fine particulate material or coat existing particles and in effect, reduces the porosity.

In this document we are interested in discussing the chemical reactions that effect contaminant migration and have for convenience copied from Peterson et al. (1982) the effluent chemical composition of permeability cell 5 in which Highland Mill tailings solution #1 (see Table 2) was percolated for nearly 838 days. Over this time period almost 19 pore volumes of effluent were collected and chemical analyses performed. The results up to 11 pore volumes are shown in Table B.1 in Appendix B. Not enough solution was available to measure radioactive daughter products. The results in Table B.1 will be compared with effluents from the vacuum extractor columns in the next sections. We will be particularly interested in investigating whether similar chemical compositions are found in the effluents despite the differences in column size and residence time. The permeability columns had a 5 cm diameter and 4.5 cm length. Each syringe column in the vacuum extractor had a 2.6 cm diameter and 10.85 cm length. The average residence time for a pore volume in permeability cell #5 was about 44 days while the residence time for a pore volume in one syringe of the vacuum extractor was about 18 hours.

TABLE 11. Preferred Analytical Techniques for Selected Constituents for Acid Uranium Mill Tailings Related Solutions

Constituent	Method ^(a)	Detection Limit (mg/l)	Comments
Li	ICP	0.01	Typically found at 0.1 to 1 mg/l; no significant spectral interfaces observed
B	ICP	0.05	Typically found at 0.1 to 0.5 mg/l Fe; U spectral interferences
HCO ₃ -CO ₃	Titration	NM ^(b)	Only found in effluents from sediment contact where acidity has been neutralized
NO ₃	IC	1	Typically found at 1 to 300 mg/l
F	IC	0.5	Typically found at <0.5 to 20 mg/l
Na	ICP	1	Typically found at 50 to 500 mg/l; precision of ICP is poor ±20 to 30%; Fe and U spectral interferences; AA flame more precise
Mg	ICP	3.0	Typically found at 50 to 2000 mg/l; U spectral interference is large
Al	ICP	0.05	Typically found at <0.05 to 500 mg/l; large U and Fe interferences; AA/GF may be useful at low concentration
Si	ICP	0.05	Typically found at 10 to 300 mg/l; U and Fe interferences
P	IC	1.	Typically <1; should try sensitive colorimetric technique if low quantities need to be determined
SO ₄	IC	NM	Typically present at 1000 to 20,000 mg/l
Cl	IC	NM	Typically present at 50 to 500 mg/l
K	ICP	3	Typically present at 10 to 200 mg/l; Fe interferes; Flame AA more precise
Ca	ICP	0.2	Typically present at 500 to 2000 mg/l; U and Fe spectral interferences
V	AA/GF	0.05	Typically present at <0.05 to 5 mg/l
Cr	AA/GF	0.03	Typically present at <0.03 to 3 mg/l; ICP suffers from spectral interference
Mn ^(c)	ICP	0.05	Typically present at <0.05 to 50 mg/l; AA/GF as good or better
Fe	AA/GF	0.02	Typically present at <0.02 to 1000 mg/l; ICP good if Fe > 0.1 mg/l
Co ^(c)	ICP	0.03	Typically present at <0.03 to 1 mg/l; AA/GF probably better but was not checked
Ni ^(c)	ICP	0.06	Typically present at <0.06 to 2 mg/l; AA/GF probably better but was not checked
Cu	AA/GF	0.05	Typically present at <0.05 to 1 mg/l; ICP OK at Cu > 0.2 mg/l; U spectral interference
Zn ^(c)	ICP	0.10	Typically present at <0.1 to 5 mg/l; AA/GF may be better but was not checked.
As	AA/GF	0.05	Typically present at <0.05 to 20 mg/l; ICP suffers numerous spectral interferences, use Ni salt matrix modification for AA/GF
Se	AA/GF	0.02	Typically present at <0.02 to 5 mg/l; use Ni salt matrix modification for AA/GF
Sr	ICP	0.04	Typically present at 5 to 30 mg/l
Mo	AA/GF	0.06	Typically present at <0.06 to 1 mg/l; ICP OK at Mo > 0.3 mg/l
Cd	AA/GF	0.01	Typically present at <0.01 to 3 mg/l; ICP OK at Cd > 0.2 mg/l
Sb ^(c)	ICP	1	Typically present at <1 mg/l; AA/GF may be better but was not checked
Ba	ICP	0.05	Typically present at <0.05 to 0.2 mg/l
La	ICP	0.2	Typically present at 1 to 10 mg/l; U spectral interference
Pb	AA/GF	0.02	Typically present at <0.02 to 0.1 mg/l; use platform graphite furnace; ICP spectral interferences are severe.

(a) Methods
 ICP Inductively Coupled Argon Plasma Emission Spectroscopy
 AA/GF Atomic Absorption with Graphite Furnace
 IC Ion Chromatography

(b) NM = not measured

(c) ICP is used because it is cost effective but AA/GF would probably be more accurate and sensitive. Because element is not a priority pollutant it is not necessary to spend extra money and time for more accurate analysis.

TABLE 12. Sample Volume Requirements to Perform
Chemical Analysis (ml)

<u>Analysis</u>	<u>Acid Tailings</u>	<u>Neutral pH Sediment Contacted Effluents</u>
IC (Anions)	5-10	10-15
HCO ₃ -CO ₃	0	5-50
ICP (metals)	5-10	5-10
AA/GF	1-5	3-5
Tracer Nuclides	10	10-15
U and Daughter Products	50-200	100-500
U (Laser Fluorescence)	1-5	5-10

pH AND CONTAMINANT BREAKTHROUGHS FROM PERMEABILITY AND VACUUM
EXTRACTION COLUMN EXPERIMENTS

Many geologic materials, especially in the Western United States, have a well documented buffering capacity [Peterson et al. 1982]. This buffering capacity enables these materials to neutralize, to varying degrees, acidic solutions. When acidic uranium mill tailings solutions interact with these geologic materials the pH of the tailings solution rises. Among the many factors that can potentially affect the final pH when acidic tailings solutions react with geologic media are carbonate and layered silicate dissolution and precipitation, aluminum and iron hydrolysis, oxidation of Fe, U, V, and Mn and the cation exchange capacity of the soil.

Many minerals and solids become less soluble as the pH of their aqueous environment is increased, with the result that their corresponding dissolved constituents precipitate out of solution. These minerals and solids provide potential solubility controls for their dissolved components. Once a solubility control has been established for a particular macro-cation or anion, trace metal or radionuclide one can predict the maximum concentration of that element or compound when a solution of a given composition encounters a specified mineral assemblage. A few of the minerals and solids likely to exert an influence on the concentrations of their dissolved components when acidic uranium mill tailings solutions encounter geologic materials have been previously identified [Peterson et al. 1982].

After the initial neutralization of a tailings solution by a particular geologic material, the pH of the subsequent solution flowing past the material may drop as the buffering capacity of the soil, sediment, or clay liner is exhausted. This drop in the pH of the sediment solution is termed the pH front breakthrough. For purposes of this report, the pH front breakthrough is defined as occurring when the effluent from the columns (permeability cell

columns or vacuum extractor columns) drops below a pH value of roughly 6.5. In general, the use of the vacuum extractor facilitates sampling (both solid and solution) and enables one to simulate long flow paths in shorter time frames than possible using conventional permeability columns.

The pH change versus pore volumes of effluent solution is shown in Figures 4 and 5 for the conventional permeability columns and selected vacuum extractor columns (columns 1-6, 8-12, and 7), respectively. All of the columns depicted in Figures 4 and 5 were packed with the Morton Ranch Clay liner. Key physical and chemical characteristics of the Morton Ranch Clay liner material have been listed in the Methods and Materials section (Table 3). This geologic material is classified by texture as a silty clay loam. Physical data pertaining to permeability cells (columns) 4, 5, and 6 are given in Peterson et al. (1982). Physical data relating to the vacuum extractor columns are presented in the Methods and Materials section of this report.

FIGURE 4. pH Versus Pore Volume for Permeability Cells

FIGURE 5. pH Versus Pore Volume for Vacuum Extractor Columns

Measurable flow through permeability cell 4 ceased after less than 1 pore volume of solution had been collected. The pH front breakthrough for cells 5 and 6 is very abrupt and occurred after approximately 6 pore volumes of solution had been eluted. The pH front breakthroughs for the vacuum extractor columns were similar to those observed for the conventional permeability columns. The pH front breakthroughs for columns 1-6, 8-12, and 7 (Figure 5) occurred at effluent pore volumes of 5, 6, and 6, respectively. Each tier of columns (1-6, 8-12, 7, etc.) is combined to form a single column as explained in the Methods and Materials section and not enough acid tailings solution has passed through columns 13-24 to generate a pH breakthrough by exhausting the buffering capacity. Table 2 lists the composition of the influent solution for the vacuum extractor columns (1-6 and 7) and the composition of the percolation solution used for permeability columns 4, 5, and 6. The two solutions came from the same mill (Exxon Highland Mill) but at different sampling times (~2.5 years apart) and have slightly different compositions. The difference in the slope of the pH front breakthrough curves (between pH 8 and pH 4) between the permeability columns and the vacuum extractor columns suggests that the buffering

reactions may be kinetically controlled over the shorter time frame it took for a pore volume to percolate through the vacuum extractor columns. A pore volume passed through the vacuum extractor columns in approximately 18 hours while a pore volume took between 40 and 90 days to percolate through permeability columns 5 and 6. Further, the pH front breakthrough curves for the two types of columns cannot strictly be compared because of the different packing densities employed in the permeability columns and vacuum extractor columns and, also, the different pH values and compositions of the acid tailings solutions. Adjusting for the differences in packing density and pH, but not the difference in solution composition, indicates that the pH front breakthrough for the vacuum extractor columns should occur about 10 percent later than the breakthroughs noted for the permeability columns. As mentioned above, the pH front breakthroughs for the vacuum extractor columns occurred at the same number of pore volumes or slightly sooner than the breakthrough for permeability cells. Slow kinetics of some of the buffering could be responsible not only for the lower slope of the pH front breakthrough curves of the vacuum extractor columns, but the buffering kinetics could also be slow enough that the reactions don't proceed to completion before the solution percolates through the columns. This would account for the breakthrough occurring slightly earlier than calculated for the vacuum extractor columns. On the other hand, the difference could merely be due to the different compositions of the solutions or the fact that the Morton Ranch Clay liner material used for packing the permeability and vacuum extractor columns was taken from two different samples of this material. This heterogeneity of materials could also be responsible for the small observed differences in the pH front breakthroughs of the two types of columns. Further, the slight differences observed in the pH front breakthroughs between the permeability cells and vacuum extractor columns were smaller than the differences noted between other laboratory columns (other than Morton Ranch Clay liner) that had been packed and percolated with acidic U tailings in other studies.

In summary, given the potential differences in clay liner samples, observed differences in tailings solution and solution residence times, the pH breakthrough curves for the permeability columns and vacuum extractor columns agree favorably. In our opinion, the vacuum extractor columns generally duplicated the pH front breakthroughs of the permeability cells. The vacuum extractor columns ran for 3 weeks and achieved in that time frame roughly the same number of pore volumes of effluent as the permeability cells reached in approximately 3 years. Thus, extrapolation of results to different path-lengths and acid solution residence times may be possible for this combination of tailings solution and clay liner and the vacuum extractor columns appear to be a useful experimental tool for simulating long term experiments in shorter time frames.

Both types of columns, permeability and vacuum extractor, exhibited a residual buffering capacity in the pH range of 3-4 that prevented the effluent pH values from reaching the influent tailings solution values (1.8-2.2) during the duration of the experiments. This residual buffering capacity has been observed before [Relyea and Martin 1982; Peterson et al. 1982] and has been hypothesized to be caused by reactions 1 and 2 shown below:

As the pH of the tailings solution rises during percolation through the clay liners, the acidity is neutralized by the liner's buffering capacity and the reverse of reactions 1 and 2 causes amorphous $\text{Fe(OH)}_3(\text{A})$ and $\text{Al(OH)}_3(\text{A})$ [where (A) = amorphous] to precipitate out of the tailings solution. As the liner's buffering capacity is exhausted and more acidic tailings solutions is percolated into the reacted sediment, the pH falls nearer to the influent pH values. Reactions 1 and 2 proceed as written to consume hydrogen ions and maintain the soil column effluent pH values above the influent pH values for extended periods of time. Eventually, given an infinite supply of acidic tailings solution the originally precipitated amorphous iron and aluminum oxides may also be exhausted and the column effluent pH should drop. Other factors may also contribute to this residual buffering capacity as explained in Peterson et al. (1982). More work needs to be done to explain the mechanisms or chemical reactions responsible for this phenomenon and the contribution of each mechanism or reaction to the total residual buffering capacity.

The following text contains plots and discussions comparing the concentrations of selected elements and constituents in the effluent solutions of the permeability cells and vacuum extractor columns. The concentrations (mg/l) and relative concentrations (C/C_0 , where C_0 = the influent concentration and C = the effluent concentration) for both types of columns are compared by plotting concentration and relative concentration versus pH and versus cumulative pore volume, respectively. For the first tier of extractor columns, columns 1-6, the cumulative pore volume is the same as the individual pore volume, that is, the volume of the eluted solution divided by the pore space of the soil columns. For subsequent tiers of extractor columns, columns 8-12, 15-18, 19-21, 22-23, and 24, the cumulative pore volume refers to the volume of solution eluted from the specified tier of columns divided by the pore space of the given tier of columns plus the pore space of all preceeding tiers of columns. In other words, the tiers of extractor columns are added together to form, in effect, a larger column with the equivalent of solution sampling ports at intermediate positions. Through the use of a cumulative pore volume one can compare the effect of different column lengths on effluent composition by considering more or fewer tiers of columns. Plots for the vacuum extractor columns were usually plotted until the effect of the improper 5 to 1 dilution of Highland Mill #2-1 tailings solution (see Methods and Materials section) began to show up (between 7.66 and 9.21 pore volumes in columns 1-6) although plots were occasionally made past this point to illustrate a specific principle. Certain elements and compounds of interest will, in the following paragraphs, be discussed in detail while the others will be lumped into a generic discussion that will follow the more detailed discussion.

Aluminum

Figure 6 contains plots of the relative aluminum concentrations (C/C_0) versus cumulative pore volumes for vacuum extractor columns 1-6 (first tier) and permeability cell 5. The tailings solution (H.M. #1) utilized in the permeability column had 600 mg/l of Al compared to the 396 mg/l found in the

FIGURE 6. Relative Concentration (C/C_o) of Al Versus Cumulative Pore Volume of Effluent For Columns 1-6 and Permeability Cell 5

vacuum extractor influent solution. Aluminum concentrations in the first tier of vacuum extractor columns (1-6) began to rise after fewer pore volumes had percolated through these columns than had passed through the permeability columns. The increases in Al concentrations for both types of columns tend to proceed at the same relative rate.

The sudden increase in the Al concentrations of the permeability cells and vacuum extractor columns coincides with a drop in pH of the effluent solutions. The most dramatic rise in concentrations occurred between the pH values of 4 to 5 (see Figure 7). At a pH value of approximately 4, both types of columns (permeability and vacuum extractor) experienced effluent Al concentrations that are higher than the influent values. This increase in Al could be due to the dissolution of amorphous $Al(OH)_3$ that had precipitated earlier when the buffering capacity of the soil increased the tailings solution pH in the columns to values above 6. This dissolution is described by reaction 1. No dissolution of layered alumino-silicate materials has been ascertained using x-ray

FIGURE 7. Concentration (mg/l) of Al Versus pH for Columns 1-6 and Permeability Cell 5.

diffraction characterization techniques [Peterson et al 1982]. It has been previously theorized in this report and Peterson et al. (1982) that the dissolution of $\text{Al}(\text{OH})_3(\text{A})$ is one of the major reactions responsible for the consumption of hydrogen ions and the existence of the residual buffering capacity noted in the Morton Ranch Clay liner material. The marked increase in Al concentrations around pH 4 in the effluent solution is a further confirmation that one of the reactions causing the residual buffering capacity to occur around pH 4 is the dissolution of $\text{Al}(\text{OH})_3(\text{A})$ (see reaction 1).

The effluent pH and Al concentrations parallel each other closely in the two types of columns and again demonstrate the ability of the vacuum extractor

columns to simulate in a few weeks what took years to produce using conventional permeability cells. The pH and Al concentrations are inversely related in these experiments which illustrates the importance of being able to predict the pH changes that occur when acidic tailings solutions encounter geologic materials with inherent buffering capacities.

As the column effluent Al concentrations are quite similar for both the vacuum extractor columns and permeability columns, one can conclude that kinetic considerations (slower than a day, but faster than three years) are not important in determining Al concentrations. All reactions responsible for the retardation and subsequent mobilization (at lower pH values) of Al appear to go to completion within the 18 hours it took a pore volume of tailings solution to transit the vacuum extractor columns.

The Al concentrations in latter tiers of vacuum extractor columns never rose above 3 mg/l. The pH values in columns 8-12 dropped to just under 5 while the remaining tiers of columns (15-18, 19-21, 22-23, and 24) had pH values that remained above 7.0. The high pH values of the later tiers of columns resulted in Al precipitation and were the cause for the low measured Al concentrations.

Iron

Figure 8 plots the relative concentrations of Fe versus cumulative pore volumes of effluent for the indicated vacuum extractor columns and permeability cell. The solution influent Fe concentration used in the permeability cell was initially measured at 2215 mg/l as opposed to an Fe level of 560 mg/l in the solution percolated through the vacuum extractor columns. These solutions are called H.M.1 and H.M.2, respectively, and are described in Table 2.

The Fe content of the H.M.1 solution decreased over time and the Fe value of 2215 mg/l that was measured very soon after collecting the solution probably had declined to a value substantially less than 2215 mg/l by the time the solution was used in the permeability cell. The decrease in the measured Fe content in tailings solutions with time coincided with the appearance of a reddish-brown precipitate in the tailings solution. Decreases in Fe concentration with time for H.M.1 could account for the marked difference in relative concentration observed between the permeability cell and the vacuum extractor columns (1-6).

A significant increase in Fe concentrations in the column effluents was seen in the pH range 4-6. This increase in concentration occurred at a slightly higher pH value in the vacuum extractor columns (see Figure 9). The explanation for the increase in iron concentrations in solution is analogous to that given for Al. The amorphous $\text{Fe}(\text{OH})_3(\text{A})$ that initially precipitated at the higher pH values began to dissolve as the pH of the tailings solution within the columns decreased due to exhaustion of the clay liner's buffering capacity. This dissolution proceeds according to reaction 1 and consumes hydrogen ions to resist further decreases in pH and to help account for the residual buffering capacity. The Fe (and Al) concentrations increased in the same pH range at which the residual buffering capacity was operable. No residual buffering capacity was evident when HCl contacted these same geologic materials

FIGURE 8. Relative Concentrations (C/C_0) of Fe Versus Cumulative Pore Volumes for Columns 1-6 and Permeability Cell 5

[Relyea and Martin 1982] as opposed to the substantial residual buffering capacity present when geologic materials were titrated with uranium mill tailings solution containing appreciable amounts of Fe and Al. Additional work is warranted to quantify the contribution of Fe and Al to the residual buffering capacity and to elucidate other possible contributions.

The effluent concentrations of Fe in the vacuum extractor columns in general were similar to those effluent concentrations observed in the permeability cell, reinforcing the value of this experimental technique in producing results in shorter periods of time than would be otherwise possible. As in the case of Al, the retardation and mobilization reactions responsible for Fe concentrations do not appear to be seriously kinetically inhibited over an 18 hour to 3 year period, but the observed differences (see Figure 8) in iron concentration versus pH for the two types of columns when compared to the almost coincidental curves in Figure 7 for Al may be due to a minor kinetic effect on Fe precipitation/dissolution. The Fe concentrations measured in vacuum extractor columns 8-12 never reached the iron concentrations of columns 1-6 or of permeability cell 5 even when measured at comparable pH values. Part of the

FIGURE 9. Concentration (mg/l) of Fe Versus pH for Columns 1-6 and Permeability Cell 5.

reason for this lies in the fact that before columns 8-12 began to decline significantly in pH the 5:1 dilution of the influent solution had begun to come through the column. The final Fe concentrations of columns 1-6 and permeability cell 5 were very similar, being 192 and 226 mg/l, respectively. The pH values of columns 15-18, 19-21, 22-23, and column 24 never dropped below approximately 7.4 and the Fe concentrations never exceeded 3 mg/l in any of these column effluents. The Environmental Protection Agency National Secondary Drinking Water Standard (40 CFR 143) established for Fe (0.3 mg/l) was exceeded in effluents from every column except the last column (24) even at pH values as high as 7.65. The biggest controlling factor for effluent Fe concentrations appeared to be pH though other mitigative factors such as adsorption may influence the effluent Fe concentrations to an as yet undetermined degree.

Uranium

The effluent concentrations of U never reached the influent concentrations for either of the two types of columns (see Figure 10). Effluent U concentrations continued to increase as increasing volumes of tailings solution percolated through the columns. This increase in U concentration also corresponded to decreasing pH values (see Figure 11). All U concentrations remained at relatively low values until an effluent pH value of ~4 was reached. At this pH value, significant increases in U concentration were measured. None of the succeeding vacuum extractor columns manifested increases in U concentration even at pH levels as low as 4.68. Even though this is above the pH value where U concentrations began to rapidly rise in vacuum extractor columns (1-6) and permeability cell 5, the U concentrations in columns 8-12 were still lower than concentrations at comparable pH values for columns 1-6 and cell 5. At least some of the decrease in U concentration is possibly attributable to adsorption or some other mechanism besides pH dependent solubility (equilibrium thermodynamics).

None of the effluents from the vacuum extractor columns exceeded the NRC Radiation Protection Standards value for ^{238}U , 4×10^4 pCi/l or 120 mg/l [Title 10-Chapter 1 CFR Part 20]. A recent EPA proposal for Standards for Inactive U Processing sites sets a total U water standard at 10 pCi/l or assuming ^{238}U only is present 0.03 mg/l (40 CFR Part 192). Such a low limit seems extremely restrictive. The pH of the vacuum extractor column effluents never dropped below 3.94. At this pH value the effluent concentrations of U from the permeability cell were below a part per million while all effluent concentrations below a pH value of 3.7 in the permeability cell exceeded ten parts per million. A pH of around 3.7 thus appeared to be critical for the mobilization of significant concentrations of uranium. The agreement between the effluent U concentrations in Figures 10 and 11 is quite good again suggesting column dimensions and residence time artifacts over the range studied are not affecting the results.

Calcium

The initial vacuum extractor column effluents had Ca concentrations that were consistently above the influent values for all tiers of columns. By the time 6 pore volumes had been eluted these values had declined to approximately the influent concentration values. The effluent relative concentration levels for permeability cell 5 paralleled closely the values for the vacuum extractor columns (see Figure 12). Higher pH values tended to have higher Ca concentrations (see Figure 13). The effluent Ca concentrations remained at the initial influent values for all columns even after the diluted (5:1) tailings solution had begun to pass through the columns. The relative concentrations (C/Co) shown in Figure 12 are based only on the initial influent concentrations levels and do not take into account the 5:1 dilution.

FIGURE 10. Relative Concentration (C/C_o) of U Versus Cumulative Pore Volumes for Columns 1-6 and Permeability Cell 5

High Ca concentrations tended to occur concomitantly with low sulfate concentrations while low Ca concentrations were accompanied by high sulfate concentrations. Since the Ca concentrations remain relatively level even after the diluted tailings solution begins to come out the columns it is obvious that the Ca concentration levels are being maintained at their initial values by Ca coming from the Morton Ranch Clay liner system. It would appear that calcium carbonate in the soil is dissolving and raising the activity product for gypsum above its solubility value. This causes the precipitation of gypsum and the concurrent lowering of the sulfate concentration. The drop in the concentration of Ca in solution for the vacuum extractor columns coincides with the exhaustion of the soils initial buffering capacity (see Figure 5).

Sulfate

Plots of the sulfate concentrations and relative concentrations are given in Figures 14 and 15. Also, see the preceding subsection on Ca for more

FIGURE 11. Concentration (mg/l) of U Versus pH for Columns 1-6 and Permeability Cell 5

discussion of SO_4 behavior. All effluent solutions from the columns exceeded the EPA National Secondary Drinking Water Standard (40 CFR 143) for (250 mg/l) SO_4 . Lower concentrations of SO_4 in the initial effluent solutions were partially due to the precipitation of gypsum brought about by the dissolution of soil calcium carbonate. Though not present in the original clay liner, substantial amounts of gypsum were identified by X-ray diffraction techniques in all the subsections of the dissected permeability cell 5 [Peterson et al. 1982].

FIGURE 12. Relative Concentrations of Ca (C/C_o) Versus Cumulative Pore Volumes for Columns 1-6, 8-12 15-18, 19-21, 22-23, 24 and Permeability Cell 5

Other Elements

For both the permeability cell 5 and vacuum extractor columns 1-6 (first tier), columns 8-12 (second tier) and columns 15-18 (third tier) the magnesium effluent concentration exceeded the influent after about 3.5 pore volumes were collected. The excess concentration continued throughout the duration of the experiments and reached maximum (C/C_o) of 2.5 and 3.1 for the permeability cell and vacuum extractors, respectively. The excess magnesium probably is caused by cation exchange or perhaps dissolution of a magnesium rich phase in the Morton Ranch Clay liner. Sodium in the effluent shows reduced concentrations after about 6 pore volumes especially in the vacuum extractor columns and perhaps is replacing magnesium on exchange sites.

FIGURE 13. Concentrations of Ca (mg/l) Versus pH for Columns 1-6, 8-12, 15-18, 19-21, 22-23, 24 and Permeability Cell 5

Trends in the manganese concentrations in the permeability cell and vacuum extractor effluents were similar to iron. At high pH values (at very low pore volumes) little manganese is observed in the effluents. As the buffering capacity of the clay liner is exhausted and the effluent pH drops to about 5, manganese starts to breakthrough. Relative peak concentrations reach 1.5 and 3 for the permeability cell and vacuum extractor first tier, respectively, probably caused by redissolution of originally precipitated manganese. The anions chloride and nitrate show very little interaction with the clay liner upon percolation. Chloride effluent values reach the influent concentration rapidly and remain there through the duration of the experiment. The vacuum extractor effluents show the effect of the improper 5:1 dilution rapidly. It appears as if the first pore volume of effluent from the various individual tiers of the vacuum extractor may dissolve some soluble nitrates from the clay liner as the first effluent sample from each tier exhibited high nitrate concentrations. Thereafter the effluent concentrations were very similar to the influent concentration.

FIGURE 14. Relative Concentrations of SO_4 (C/Co) Versus Cumulative Pore Volumes for Columns 1-6 and Permeability Cell 5

Trace metal analyses of permeability cell 5 were performed strictly by ICP and because of low concentrations and significant spectral and matrix interferences are not very reliable excepting perhaps Zn. Therefore the discussion of the fate of trace metals aside from Zn will rely solely on the vacuum extractor results with the more preferred AA/GF analyses. Zinc effluent concentrations for both the permeability cell and vacuum extractor columns are low until pH values of 4.8 and 4.7, respectively are reached. At these pH values and below the effluent zinc concentrations reach or exceed a relative concentration ratio (C/Co) >1 .

FIGURE 15. Concentrations of SO_4 (mg/l) Versus pH for Columns 1-6 and Permeability Cell 5

Cadmium concentrations in the vacuum extractor column effluents are similar to other elements such as iron, manganese, aluminum and zinc. At high pH (low pore volumes collected) the effluent cadmium concentrations are low but as the pH in the effluent drops cadmium concentrations increase rapidly. For the first tier of the vacuum extractor columns (columns 1-6) a pulse of cadmium with a relative concentration (C/C_0) of 7 is reached as the pH drops to 4.5. For the second tier (columns 8-12) the pulse is reached at pH 5 (see Figures 16 and 17). The incorrect 5:1 dilution occurred soon after the cadmium peak concentration would have dropped as observed so it is difficult to assert that the cadmium concentration would have dropped as shown in Figure 17. The trace metals Co, Cu and Ni showed trends very similar to Cd and Zn.

FIGURE 16. Relative Concentrations of Cd (C/Co) Versus Cumulative Pore Volumes for Selected Vacuum Extractor Columns

Trace metals such as V, Cr, As and Pb showed no detectable or very low concentrations in the effluents regardless of effluent pH. All but the Pb showed measurable concentrations in the influent.

The effluent Mo and Se concentrations were distinctly different from all other trace metals. The first effluent sample from each vacuum extractor tier showed measurable and most often the highest Mo and Se concentrations measured for each tier. Other Se samples, especially those from the first tier

FIGURE 17. Concentration of Cd (mg/l) Versus pH for Selected Vacuum Extractor Columns

(columns 1-6), showed rapidly fluctuating values although there appears to be increased Se concentrations in columns 1-6 as the pH front (rapidly decreasing pH) passes out of the columns.

Besides uranium we were unable to measure the effluent concentrations of the radionuclides typically present in U mill tailings solutions (^{226}Ra and ^{230}Th) because of a shortage of sample. We did add additional ^{210}Pb to the solutions as will be discussed in the next section.

In summary pH dependent reactions such as described in equations 1 and 2 and precipitation of gypsum explain most of the variation in Al, Fe, Mn, Ca and SO₄. Ion exchange reactions may be necessary to predict quantitatively the behavior of Mg, Na, Sr, K and Ca.

The largest factor influencing the effluent concentrations of most of the trace metals was pH but further effluent cleansing in lower tiers of columns may indicate that both equilibrium thermodynamic precipitation-dissolution reactions and surface adsorption are contributing to the observed effluent concentrations. Selenium and molybdenum effluent concentrations did not exhibit the inverse relationship with pH.

Geochemical modeling has been performed on some column effluents and is currently underway for other column effluent solutions to define more clearly under what conditions equilibrium thermodynamic considerations are valid and to quantify the thermodynamic contribution. Results of the geochemical modeling will be presented in the next report on this project by S. R. Peterson et al. expected in June 1983. Tables B.1 and B.7 in Appendix B contain the concentrations of the analyzed constituents including radiotracers at various pore volumes, tiers, and observed Eh/pH values for the permeability cell 5 and vacuum extractor columns.

RADIOTRACER RESULTS IN VACUUM EXTRACTOR COLUMN EXPERIMENTS

The radiocounting data for radiotracer activity in the Highland Mill tailings solution and vacuum extractor column effluents are shown in Table 2 and Tables B.2 through B.8, respectively. In general, the data show that very little if any of the radiotracers passed through all of the tiers and exited the bottom columns. None of the radioisotopes ^{110m}Ag, ⁷³As, ²¹⁰Pb or ²²⁸Ra added to the acid tailings solution were measured in effluents from the first tier columns (1-6 and 7), although poor mass balances on ²²⁸Ra make the data suspect. From analysis of effluent solutions for ²¹⁰Pb we conclude that ²¹⁰Pb is immobilized at the top of clay liner and will not migrate. Atomic absorption-graphite furnace analyses agree with the radiotracer data in that Ag and Pb are never found above their detection limits and As is found in only three effluents at detectable concentrations.

Measurable ¹⁰⁹Cd activity was observed in the effluents from the upper three tiers but not in the lower three tiers. The ¹⁰⁹Cd tracer data corroborate qualitatively the effluent trends discussed in the previous section. Significant ¹⁰⁹Cd breakthrough occurs when the pH front breaks through columns 1-6. Quantitative comparisons of the relative concentrations, C/Co, are shown in Table 13. The stable Cd results were confounded because of the improper 5:1 dilution of the influent tailings solution that occurred midway in the experiment. The results seem to show a greater release of stable cadmium as the pH of the column effluents drops. Such could be explained by release of stable cadmium originally present in the clay liner or less likely to a preferential retardation of ¹⁰⁹Cd in the system.

The ⁷⁵Se tracer effluent data show measurable counts in the first sample from all tiers and every aliquot collected from the first three tiers of

TABLE 13. Relative Concentration (C/Co) Data for Radiotracers Compared with the Total Elemental Concentration Ratio

Pore Volume	Cd	^{109}Cd	Se	^{75}Se	Cr	^{51}Cr	Fe	^{59}Fe	Mn	^{54}Mn
<u>Column 1-6</u>										
1.36	DL	DL	1.36	0.06	DL	DL	<0.001	DL	0.01	DL
3.04	DL	0.004	0.36	0.03	DL	DL	<0.001	DL	0.04	0.03
4.04	DL	0.066	0.62	0.05	DL	DL	0.026	0.01	0.11	0.08
5.19	0.50	0.180	0.82	0.06	DL	DL	0.190	0.05	1.03	0.85
6.28	5.50	1.80	0.89	0.08	DL	0.02	1.52	0.37	3.02	2.61
7.66	7.00	2.77	1.21	0.13	0.07	0.17	2.26	0.76	1.69	1.56
9.21	1.70 ^(a)	1.65	0.88 ^(a)	0.16	0.08 ^(a)	0.04	1.69 ^(a)	0.61	1.25 ^(a)	1.10
10.43	0.65 ^(a)	0.68	0.30 ^(a)	0.10	0.05 ^(a)	0.02	0.83 ^(a)	0.29	0.59 ^(a)	0.54
11.75	ND ^(b)	0.39	ND	0.09	ND	0.01	0.42 ^(a)	0.17	0.36 ^(a)	0.33
13.21	DL ^(c)	0.47	0.19 ^(a)	0.10	0.04 ^(a)	0.01	0.46 ^(a)	0.15	0.31 ^(a)	0.41
16.05	DL ^(c)	0.70	0.19 ^(a)	0.11	DL	0.01	0.34 ^(a)	0.14	0.22 ^(a)	0.65
<u>Columns 8-12</u>										
1.91	DL	0.02	0.50	0.04			0.02	DL	0.05	0.03
4.06	DL	0.03	0.90	0.06			0.02	0.002	0.29	0.21
4.70	0.60	0.18	0.66	0.06			0.08	0.027	0.85	0.68
5.37	ND	0.29	ND	0.09			0.17	0.054	1.56	1.29
6.11	1.75	0.47	0.16	0.10			0.28	0.069	1.61	1.46
6.80	2.75	0.58	0.16	0.09			0.36	0.073	1.16	1.01
7.59	1.75	0.68	0.18	0.10			0.40	0.093	0.68	0.58
<u>Columns 15-18</u>										
0.47	DL	DL	1.63	0.04			<0.001	DL	0.00	0.000
1.85	DL	DL	0.51	0.03			<0.001	DL	0.01	DL
2.36	ND	DL	ND	0.05			<0.001	DL	0.01	0.002
2.87	ND	DL	ND	0.06			0.002	DL	0.03	0.016
3.33	ND	0.01	ND	0.06			<0.001	0.004	0.01	0.005
3.85	DL	0.01	0.24	0.05			0.004	0.004	0.03	0.016

(a) Based on full strength influent not 5:1 dilution.

(b) ND - not determined (solution analysis not performed).

(c) DL - effluent solution concentration below detection limit.

columns, in the latter half of the samples from tier four and the last samples from tiers five and six. The ^{75}Se breakthrough expressed as the relative concentration ratio is low (0.03 to 0.16) and shows no trend. The AA/GF data on total Se shows much variation but as stated in the previous section the first sample collected from each tier (excepting tier two) shows the highest breakthrough. The relative breakthrough of total Se for the first three tiers is shown in Table 13 beside the ^{75}Se data. The ratios are much higher for the stable Se and often exceed one suggesting Se was leached from the clay liner in selected aliquots. The ^{75}Se tracer used does not seem to act as a good tracer of the stable Se. A partial explanation could be that the ^{75}Se and stable Se were not present with the same proportions between possible species that could include selenate and selenite that the kinetics of redistribution are so slow that equilibrium is not reached. Before radioactive selenium is used as a tracer in future studies more characterization of selenium species distribution would be necessary.

Measureable ^{51}Cr was observed in the effluents from the first tier of columns and a low activity sample was observed in one sample in each of the next two tiers (see Appendix B). There appears to be a slight peak of ^{51}Cr in the effluents from columns 1-6 in the samples that contain the pH breakthrough (the first samples at pH values between 4.5 and 4.0). The radiochromium peaks with a relative concentration ratio of 0.17 while the total Cr peaks at 0.08. Again the incorrect 5:1 dilution confounds the total Cr data. We conclude that the radioactive Cr may be a suitable tracer for the behavior of Cr in this circumstance. Relative concentration ratios for the first tier of columns are shown in Table 13.

Detectable ^{59}Fe was found in effluents from samples taken from the first three tiers. The first tier of columns shows a peak shaped partial breakthrough ($C/\text{Co} = 0.76$) at 7.66 pore volumes at pH 4.22. Less than 10% and less than 1% ^{59}Fe breakthroughs are observed in the next two tiers, respectively. The total iron effluent concentrations show similar trends but the relative concentration ratios for the first two tiers are significantly higher (3 to 5 times) than the corresponding ^{59}Fe data. Thus, the ^{59}Fe isotope is an adequate qualitative tracer for this experiment. The relative concentrations of ^{59}Fe and total iron for the first three tiers are shown in Table 13.

Detectable ^{54}Mn was observed in most of the samples from the first three tiers of columns and a few sporadic samples in lower tiers. The comparison between the total manganese and ^{54}Mn relative concentrations for the first three tiers is shown in Table 13 and is quite good even for samples in which the stable Mn should have been influenced by the incorrect 5:1 dilution. Both show sharp increases in Mn effluent concentrations when the pH front is exiting the columns. Both show a C/Co that peaks above 1 signifying redissolution of previously precipitated manganese similar to the reversible reactions (equations 1 and 2) previously discussed.

In summary, the radiotracer experiments qualitatively agreed with the behavior of the stable elements excepting Se. The quantitative agreement was

poorer aside from Mn and the very slowly migrating Cr. We can not recommend radiotracer substitution as a convenient method for determining quantitatively the behavior of trace elements in similar experiments.

RADIOTRACER DISTRIBUTIONS RETAINED IN THE VACUUM EXTRACTOR SEDIMENTS

If we consider that the six tiers of vacuum extractor columns in system 1 and the three tiers in 2, respectively, represent long columns of clay liner, the observed solution exiting the bottom column 24 or column 14 was essentially cleansed of radioactivity. Thus, we can assume that essentially all of the tracers added to the acidic tailings solution remained in the soil column. The soil columns were dissected, dried and radiocounted as described in the Methods and Materials section. The actual counts/g of soil observed at the end of the experiment in the various dissections are given in Tables C.1 and C.2 in Appendix C. Table 14 lists cumulative % of the total radionuclide retained versus depth for each isotope. The ^{51}Cr , ^{54}Mn , ^{59}Fe , ^{73}As , ^{79}Se , $^{110\text{m}}\text{Ag}$, ^{109}Cd and first entry for ^{210}Pb refer to the vacuum extract or columns shown in Figure 2. The latter ^{210}Pb and ^{228}Ra data refer to a column consisting of vacuum extractor columns 7, 13 and 14 in series (see Figure 3). These data are also presented in Figures 18-20. The data show $^{110\text{m}}\text{Ag}$, ^{73}As and ^{210}Pb are retained totally in the upper 10% of the column. Selenium-79, ^{228}Ra , ^{109}Cd and ^{54}Mn migrate into the lower half of the soil columns. The ^{228}Ra data is somewhat suspect because of very low count rates found on the soil and no detectable counts in the effluent solutions. We suspect that the ^{228}Ra added to the acidic tailings solution may have precipitated within the container used to store the traced tailings solution. The ^{210}Pb data show that the incorrect 5:1 dilution midway in the experiment for the vacuum extractor system 1 did not significantly affect lead mobility. One might speculate that the 5:1 dilution represented a much less harsh test solution but as columns 7, 13 and 14 were percolated with full strength tailings solution throughout the experiment and their ^{210}Pb results are very similar (see Figure 20) we conclude that all the data herein are useful. We plan to perform additional work on acid tailings solution contacting other sediments to further test the applicability of the results presented in this document.

Total chemical analysis (XRF) data on the distribution of elements versus depth in the vacuum extractor column systems are found in Tables D.5 and D.6. These data may be compared with the radiotracer data presented in Tables C.1 and C.2 and Table 14.

The total Cr data (Table D.5) show elevated Cr values when compared to the original Morton Ranch Clay liner value of 54 ppm for the upper most 108 mm. Below a depth of 108 mm the total Cr is not distinguishable from the original Morton Ranch Clay liner. The ^{51}Cr data in Table C.1 show measurable ^{51}Cr in the upper 108 mm also, suggesting that the elevated chromium's source is the tailings solution and that both the tracer and the total chromium data agree on the extent of migration. Conversely, the total chromium distribution in the vacuum extractor column system 2 sediments appears elevated throughout its 325 mm length.

The total manganese data (Table D.5) show peak concentrations in the samples between 217 and 325 mm for both extractor systems. The ^{54}Mn data in

TABLE 14. % Radionuclide Retained Versus Depth for Composite Vacuum Extractor Columns

Column Depth (mm)	Cumulative % Nuclear Retained Within and Above Given Depth									
	⁵¹ Cr	⁵⁴ Mn	⁵⁹ Fe	⁷³ As	⁷⁹ Se	^{110m} Ag	¹⁰⁹ Cd	²¹⁰ Pb	²¹⁰ Pb (a)	²²⁸ Ra (a)
0 - 18.1	21.9	6.9	38.4	89.4	87.0	95.1	6.4	96.4	98.6	0.0
18.1 - 36.2	42.9	13.5	59.1	99.5	92.3	100.0	14.9	99.8	99.5	0.0
36.2 - 54.2	62.3	19.5	71.5	100.0	93.0		21.1	100.0	99.7	0.0
54.2 - 72.3	85.7	25.0	76.1		93.2		27.2		99.9	4.3
72.3 - 90.4	96.7	30.1	78.8		93.6		33.1		100.0	15.9
90.4 - 108.5	99.0	34.3	81.0		93.9		38.2			30.6
108.5 - 126.6	99.6	38.0	84.9		94.0		42.4			
126.6 - 144.7	99.8	41.7	87.7		94.1		48.4			32.3
144.7 - 162.7	100.0	45.4	90.7		94.2		54.7			
162.7 - 180.8		49.6	93.9		94.4		63.2			48.4
180.8 - 198.9		53.5	95.5		94.7		73.0			
198.9 - 217.0		57.6	98.4		95.1		82.4			62.0
217.0 - 253.2		77.8	99.7		95.4		94.9			62.0
253.2 - 289.3		94.1	100.0		95.9		99.6			79.6
289.3 - 325.5		99.6			96.6		99.9			100.0
325.5 - 361.7		100.0			96.8		100.0			
361.7 - 397.8					97.2					
397.8 - 434.0					99.1					
434.0 - 470.2					99.4					
470.2 - 506.3					99.6					
506.3 - 542.5					99.9					
542.5 - 596.7					99.9					
596.7 - 651.0					100.0					

(a) Vacuum extractor system 2 (columns 7, 13, 14) all other from vacuum extractor system 1.

FIGURE 18. Distribution of ^{73}As , ^{51}Cr , ^{59}Fe and ^{54}Mn Retained in Morton Ranch Clay Liner

FIGURE 19. Distribution of ^{110m}Ag , ^{79}Se , ^{109}Cd and ^{228}Ra Retained in Morton Ranch Clay Liner

FIGURE 20. Distribution of ^{210}Pb Retained in Morton Ranch Clay Liner

Table C.1 show peak activity at the same depths suggesting that this zone was actively sequestering manganese percolating through the sediments. The total iron composition of the sediments does not vary significantly with depth probably the result of the high original clay liner iron content. Such a large baseline iron content overshadows the mass of iron added by the tailings solution.

Both extractor systems show inflated total arsenic concentrations indistinguishable from the uncontacted clay liner. The ^{73}As tracer results show 90% of the retained tracer is found in the first 18 mm. Thus, the data agree that arsenic in U mill tailings solution very quickly gets retained in sediments upon disposal.

The total selenium data in Tables D.5 and D.6 prior to extraction show elevated levels compared to the uncontacted clay liner. For the vacuum extractor system 1 the elevated total selenium profile versus depth is very irregular throughout but the 0-18 mm depth does clearly have the largest concentration. For the vacuum extractor system 2 all the tailings solution contacted sediments show elevated total Se results but again the first 18 mm sample had the largest value. The ^{79}Se data in Table C.1 show 87% of the retained tracer occurs in the first 18 mm and measurable ^{79}Se occurs throughout the rest of the sediment profile. Thus, there is qualitative agreement between total and tracer selenium results in that measurable and erratic levels of selenium may be migrating through the sediments but a significant proportion does get retained upon initial contact with the sediment.

Total silver concentrations versus depth are quite erratic for vacuum extractor system 1 and below detection limits in system 2. The ^{110m}Ag tracer data show that silver is rapidly retained by the first 18 mm of sediment contacted. We have no total cadmium values to compare with the tracer data. Thus, comparisons for silver and cadmium total concentration versus radio-tracers are not possible.

Sediment stable lead data show no striking trends nor significantly elevated concentrations after tailings solution contact probably reflecting the low mass of lead present in the U tailings solution. The ^{210}Pb show very rapid removal occur in the upper portions of the columns.

It is of interest to uranium mill tailings disposal to discuss the distribution of several other elements. Total sulfur (indicative of sulfate) is depleted in the first 36 mm of clay liner in vacuum extractor system 1, then elevated throughout the rest of the column system. This distribution probably reflects the dissolution of gypsum in the upper part of the column by the one-fifth strength tailings solution incorrectly used in the latter stages of the experiment whereas the elevated sulfur values throughout the rest of the system reflect gypsum precipitates formed upon release of Ca by sediment carbonates being used to neutralize the tailings solution. The increased calcium level would cause precipitation of gypsum as the sulfate levels in the full strength tailings are quite high.

For extractor system 2 (percolated with H.M. #2-2), total sulfur concentrations are elevated throughout the profile. As full strength tailings solution was present throughout the experiment and as the full strength solution is at the saturation limit for gypsum there is no capacity to dissolve more upon contact with the sediment. Upon extraction all the excess total sulfur is removed from the sediments suggesting gypsum (a readily soluble phase) is present. [As previously stated, gypsum has been positively identified as a key precipitate in other work (Peterson et al. 1982 and Sherwood and Serne 1982).]

Elevated total vanadium concentrations are found only in the upper 50 mm of both extractor system sediments suggesting that vanadium migration is retarded significantly. Solution effluent data in Appendix B show no measurable V concentrations exit the columns. The total nickel data show diminished concentrations in the upper 50 mm of sediment and inflated concentrations in the 200 to 325 mm zone (similar to Mn). The longer column, system 1, shows baseline nickel concentrations in the last 300 mm. We conclude that nickel is mobilized in the acidic ($\text{pH} < 4$) zone and redeposited at the basic side of the pH front breakthrough. The total zinc data trends are identical to the nickel data. The total copper data show slightly reduced concentrations in the first 50 mm and slightly elevated concentrations between 75 and 100 mm in the first vacuum extractor system suggesting copper may lag behind nickel, zinc and manganese in terms of acidic dissolution and may become reattached to sediments earlier than these metals. The total barium, lanthanum and molybdenum sediment concentrations show no trends and allow us no speculation on migration potential.

The total uranium concentration profiles in the two vacuum extractor column experiments show elevated concentrations in both columns at depths up to 200-300 mm. The peak uranium concentrations are quite distinct and occur at 72 to 108 mm in both systems. This is about the depth zone of the copper peak and is on the acidic side of the pH breakthrough front. A similar depth profile trend has been observed in the field below a tailings solution evaporation pond (Erikson and Sherwood 1982).

Nuclear waste managers often discuss contaminant migration in terms of the relative migration rate of the contaminant to that of the groundwater [see Burkholder et al. (1979), Inone and Kaufman (1963) and Relyea (1982)].

In general, for column experiments it is customary to measure the number of pore volumes that pass through the column to reach the point where the relative concentration $C/C_0 = 0.5$ for a contaminant present in the percolating solution throughout the experiment at a concentration of C_0 . When the contaminant is readily adsorbed such that no or little mass exits the column one can determine the distance at which 50% of contaminant has been retained in the sediments and then to compare this distance to the total distance travelled by the water (column length x pore volumes of solution percolated through the column). This ratio (distance travelled by the water/distance travelled to retain 50% of the contaminant mass), R or R_f , is related to the distribution coefficient, R_d or K_d , for the contaminant by equation 3.

$$R = 1 + \frac{\rho}{\theta} R_d \quad (3)$$

where

ρ = bulk density of the column

θ = porosity of the column.

Table 15 lists the calculated values of R and R_d for the radionuclides listed in Table 14 and Figures 18-20. Although the data in Table 15 were derived by the commonly accepted convention there are several drawbacks. First we had to assume that for those isotopes for which >50% of the mass was retained in the first segment (18.1 mm) that linear interpolations to find the depth of 50% mass were correct. The shapes of Figures 18-20 are far from linear thus one would need much finer segments to determine an accurate depth for 50% retention. Further the assumptions behind the derivation of equation 3 and R_d theory necessitate reversible retention and the preponderance of a single species for each contaminant. It is questionable whether either of these requirements are met for these circumstances especially for Se. Further the breakthrough data for the first tier columns (shown in Table 13) are not

TABLE 15. R and R_d Values for Radiotracers Used in the Vacuum Extractor Experiments

Isotope	Depth to 50% Mass Retained (mm)	R (a) (unitless)	R_d (b) (ml/g)
^{51}Cr	45.3	19.3	7.9
^{54}Mn	182.6	4.8	1.6
^{59}Fe	28.2	30.9	12.9
^{73}As	10.1	86.4	36.9
^{79}Se	10.4	83.9	35.8
^{110m}Ag	9.5	91.8	39.3
^{109}Cd	149.3	5.8	2.1
^{210}Pb	9.4	92.8	39.7
$^{210}\text{Pb}(c)$	9.2	30.4	12.7
$^{228}\text{Ra}(c)$	185.1	4.7	1.6

(a) Based upon: water in columns from Figure 2 travelled 651 mm x 1.34 pore volumes = 872.3 mm, Figure 3 travelled 325 mm x 0.86 pore volumes = 279.5 mm

(b) Based upon $\rho = 1.25 \text{ g/cm}^3$ and $\theta = 0.54$

(c) Columns 7, 13, 14

the typical "s" shaped curves found for reversible ion exchange loading thus our use of equation 3 for the cumulative columns is suspect. We know of no complete and commonly used method to critically assess migration data for contaminants where pH sensitive precipitation reactions are as or more important than ion exchange. We feel that our approach of coupling geochemical thermodynamic codes and ion exchange descriptors such as possible in computer codes such as MINTEQ (Felmy et al. 1983) or MINEQL (Westall et al. 1976 and Silva et al. 1980) are necessary. Our future efforts will investigate such an approach.

SELECTIVE EXTRACTION RESULTS - STABLE ELEMENTS

Lee and Plumb (1974) concluded after extensive literature review that the bulk chemical composition of sediments is not a useful index of environmental water quality degradation potential because total analysis does not account for the varying impact of different phases or chemical forms of a constituent. The weakness of total contaminant analysis in sediments to predict potential degradation of the environment has led to attempts to differentiate geochemically the various forms of trace contaminants in soils and sediments. We feel such differentiation would be quite useful in empirically determining the ease of remobilization of sediment bound heavy metals and radionuclides deposited during the neutralization of acidic uranium mill tailings by natural sediments and clay liners. Further, geochemical investigations that reveal with which phases the trace contaminants associate would be quite valuable in identifying the controlling mechanisms or chemical reactions. As our future modeling efforts will investigate the use of sophisticated geochemical thermodynamic codes that include dissolution-precipitation, complex formation and generalized ion exchange and/or surface adsorption reactions such knowledge of the controlling chemical reactions will be necessary as they wish to rely upon quantitative predictor relationships based on scientific principles as opposed to empirical observations.

Briefly, the various geochemical phases are differentiated by sequential attack of the sediment with chemical reagents that selectively dissolve or release trace metals (including radionuclides) bound to different geological phases such as ion-exchange sites, carbonates, hydrous oxides, sulfates, sulfides and organic matter. Several extraction schemes were reviewed and we chose the sequence and reagents shown in Table 10. The more mobile forms of the trace constituents in the bulk sediment would include those associated with exchange sites and weak acid soluble phases (steps 1 and 2 from Table 10). The least mobile forms of the metals would be those associated with the crystalline iron oxides and residual clay or silicate lattice sites (steps 5 and 6 from Table 10). Of intermediate mobility would be trace constituents associated with the manganese and amorphous iron and aluminum oxides. These phases are most sensitive to oxidation-reduction and acid-base changes.

As pointed out by Serne (1977) any extraction scheme used is at best semi-selective and introduces experimental artifacts such that the results obtained should be considered semi-quantitative in differentiation of discrete geologic phases even though one can present distinctly quantitative results.

The dissected vacuum extractor columns were extracted as described in the Methods and Materials section. To date, radionuclide counting and ICP analyses have been performed on all the solution extracts and radionuclide and XRF counting have been performed on the original Morton Ranch Clay liner, the liner material after contact with the Highland Mills U tailings solution and the residual solids (step 6) after semi-selective extraction. Not performed to date are sulfate analyses of the step 1 and 2 leachates and AA/GF for all leachates.

In order to remove matrix and spectral interferences on the ICP results for the various extractants preliminary work was performed on each solution. The $MgCl_2$ solutions used in steps 1 and 2 required 10 fold dilution to get stable solution nebulization and to get Mg concentrations in a workable range. The reagents in solutions 1 and 2 either contained significant potassium and sodium impurities or the magnesium caused large spectral interferences on these two elements. Further, significant interferences were found for Al (2.6 ppm), Ca (5.6 ppm), Pb (3.0 ppm), and Si (10.4 ppm). The numbers in parentheses indicate the apparent concentration of these elements in the $MgCl_2$ solutions. Using the computer software available in the ICP system we elected to subtract the apparent blank signals for each element for each extractant. In other words, only a net increase over the reagents themselves would be reported. The step 3 solution hydroxylamine hydrochloride could be run directly on the ICP and gave significant signals for Cu (0.3 ppm), Mg (2.7 ppm) and Si (0.5 ppm). The ammonium oxalate solution used in step 4 required a ten fold dilution to get stable plasma and nebulization and gave significant apparent signals for As (0.4 ppm), Ca (0.3 ppm), Fe (0.4 ppm), P (0.5 ppm) and Si (0.4 ppm). Solution 5, the ammonium oxalate plus ascorbic acid could be run directly but gave numerous apparent peaks, As (1.2 ppm), Ca (0.5 ppm), Fe (0.2 ppm), Mg (4.4 ppm), Na (1 ppm), P (0.2 ppm) and Si (0.4 ppm). As was done for the step 1 and 2 extractants the observed blank signals were automatically subtracted from the signals obtained on solutions after contact with the various subsamples of Morton Ranch Clay liner.

Upon analyses of the extractants it was found that detectable values for only Al, Ba, Ca, Fe, Mn, Si, Sr and Zn were obtained for all five extractants. For particular extractants other elements were observed at measurable concentrations, notably B in step 1, P in steps 4 and 5 and Cr, Mo, Ni, Ti and Zr in step 5. The reported values for the 8 elements found in all five extractants are listed in Appendix D Tables D.2 through D.4.

Unfortunately, matrix and spectral interferences coupled with low resultant trace metal concentrations precludes a definitive discussion of the association of trace metals other than Fe, Mn and Zn.

We attempted to combine the XRF data on the sediment samples before extraction (at the end of the vacuum extractor percolation of the radiotracer solutions) and step 6 residuals and their respective weights with the ICP data on solutions and their respective volumes to obtain mass balances on the association of Al, Si, Fe, Mn and Zn with the six extractants. For unknown reasons the mass balances for the amount of elements remaining in the sediment

(residuals) and the amount removed by the extractants do not sum to equal the original mass present in the sediment at the start of the experiment. We acknowledge that the wash steps after steps 3 and 5 and subsampling of sediments to determine moisture content after step 2, 3 and 4 confound mass balance results and that some of the reported weight losses in Table D.1 (7 to 14%) may reflect sediment loss during the experiment as opposed to solid phase dissolution. For Mn, Si and Fe the mass found in the solutions (steps 1-4) is significantly less than the difference in mass on the solids (original elemental content x original weight-residual elemental content x residual weight). For Zn the opposite mass balance discrepancy was found (i.e., Zn mass in extractant solutions exceeded Zn calculated to have been removed from the sediments). The Al data show scattered data sometimes showing more Al removed by extractants than one would expect and other times much less Al found in extractants than calculated from the difference in pre-extraction and residual sediment contents.

Therefore we will not attempt to discuss the data in terms of absolute percentages in the various extracts and residual sediment. Rather we will discuss the data in relative terms.

Relatively small percentages of Al were removed from the Morton Ranch Clay liner material that had been contacted with acidic Highland Mill tailings solutions as one might expect. In fact, a student's t test shows no significant change in sediment Al content before and after extraction (see Tables D.5 through D.8). The uncontacted Morton Ranch Clay liner material contained 6.42% Al probably as crystalline alumino-silicate material that should resist dissolution in the extractants. After percolation of the acidic tailings solution we expected that the Al present in the acid solution would precipitate within the upper portions of the vacuum extractor columns as amorphous oxides and replace lesser charged cations on exchange sites. The results in Tables D.2 through D.4 clearly show that exchangeable and weak acid soluble Al (steps 1 and 2) are important in the upper third of the two vacuum extractor systems, columns 1-6 and 8-12 and column 7, (see Figures 2 and 3). For the original Morton Ranch Clay liner (see Table D.4) and the lower two-thirds of the vacuum extractor systems very little Al is present in these two extracts. Only after contact with Al-rich acid solutions do we find exchangeable Al on the clay liner in the zone where buffering capacity has been exhausted. As, Al via equation 1, is involved in acid/base reactions, the sequestration of Al on exchange sites must be considered in predicting a soil, sediment or clay liner's overall buffering capacity. The extracts from step 3 show very little Al present and we conclude Al is not associated with manganese oxide phases. The step 4 extractant consistently shows about 30 ppm Al for all but the top sample (where the most acid conditions probably exists). Step 4 should remove amorphous forms of Al and Fe oxides thus we would expect Al to be present. The uncontacted Morton Ranch clay liner extract showed 35 ppm and is not lower than other acid contacted sediment extracts. We expected to observe a higher percentage of amorphous Al oxides in sediments after contact with acidic tailings solution but these data for step 4 do not support our expectation. The probable cause is the extremely high Al content of the natural clay liner makes the contribution added by the neutralization unrecognizable. It is worth noting that the first sediment samples of tailings solution from both vacuum extractor

(0-18 mm) systems do show lower Al contents in step 4 extracts suggesting that the Al oxides originally precipitated were redissolved by the acid solution and moved further down the column.

Silicon data in Tables D.2 through D.4 show little Si removal by steps 1 through 3 for any of the sediment samples. Step 4 extracts some Si (2-35%) of the total Si extracted and shows lower percentages for the upper 1/6 of both vacuum extractor systems. Significantly more Si is found in the uncontacted Morton Ranch clay liner and lower two-thirds of the vacuum extractor systems sediments in extract 4. The geochemical significance of this trend in the step 4 extract that should dissolve amorphous Fe and Al oxides is not straightforward. Roughly 70-80% of the Si removed during extraction is found in the step 5 extractant. There are no trends across the liner depth profiles. The lower two-thirds of both vacuum extractor systems show Si extract distributions for all steps that are indistinguishable from the uncontacted Morton Ranch clay liner. The clay liner contained originally between 31 and 32% Si and after extraction the residual sediment contained 32 to 36% Si showing that Si is indeed resistant to the chemical attack. Thus, the amount of Si extracted is actually a very small percentage of the total Si in the clay liner and perhaps not much weight should be placed upon interpretation of the solution silica data.

The calcium data show that the majority of the extracted calcium occurs in the first two extraction steps and represents exchangeable and gypsum dissolution derived calcium. The upper two sediment samples (0-38 mm) in both extractor systems show slightly less Ca release than lower sediment samples perhaps reflecting the removal of exchangeable Ca and gypsum during the percolation of the acid tailings solution. It is interesting to note that the total calcium content of the sediment samples (depth = 0-18.1 mm) from the first vacuum extractor system (Figure 2) prior to selective extraction shows a distinctly lower concentration than any other subsample. Conversely the top sediment sample from the second vacuum extractor system (columns 7, 13 and 14; see Figure 3) does not show the low calcium concentration. This probably is a result of the incorrect 5:1 dilution of the acid tailings solution midway through the experiment in system 1. The lower ionic strength solution was slightly undersaturated in respect to gypsum and probably redissolved gypsum that precipitated initially from the full strength acid tailings solution contacting the clay liner. In the second vacuum extractor system the full strength U tailings solution was used throughout and was already at the saturation level for gypsum and thus did not require significant redissolution to satisfy equilibrium conditions. The large difference in clay liner Ca content prior to extraction and after extraction (steps 6 residuals) shows most of the calcium is present in exchangeable and readily dissolvable forms.

The extract data for manganese show manganese is present in solutions from all five solutions with the greatest mass found in steps 1, 2 and 5 signifying exchangeable, readily soluble in weak acid and associated with crystalline iron oxide phases. The greatest total removal of manganese occurs in the midzone between 1/3 and 1/2 the distance into the vacuum extractor systems and shows agreement with the highest concentration of total manganese in the sediments

before extraction and with the radioactive manganese to be reported later. The data suggest that a large portion of the solid phase manganese is present in exchangeable or readily acid soluble forms after contact with the acid tailings solution. It is interesting to note that the content of the uncontacted (original) Morton Ranch Clay liner is not found to extract significantly in steps 1 and 2 but does extract in steps 4 and 5 which suggest association with amorphous and crystalline iron oxides. It is interesting to note that step 3 that was used to extract specifically manganese oxides shows in general the least manganese. Perhaps the step 2 extractant (pH 2) removes the manganese oxides or perhaps they are not important in this system. The residual Mn for sediments contacted with U mill tailings solution contain 40% to 50% of the original Mn while the residual from the uncontacted clay liner contains 70% of the total manganese suggesting that the uncontacted clay liner contains a significantly greater percentage of its manganese in firmly bound crystalline forms. The manganese added by neutralization of the acid mill tailings remains predominately in relatively mobile forms.

The extraction results for iron are similar to those for aluminum in that extraction steps 4 and 5 contain 80% to 90% of the extractable iron. As these extracts are supposed to remove amorphous and crystalline iron oxides it is understandable that these steps contain the bulk of the iron. As equation 1 describes the fate of iron upon neutralization, one can readily see that iron oxides are expected in this system. Further, like Al, the top third of the column systems shows greater contributions in steps 1 and 2, exchangeable and weak acid extractable. Again at pH values <4 iron becomes a strong competitor for ion exchange sites in sediments as was discussed for Al. In contrast the uncontacted clay liner shows no exchangeable iron contribution. Roughly 25% to 50% of the total iron present in the contacted sediments is extractable with the rest undoubtedly associated with crystalline alumino-silicates.

The zinc extraction results show that zinc was extracted in very step and that the distribution is fairly even in all solutions. We suspect that the ICP technique may be generating a small positive bias (false positive readings) because we calculate from the mass of zinc in solution that much greater differences would be expected between the residual and original sediments. A slight trend is evident that shows larger contributions from the exchangeable and weak acid soluble (steps 1 and 2) in the upper third of the samples where acid conditions predominate as opposed to the lower parts of the columns where a greater percentage of the zinc is found in the steps 4 and 5 extracts and neutral conditions exist. This trend may be real as Zn would act much like Al and Fe previously discussed. The residual sediments contacted by tailings solution contain 40% to 60% of the total zinc found prior to extraction whereas the original uncontacted Morton Ranch clay liner shows 75% of its zinc is not extracted and most likely found in crystalline lattice sites. The zinc that precipitates from the U mill tailings solutions is more readily extractable as one would expect.

The strontium data show that most of the extractable Sr is released in steps 1 and 2 as one might predict a priori. Strontium, like calcium, would be expected to be present in the sediment bound to exchange sites and precipitated

as celestite, SrSO_4 , and/or coprecipitated with gypsum. The Sr released in steps 1 and 2 in the upper third of the columns is less than that released in the lower two-thirds. As discussed for the calcium perhaps this reflects strontium sulfate dissolution by the uranium mill tailings solutions prior to initiation of the extraction experiment or perhaps depletion of exchangeable Sr in the upper sediment samples which would be in agreement with the observed increase in exchangeable Al, Fe and Zn. Extraction reduces the residual sediments Sr content to levels about one-half those found in the pre-extraction sediments thus some Sr is probably bound in crystalline lattice sites also. The Sr extraction data for the uncontacted clay liner material is very similar to that of the lower samples from the vacuum extractor columns with steps 1 and 2 predominating.

The Ba extraction data show that extractable barium is present in all steps with step 5 showing the largest contribution in most cases but steps 2, 4 and sometimes step 1 show only slightly lower concentrations. The ICP data are all low and perhaps the solution data should not be given much weight. There does appear to be less Ba released in step 1 for the upper sediment samples that react first with the acid tailings solutions. Again cation competition for exchange sites and sulfate phase redissolution may account for this trend. The residual sediment barium concentrations do not differ significantly from the pre-extraction data thus the bulk of the barium present in the sediment is bound in the crystalline lattices and not reactive. The acid tailings solutions (see Table 2) contain very little Ba because its sulfate is very insoluble and thus percolation of tailings solution does not appear to perturb or add significantly to the barium originally present.

Tables D.5 and D.6 present all the X-ray fluorescence data for the original unreacted clay liner material and vacuum extractor column samples both prior to and after selective extraction. Table D.7 lists the results of student's t statistics on the differences between the residual sediments (after extraction) contents and the before-extraction samples for all elements measured for the first vacuum extractor system while Table D.8 lists the student's t results for the second vacuum extractor system. We used the student's t statistic to investigate whether selective extraction actually removed significant amounts of each element.

The larger the t statistic the greater the difference. We were particularly interested in seeing whether significant differences were observable for the two vacuum extractor systems as the tailings solution used in the first system was inadvertently diluted to one-fifth strength. In general, most of the t statistics agreed for the two systems especially considering that only four results were available for the second system. The notable differences were that neither V or Cr were removed in statistically significant amounts during extraction of the first column system but they were significantly removed from the second column system. Conversely, Mo was removed during extraction of the first column system but not the second.

The t statistics also identify elements that are resistant to extraction because they are present predominately in crystalline lattice sites in

chemically resistant phases such as aluminosilicates. Elements that exhibit a t statistic that is negative or close to zero can be considered very resistant to leaching. Tables D.7 and D.8 show that Al, Si, Ti, Ba, Nb and Nd are very resistant to leaching while K, V, Cr, Ga, Se, As, U and Mo are somewhat resistant.

SELECTIVE EXTRACTION RESULTS - RADIONUCLIDES

The data for the radiotracers used in the vacuum extractor systems are presented in this section. The data were treated in a fashion similar to the data from the ICP and XRF analyses on the total elements present in extract solutions and sediments.

Again, mass balance calculations based on the radioactivity measured do not agree very well. In almost all cases the sum of the calculated activity extracted and found in solutions 1-4 exceeds the difference in activity between the original sediments and the step 6 residual sediments. Although we have not determined the cause, perhaps our peak stripping program is giving positive biases at very low count rates (a condition prevalent for most of the solutions) or alternately our detectors' calibration for solid pellets may need recalibration. The radiocounting data on pellets of pre-leached sediment shown in Tables D.9 and D.10 agree well qualitatively with the data shown in Tables C.1 and C.2 suggesting that the efficiency factors used to convert counts to picocuries for the specific pellet geometry are reasonable. At any rate, as was performed on the total element data we will compare the data in a qualitative way.

The extracts show excepting for one sample that ^{51}Cr is removed from the sediment only by steps 4 and 5 that should dissolve amorphous Fe and Al and crystalline Fe oxides. There is no evidence that any chromium is found as exchangeable or weak acid soluble. The data suggest that Cr present as CrO_4^{2-} anion is associated with hydrous iron oxides. The ^{75}Se data although less conclusive due to very low solution count rates also suggest that steps 4 and 5 are important and therefore amorphous and crystalline iron oxides are sequestering the selenium probably in the selenate SeO_4^{2-} form. We suggest that the binding mechanism is a coprecipitation in which CrO_4^{2-} and SeO_4^{2-} replace OH^- but can not rule out electrostatic surface adsorption of the anions by Fe-OH_2^+ sites during solid phases formation at acidic pH's. Adsorption of anions on the hydrous oxides' positively charged surface occurs at pH values below the pH of zero charge. Adsorption should predominate in the upper part of the columns where acidic pH values occur but conversely the high concentrations of SO_4^{2-} and Cl^- may outcompete for the sorption sites in the presence of the trace concentrations of selenium and chromium. Therefore, we suggest that coprecipitation/replacement mechanisms where the chromate and selenate enter the solid structure in lieu of hydroxyl anions may be the binding mechanism. In general, >85% of the ^{51}Cr bound to the acidic tailings solution treated sediments is removed from the sediments (on a per gram basis) upon extraction with the five extracts whereas <50% of the ^{75}Se bound to the sediments is released. The student's t statistics for the total Cr and Se in the acid contacted sediments also suggest that these two metals are bound more strongly than other trace metals like Zn, Ni, etc.

The ^{54}Mn extraction data is similar to the data on total Mn in that the largest extractable manganese occurs in step 1 and significant contributions are released in steps 2, 4 and 5. The ^{54}Mn data seem to increase the contribution of step 2 slightly when compared to the Mn total data but this might be caused by the residual step 1 solution left in the container after separation. The small volume of high activity step 1 solution left within the container would inflate the activity of the step 2 solution which extracts only ~10% to 20% additional activity. In terms of geochemistry the ^{54}Mn and total manganese data suggest that upon neutralization that manganese associates with sediment exchange sites, amorphous and crystalline iron oxides and weak acid soluble phases such as gypsum and perhaps manganese amorphous oxides themselves.

The ^{59}Fe extract data in general are similar to the total iron data in that steps 4 and 5 release most of the iron. The radionuclide data in the lower two-thirds of the column do suggest larger contributions from step 1 and perhaps step 2. We feel that the total iron content in the natural clay liner may be biasing the results in favor of steps 4 and 5 due to the presence of ~0.8% by weight extractable Fe in amorphous and crystalline oxides (see Table D.6) in the uncontacted Morton Ranch Clay liner. The iron added to the sediment by the neutralization of the acid U tailings solution is still predominately associated with crystalline and amorphous iron oxides but measurable amounts appear to be found associated with exchange sites and weak acid soluble phases in the portions of the sediment where acid breakthrough has not gone to completion. The amount of ^{54}Mn and ^{59}Fe removed from the sediments was 70% to >90% compared to 40% to 50% for the total manganese and 25% to 50% for the total iron.

The ^{73}As extraction data show steps 4, 5 and 3 (in this order) contribute to the removal of bound arsenic. Step 4 (amorphous iron oxides) clearly predominates and step 3 (manganese oxides) contributes only ~5% additional release. The data suggest that arsenic in the waste solution is present as the H_2AsO_4^- anion and reacts with the sediments in a similar fashion to Se and Cr described previously in that anion exchange onto iron oxide surfaces and precipitation as ferric arsenates may control the fate of arsenic. About 78% of the ^{73}As bound to the sediment is released during the extractions whereas the total arsenic data in Tables O.5 and D.6 show a lesser percentage removal.

The ^{110m}Ag extraction data show that steps 1 and 2 remove silver bound to the sediments. Therefore, we conclude that ion exchange-like processes and perhaps weakly acid soluble phases control the fate of silver in the neutralization of acid U mill tailings solution although 40% to 60% of the Ag bound in the soils on a per gram basis is not extracted in the five steps. Thus, a significant fraction appears to become tightly bound in the sediments. As mentioned previously, ^{110m}Ag moves into the sediment for a very short distance (see Figure 19 and Tables 14 and C.1) suggesting it becomes tightly bound to sediments.

The ^{109}Cd data show that step 1 removes significantly more cadmium than other extractants and that step 2 also contributes to the removal of cadmium. The latter three extractants each remove a little cadmium. Thus, it appears that ion-exchange reactions and readily weak-acid soluble phases control the removal of trace cadmium upon sediment contact with acidic tailings solution. Typically, >90% of the sediment bound ^{109}Cd was extracted but up to 35% remained bound in the lower portions of the column system where the total ^{109}Cd activity was low and pH values higher in the sediment system.

The ^{210}Pb data for vacuum extractor system 1 and vacuum extractor system 2 give different extraction results. System 1 that contained the incorrect 5:1 diluted tailings solution showed step 5 releasing the most lead and steps 1 and 4 each releasing about one-third as much. Such a distribution suggests lead associates with crystalline iron oxides, exchange sites and amorphous iron and aluminum oxides. The extraction data from the second system for the first sediment subsample show the largest release in step 3 although the other sediment samples from system 2 agree with system 1 results in that steps 5, 4 and 1 contribute the most. At this time we do not have an explanation for the discrepancy. The total percentage of ^{210}Pb removed from the sediments by extraction varies between 25% to 85% by weight on a per gram basis with no obvious trends versus depth. Total lead results seen in Tables D.5 and D.6 show in general 30% to 50% removal.

The ^{228}Ra data were obscured by low observed counts and do not allow any discussion. Presently, our only data on radium removal from acidic uranium mill tailings are found in Sherwood and Serne (1982). Upon neutralization with seven chemical reagents, two different tailings solutions (including H.M. #2) showed an average radium removal rate of 85 to 96%. Neutralized effluents with high total carbonate concentrations removed less percentages of radium. Because radium has such a low maximum permissible concentration level we will defer further speculation on its migration potential through sediments until we have actual data.

The uncontacted Morton Ranch Clay liner was also used in the extraction procedure and samples of each liquid extract and sediment prior to and after extraction were radiocounted. The only identifiable peak in any samples was ^{40}K naturally present in the sediments. Thus, there were no background radioactive isotopes present to obscure results for those tracers chosen and discussed herein.

SUMMARY

This document presents FY82 progress in laboratory experimentation to understand contaminant attenuation processes specific to disposal of acidic uranium mill tailings solutions into earthen pits. Chemical reactions known to attenuate contaminant migration include precipitation and surface adsorption. Using laboratory experimentation, field observation and geochemical thermodynamic modeling we are attempting to develop quantitative (mathematical) relationships that describe these attenuation processes. The goal is to formulate relationships amenable to inclusion into computer transport models that can be used to increase the NRC's predictive capabilities on the long-term effects of uranium mill tailings disposal.

High-acid high-salt tailings solutions present significant analytical problems so preliminary efforts were directed at evaluating the strengths and weaknesses and element-by-element specific capabilities of inductively coupled plasma emission spectroscopy (ICP) and atomic absorption-graphite furnace (AA/GF) techniques for metals and ion chromatography for anion analysis. For metals analysis we determined that dilution of the tailings and column effluent solutions was required to reduce spectral, physical and non-specific absorption interferences to acceptable ranges to allow accurate results. The dilution procedure directly increased detection limits for most trace metals to the range 10-50 parts per billion. Thus, for routine analysis of large numbers of samples practical detection limits for most trace metals are at or slightly exceed recommended drinking water maximum concentration levels. In general, the trace metals concentrations of the acidic U mill tailings solutions are present in the low parts per million range and thus readily measured. Notable exceptions include Ba and Pb which are present at <50 part per billion. (see Table 2). In general, the neutralized effluents emanating from the sediment columns show trace metal concentrations at or below the practical detection limits (10-50 ppb). Notable exceptions in the initial effluents include Se and Mo and perhaps Zn (see Appendix B).

Ion chromatography is capable of detecting sulfate, chloride, fluoride, nitrate and bromide down to the low parts per million in the acid tailings solution and sediment contacted effluents. Sulfate predominates (2,000 to 20,000 ppm) in the solutions and chloride is present at 100-300 ppm concentrations. Nitrate varies from the low ppm's to 50 ppm, fluoride from less than detectable to 10 ppm and Br is usually not detectable (<0.5 ppm). Recommended analytical techniques, practical detection limits for macro cations, metals and anions and trace metals are given in Table 11 to guide future solution analysis.

To pursue one of our main objectives, to understand contaminant attenuation processes specific to disposal of acidic uranium mill tailings solutions into geologic disposal pits, numerous laboratory column experiments have been performed. We have observed that when acidic uranium mill tailings solution is percolated through sediments or clay liners that the pH of the effluent solutions is initially increased. We have identified several factors that may be

contributing to these neutralization phenomena: carbonate and layered silicate dissolution, aluminum and iron hydrolysis, oxidation of iron, uranium, vanadium and manganese and cation exchange. We are now in the process of evaluating the importance of these processes in hopes of developing predictor relationships for the neutralization phenomena. A few of the above identified solids likely to exert an influence on the neutralization and likely to control the concentrations of their dissolved components when acidic uranium mill tailings solutions contact geologic material have been verified as important in past studies (Peterson et al. 1982). The experimental results herein are also being studied with the aid of geochemical thermodynamic models to further our understanding. Modeling results will be forthcoming in 1983.

After the initial pore volumes are neutralized, the pH of subsequent effluent drops somewhat as the sediment or clay liner buffering capacity is exhausted. In these studies using two different column designs, permeability cells with 5 cm diameter and 4.5 cm length and vacuum extractor columns with 2.6 cm diameter and 10.8 cm length, with two different solution residence times, 44 days and 0.75 days, respectively, the points at which acidic pH values started to breakthrough were quite similar. The permeability cells showed pH to rapidly start declining after 6 pore volumes while the vacuum extractor columns showed the pH decline between 5 and 6 pore volumes for the specific combination of Morton Ranch Clay liner and Highland Mill tailings solution. Considering the differences in column design, residence times and acidic tailings solutions (see Methods and Materials), the agreement in pH front breakthrough is very encouraging. We feel that extrapolation of our laboratory results to field cases may be defensible. In other words, the laboratory columns are not severely effected by the short pathlengths and relatively short residence times.

In these experiments, both column types exhibited a residual buffering capacity in the pH range of 3-4 that kept the effluent pH values from dropping to the influent values, 1.8-2.2. This residual buffering capacity has been observed before (Relyea and Martin 1982 and Peterson et al. 1982) and we hypothesize that it is caused by reactions 1 and 2.

As the pH of the tailings solution rises during percolation through the clay liners, the acidity is neutralized by the liner's buffering capacity and the reserve of reactions 1 and 2 causes amorphous Fe(OH)_3 and Al(OH)_3 to precipitate out of the tailings solution. As the liner's buffering capacity is exhausted and more acidic tailings solutions is percolated into the reacted sediment, the pH falls nearer to the influent pH values. Reactions 1 and 2 proceed as written to consume hydrogen ions and maintain the soil column effluent pH values above the influent pH values for extended periods of time. Eventually, given an infinite supply of acidic tailings solution, the originally precipitated amorphous iron and aluminum oxides may also be exhausted and the column effluent pH should drop. Other factors may also contribute to this residual buffering capacity as explained in Peterson et al. (1982). More work

needs to be done to explain the mechanisms or chemical reactions responsible for this phenomenon and the contribution to each mechanism or reaction to the total residual buffering capacity.

The acidic U mill tailings solution contained 400-600 mg/l aluminum yet the effluents from either type of columns showed <10 mg/l values until the effluent pH decreased to values between 4 and 5. At pH 4 effluent Al values increased above the influent concentrations. These trends corroborate the process described in equation 2 and the accompanying discussion on the effects of aluminum precipitation and subsequent dissolution on the original and residual buffering capacity. Effluent iron concentrations follow the same trend as Al as one would expect from the similarity of equations 1 and 2. The agreement between the effluent iron curves for the two types of columns showed slightly larger differences than the aluminum data suggesting perhaps that kinetics may play a slight role in our observed results. Further, iron concentrations in lower vacuum extractor cells' effluents were lower at pH values 4.7 to 6 suggesting some further attenuation mechanism than pH sensitive hydrous oxide precipitation is occurring. The selective extraction data suggest that measurable quantities of the iron are indeed found associated with cation-exchange sites. Therefore continued removal of iron after the formation of hydrous oxides would be expected.

Effluent uranium concentrations from both types of columns were lower than the influent values. At pH values above 3.7 the effluent concentrations remained below 1 part per million but sharply increased to above 10 ppm at pH values below 3.7. Both the influent and effluents were below the Radiation Protection Standard for release at an unrestrictive boundary (4×10^4 pCi/l or 120 mg/l) assuming that our total uranium values are predominately ^{238}U . The effluent concentrations do exceed the proposed EPA Standards for Inactive Uranium Processing Sites (40 CFR Part 192) set at 10 pCi/l.

The effluent calcium and sulfate concentrations in both types of columns appear to be controlled by dissolution of calcium carbonate (calcite) in the clay liner and precipitation of calcium sulfate (gypsum) in the presence of the high sulfate added by the tailings solution. Once the calcite has been exhausted sulfate concentrations in the effluents rise to values close to the influent values. An excess of magnesium in the later effluents for both types of columns and a shortage of sodium especially in the vacuum extractor columns suggests ion exchange replacement of Na for Mg on clay liner sites may be occurring.

Manganese concentrations in the column effluents are similar to iron, low concentrations are observed at neutral pH values and large concentrations appear when the acid front breakthrough. In the upper tiers manganese starts to increase slightly earlier than iron suggesting that it remobilizes slightly quicker than iron.

The anions chloride, fluoride and nitrate show very little interaction with the clay liner and after percolation through the column soon reach steady concentrations similar to the influent values.

The trace metals Zn, Cd, Co, Cu and Ni showed similar trends in that their effluent concentrations were very low initially while the pH of the effluent was neutral. At the time that the effluent pH dropped to 4-5 the effluent concentrations of these metals started to rise. At pH values around 4-4.5 the relative concentrations of these trace metals exceeded the influent concentration. The concentrations then dropped but we can not assert that such would occur normally as this drop coincided with the inadvertant 5:1 dilution of the influent tailings solution.

Trace metals such as V, Cr, As and Pb showed no detectable or very low concentrations in the effluents regardless of the effluent pH. Tracer data for As and Pb corroborate these findings. In addition, the radiotracer data suggest that silver is retained readily in the soil similarly to Pb, As, Cr and V. The effluent Mo and Se concentrations were distinctly different from all other trace metals. The first effluent sample from each vacuum extractor tier showed the highest Mo and usually highest Se concentrations observed throughout the experiment. Qualitatively ⁷⁵Se radiotracer data confirms the typical trends observed for the stable Se.

In these experiments, we did not have adequate volume to measure the radioactive daughter products of uranium present in acidic tailings solution (e.g., ²²⁶Ra, ²³⁰Th) although we added additional ²¹⁰Pb to the solutions and these results will be discussed.

The largest factor influencing the effluent concentrations of most of the trace and transition metals (manganese and iron) was pH but further effluent cleansing in lower tiers of the columns seem to indicate that both equilibrium thermodynamic precipitation-dissolution reactions and surface adsorption are contributing to the observed effluent concentrations. Selenium and molybdenum effluent concentrations did not exhibit the inverse relationship with pH.

The radiotracer data on column effluents qualitatively agree with the behavior of the stable elements excepting Se. The quantitative agreement of ⁵⁴Mn and ⁵¹Cr with their stable elements was adequate but in general we can not recommend radiotracers as surrogates for determining the quantitative behavior of trace metals in similar experiments. Radium-228 data are not definitive because of very low count rates and should not be given much weight. Our experiments to date have been unsuccessful in ascertaining the fate of radium. Thus, future experiments will pay increased attention to radium.

Good agreement was obtained in comparing the total elemental concentration profiles versus depth with the profiles for the radiotracers retained in the acid tailings exposed clay liner. Lead, vanadium and chromium present in the acid U mill tailings solution were retained in the upper 20%, silver and arsenic were retained in the upper 5%, the bulk of the selenium was retained in the upper 5% of the clay liner but measurable percentages seem to migrate through the total distance. Iron, manganese, nickel, zinc, copper and uranium are leached from the acidic sediments and redeposited at the pH breakthrough transition zone. It appears that copper and uranium redeposit first and travel slightly shorter distances. Sulfur, presumably as sulfate, precipitates throughout the clay liner but can be readily remobilized by contact with waters with lower sulfate concentrations than found in the acidic tailings solutions.

For comparative purposes the migration potential of the radiotracers was calculated in commonly used terms, the ratio of ground water velocity to nuclide velocity (R) and the distribution coefficient (R_d). The drawbacks to these approaches for describing conditions where ion exchange reactions are not the major contributor to retention are discussed. Our goal, to couple geochemical thermodynamic and ion exchange descriptors, to improve migration predictions is briefly discussed.

Geochemical extraction studies were performed to reveal with which solid phases and minerals the trace contaminants became associated. Such knowledge is important in our evaluation of the usefulness of geochemical thermodynamic codes in predicting the interactions that occur when acid U mill tailings solution contacts sediments and clay liners. The selective extraction studies also provide valuable empirical results that directly provide data on the migration potential of contaminants.

The selective extraction data for aluminum show that in the sediments in the tops of the columns (zone where the buffering capacity has been exhausted and acid pH 3.5-4 conditions exist) some Al is associated with ion exchange sites. Lower in the columns where neutral pH values still occur (buffering capacity is not exhausted) Al is associated with amorphous iron and aluminum oxides and not exchange sites. The results confirm the process previously discussed (equation 2) and suggest further that for quantitative predictions we must include the sediment/clay liners cation exchange reactions in transport calculations.

The selective extraction data for calcium and strontium suggest that they are bound to exchange sites and present in sulfate phases such as gypsum and celestite. More calcium and strontium is removed from sediments in the depth profile deeper than 36 mm likely due to displacement of exchangeable calcium and strontium in the upper region or dissolution of sulfate phases during the percolation of acid U mill tailings solution. The inadvertent 5:1 dilution of the acidic tailings solution dissolved measurable concentrations of gypsum from the top 18 mm of the sediments in columns 1-6 as shown by the diminished total calcium and sulfur contents at the end of the tailings percolation experiment (Table D.5). Gypsum dissolution is not evident for the second extractor system where full strength tailings solution was used throughout the experiment. We would predict no dissolution because the full strength tailings solution is at saturation with gypsum already.

The portion of the manganese, bound in the sediments after contact with acidic tailings solution, that precipitates during neutralization is associated with ion exchange sites, amorphous and crystalline iron oxides and weak acid soluble phases (perhaps gypsum and manganese oxides). Both the total and radiotracer selective extraction data support these conclusions. The depth profiles for bound manganese also show that elevated concentrations of manganese are present in sediments in the region of the pH breakthrough front. Behind the pH front (in the acidic region) manganese is being actively remobilized and then redeposited in the front where neutral pH values still exist. The remobilization/deposition appears to be a combination of cation exchange

and oxide formation/dissolution. In the acidic zone the high solution concentrations of competing cations knock manganese off exchange sites and redissolve oxides via equations 1 and 2.

The selective extraction data for iron are very similar to aluminum and somewhat similar to the manganese data. Iron bound to the sediment, especially that iron added by neutralization of iron-rich acidic tailings solutions as opposed to naturally bound iron, is associated with numerous phases, amorphous and crystalline iron oxides, cation-exchangeable and weak acid soluble. The latter two phases are more important for the iron added by uranium mill tailings solution as evidenced by the slightly different proportions of ^{59}Fe extracted versus total iron and the extractable iron from uncontacted clay liner. Again, we emphasize that quantitative predictions will have to account for the cation exchange reactions of Al, Mn and Fe in their interactions between the acidic uranium mill tailings and geologic materials.

Radiotracer data allow us to hypothesize on the types of phases which bind the trace metals chromium, selenium, arsenic, silver, cadmium and lead in the clay liner and the relative migration rates through the clay liner.

Chromium-51, arsenic-73 and selenium-75 extraction data all show that steps 4 and 5 (those purported to dissolve amorphous iron and aluminum oxides and crystalline iron oxides) remove the largest percentages of these elements. The residual sediments after extraction contain (on a per gram basis) concentrations <50% of the pre-extraction clay liner for ^{75}Se , 22% for ^{73}As and <15% for ^{51}Cr . The radiotracer data in Table C.1 show that most of the arsenic and selenium is adsorbed in the upper 36 mm of the column while chromium is bound in the upper 90.4 mm, although measurable selenium is found throughout the sediments at all depths. The association of these three radionuclides with hydrous oxides suggest that they may be bound by anion exchange reactions onto hydrous oxides surfaces especially at pH values below the point of zero charge for these oxide surfaces where net positive surface sites exist on the solids. A second process, formation of insoluble salts such as ferric arsenate and ferric selenite, is also a possible explanation.

The ^{110m}Ag and ^{109}Cd extraction data show removal of bound tracer in steps 1 and 2 purported to remove cation exchangeable and weakly acid soluble phases. The four extraction steps resulted in a residual sediment with concentrations on a per gram basis of 50% of the pre-extraction silver and 10% of the cadmium. The nuclide versus depth data in Table C.1 also suggests that silver is retained rapidly and strongly in the clay liner whereas cadmium seems to migrate faster and to deposit more prominently in the pH breakthrough zone where acid conditions grade into neutral conditions.

Lead-210 extraction data suggest that bound lead associates with several phases, crystalline iron oxides predominately with amorphous oxides and cation exchange sites also contributing significantly. Variable percentages of the lead radiotracer remained in the residual sediment in the depth profile samples but no trends are evident. The data in Tables C.1 and C.2 suggest that lead migrates slower than chromium and cadmium but slightly faster than arsenic and silver.

Table 16 is a summary of the migration potential of selected macro anions, trace metals and radionuclides based on the various types of empirical data presented in the text.

TABLE 16. Summary of Migration Potential

<u>Element or Constituent</u>	<u>Immobilized at all pH Values (3.5 - 8.5)</u>	<u>Immobilized at near Neutral pH Values (4.5 - 8.5) but Mobile at Low pH Values (pH <4.5)</u>	<u>Mobile</u>	<u>Insufficient Data</u>
NO ₃			X	
Al		X		
SO ₄ ²⁻			X	
V	X			
Cr	X			
Mn		X		
Fe		X		
Co		X		
Ni		X		
Cu		X		
Zn		X		
As	X			
Se			X	
Mo			X	
Ag	X			
Cd		X		
Ba	X			
Pb	X			
Ra				X
Th	X			
U		X		

FUTURE STUDIES

1. The results presented herein suggest that ion exchange reactions as well as solubility (precipitation/dissolution) reactions such as equations 1 and 2 must both be used to adequately model the mass transport of constituents in the acidic tailings solution upon contact with sediments. Most existing geochemical codes at present stress solubility reactions. Modeling results of the predicted effluent concentrations of elements for which the thermodynamic data base is available should be compared with observed effluent concentrations to assess the need for further reliance upon ion exchange reactions prior to complete coupling of hydrologic and geochemical codes to allow sophisticated mass transport with chemical reactions.
2. The Morton Ranch Clay liner has a relatively high cation-exchange capacity (31.6 meq/100 g) which may be the cause for the apparent importance of ion exchange reactions. Similar column experiments should be performed on sediments with lower cation-exchange capacities.
3. Further experiments are needed to investigate the fate of radium and to establish the case of the apparent rapid mobility of a fraction of the selenium and molybdenum.
4. The cause of the poor mass balance checks on the selective extraction procedures needs to be determined and studies performed to determine in which extractant step manganese hydrous oxides and sulfate bearing phases dissolve. The latter studies are needed to ascertain more clearly how selective the results really are and to determine why the step 3 extractant did not dissolve appreciable manganese.
5. Should ion exchange reactions provide necessary to describe the observed effluent breakthrough curves a cost effective technique to measure the selectivity constants for the various cations must be explored.
6. To lend more credence to the results presented herein, other tailings solution-sediment combinations should be investigated in similar column studies to verify the generalization of these results to all typical U mill disposal sites.
7. Finally, more field validation studies, similar to Erikson and Sherwood (1982), should be performed to conclusively show the applicability of extrapolation of laboratory results to field conditions.

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APPENDIX A

COMPARISON OF ICP AND AA/GF RESULTS ON ACIDIC URANIUM TAILINGS SOLUTIONS AND COLUMN EFFLUENTS

TABLE A.1. Comparison of ICP Versus AA/GF Analyses for Selected Solutions;
Concentrations are in mg/l

Element	ICP AA/GF	Comparison No.											
		1	2	3	4	5	6	7	8	9	10	11	12
Fe	ICP	1224	900	679	404	220	185	54	1.8	0.11	0.07	0.06	
	AA/GF	1266	948	825	466	256	192	46	2.1	0.14	0.12	<0.10	
Mn	ICP	130	73	69	54	37	29	13.5	9.6	1.2	0.28	0.12	0.08
	AA/GF	97	48	70	44	41	28	10.2	8.8	1.3	0.26	0.12	0.09
As	ICP	0.90	0.77	0.46	0.42	<0.40	0.20						
	AA/GF	<0.10	<0.10	0.30	<0.10	<0.10	0.15						
Cd	ICP	0.32	0.31	0.28	0.18	0.06	0.04						
	AA/GF	0.28	0.22	0.28	0.07	0.03	<0.02						
Cr	ICP	0.30	0.22	0.19	0.04	0.03	0.03						
	AA/GF	0.30	0.11	0.11	0.06	0.12	<0.06						
Mo	ICP	0.39	0.16	0.15	0.10	0.05	0.03						
	AA/GF	0.28	0.07	<0.06	<0.06	<0.06	<0.06						
Pb	ICP	0.94	0.78	0.56	0.37	0.31	0.26						
	AA/GF	0.07	0.04	0.05	<0.04	0.04	<0.04						

APPENDIX B

CHEMICAL COMPOSITION OF COLUMN EFFLUENTS

TABLE B.1. Chemical Analyses of Effluent Solutions from Permeability Column 5 (mg/l)

Constituent	Pore Volume							
	1.35	3.46	5.54	6.24	7.91	8.89	10.39	11.17
Li	DL ^(a)	0.4	1.2	1.0	1.1	1.4	1.4	1.3
B	ND ^(b)	ND	ND	ND	ND	ND	ND	ND
HCO ₃ /CO ₃	ND	ND	ND	0.0 ^(c)	0.0	0.0	0.0	0.0
NO ₃	ND	ND	ND	ND	ND	ND	ND	ND
F	ND	ND	ND	ND	ND	ND	ND	ND
Na	158	283	424	308	296	332	329	319
Mg	203	519	1,420	1,554	1,771	1,738	1,601	1,420
Al	DL	DL	DL	47	167	392	564	703
Si	3.2	7.2	15.2	23.2	28.8	40	43	45
P	DL	DL	1.5	2.1	2.1	3.0	3.8	3.8
SO ₄	2,220	3,704	7,864	9,492	12,192	13,900	14,800	10,100
Cl	132	292	402	303	306	389	355	333
K	ND	ND	ND	ND	ND	ND	ND	ND
Ca	657	612	820	512	467	507	528	517
V	ND	ND	ND	ND	ND	ND	ND	ND
Cr	DL	DL	0.08	0.1	0.1	0.5	0.5	0.5
Mn	DL	2.4	41.2	64.4	89.6	101	101	96
Fe	DL	DL	127	538	950	1,330	1,560	1,720
Co	ND	ND	ND	ND	ND	ND	ND	ND
Ni	0.2	0.5	4.1	0.8	10.9	12.9	12.4	10.8
Cu	DL	DL	0.09	0.1	0.2	0.2	0.3	0.3
Zn	0.5	0.7	9.1	15	21	29.5	31.8	29.5
As	DL	DL	DL	0.6	0.7	DL	DL	DL
Se	DL	DL	DL	DL	DL	1.6	2.1	2.1
Sr	14	19	38	32	31	31	25	19
Mo	DL	DL	DL	DL	DL	DL	DL	DL
Cd	DL	DL	0.2	0.4	0.9	0.8	1.0	1.0
Sb	ND	ND	ND	ND	ND	ND	ND	ND
Ba	ND	ND	ND	ND	ND	ND	ND	ND
La	ND	ND	ND	ND	ND	ND	ND	ND
Pb	DL	DL	DL	DL	0.5	2	2	2
U	0.4	0.6	DL	DL	DL	19.7	23.8	27.2
pH (units)	8.20	8.00	4.80	4.20	3.80	3.53	3.70	3.42
Eh (mv)	318	331	532	570	594	612	601	618

(a) DL - less than detection limit.

(b) ND - not determined.

(c) By definition HCO₃/CO₃ = 0.0 when pH < 4.3.

TABLE B.2. Chemical Composition of Vacuum Extractor Columns 1-6 Effluents (mg/l) at Selected Pore Volumes

Constituent	Pore Volume										
	1.36	3.04	4.04	5.19	6.28	7.66	9.21	10.43	11.75	13.21	16.05
Li	0.28	0.91	1.0	1.1	0.92	0.79	0.66	0.32	0.37	0.24	0.20
B	0.12	0.11	0.30	0.58	0.52	0.52	0.42	0.28	0.20	0.18	0.12
HCO ₃ /CO ₃	ND ^(a)	ND	ND	ND	ND	0.0 ^(b)	0.0 ^(b)	0.0 ^(b)	0.0 ^(b)	0.0 ^(b)	0.0 ^(b)
NO ₃	43.6	25.0	28.2	28.2	32.0	33.8	31.2	26.2	ND	23.8	25.0
F	4.0	3.8	9	9	7.8	13.4	5.6	3.2	ND	2.2	1.8
Na	174	451	439	481	462	388	352	136	90	76	74
Mg	307	409	1,260	1,320	1,010	765	584	290	186	160	112
Al	0.20	0.05	0.29	23.1	46.6	171	444	250	147	128	91
Si	15.2	13.3	17.7	27.0	59.7	106	126	108	89	89	76
P	0.81	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1.1	<0.5	<0.5	<0.5
SO ₄	2,600	3,400	6,540	7,400	7,880	8,480	8,480	4,540	3,880	2,780	2,420
Cl	320	280	320	320	320	320	220	92	66	58	56
K	122	74.8	160	211	112	36.4	11.6	6.5	10.8	4.9	3.0
Ca	913	830	607	534	503	466	482	514	483	566	554
V	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	ND	<0.1	<0.1
Cr	<0.06	<0.06	<0.06	<0.06	<0.06	0.11	0.12	0.08	ND	0.06	<0.06
Mn	0.42	1.78	4.50	44.5	130	72.8	53.6	25.4	15.6	13.5	9.6
Fe	0.16	<0.10	14.7	108.2	852	1,266	948	466	236 ^(c)	256	192
Co	<0.1	<0.1	0.2	1.0	6.9	4.1	2.1	1.0	0.7	0.6	0.4
Ni	<0.2	<0.2	0.18	1.45	11.8	7.5	3.7	1.7	1.0	0.8	0.6
Cu	0.02	0.01	0.02	0.07	0.23	0.43	0.78	0.76	0.62	0.64	0.59
Zn	1.88	0.29	0.78	2.74	20.9	17.8	9.2	4.1	2.6	2.5	1.8
As	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.31	0.15	ND	0.10	<0.10
Se	1.57	0.42	0.73	0.97	1.05	1.43	1.04	0.35	ND	0.23	0.22
Sr	16.3	17.8	30.9	29.3	18.1	11.9	9.1	6.1	4.9	5.0	4.6
Mo	0.28	<0.06	<0.06	<0.06	<0.06	<0.06	0.06	<0.06	<0.06 ^(c)	<0.06	<0.06
Cd	<0.02	<0.02	<0.02	0.024	0.218	0.276	0.068	0.026	ND	<0.02	<0.02
Sb	<0.5	<0.5	<0.5	<0.5	<0.5	0.6	0.9	0.8	0.5	0.6	<0.5
Ba	0.17	0.11	0.09	0.07	0.10	0.09	0.10	0.08	0.07	0.08	0.05
La	7.7	7.2	5.4	4.9	4.7	5.4	6.4	5.4	0.71	5.5	5.0
Pb	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	0.07	0.05	ND	0.04	0.04
U	0.17	0.15	0.09	0.40	0.82	1.16	3.80	3.60	ND	1.90	2.20
pH (units)	7.86	7.79	7.33	6.51	4.72	4.22	3.95	3.94	3.95	3.96	3.97
Eh (mv)	+421	+418	+165	+254	+439	+459	+470	+455	+453	+442	+441
Radionuclides (cms/ml)											
⁵¹ Cr	DL ^(b)	DL	DL	DL	0.132	1.12	0.277	0.165	0.092	0.086	0.046
⁵⁴ Mn	DL	1.319	3.38	36.72	112.5	67.236	47.626	23.36	14.266	17.714	28.187
⁵⁹ Fe	DL	DL	0.016	0.115	0.832	1.703	1.377	0.655	0.374	0.333	0.317
⁷³ As	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL
⁷⁵ Se	0.514	0.269	0.408	0.530	0.653	1.061	1.273	0.832	0.751	0.840	0.922
^{110m} Ag	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL
¹⁰⁹ Cd	DL	0.016	0.265	0.722	7.22	11.11	6.616	2.727	1.564	1.885	2.807
²¹⁰ Pb	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL

(a) ND - not determined.

(b) Not measured but by definition = 0 as pH < 4.3.

(c) Analysis reported was obtained on ICP but atomic absorption/graphite furnace is preferred method.

(d) DL - activity was below detection limit as determined by PEAK SEARCH® Nuclear Data, Inc., Schaumburg, IL 60196, December 22, 1978 version.

TABLE B.3. Chemical Composition of Vacuum Extractor Columns 8-12 Effluent (mg/l) at Selected Cumulative Pore Volumes

Constituent	Cumulative Pore Volume						
	1.91	4.06	4.70	5.37	6.11	6.80	7.59
Li	0.60	0.94	0.81	0.80	0.35	0.26	0.28
B	0.10	0.44	0.54	0.51	0.29	0.26	0.27
HCO ₃ /CO ₃	ND ^(a)	ND	ND	ND	ND	ND	ND
NO ₃	26.2	28.8	23.8	ND	21.2	22.6	22.6
F	3.8	9.4	8.0	ND	3.6	2.8	2.4
Na	360	390	315	205	106	80	76
Mg	296	1,354	1,133	758	456	345	287
Al	0.9	1.0	0.6	2.3	0.9	2.8	2.9
Si	14.3	17.1	19.8	27.8	31.7	40.1	39.5
P	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SO ₄	2,960	7,980	6,780	5,860	4,060	3,460	3,220
Cl	300	260	170	84	66	66	66
K	67	183	171	116	63	39	27
Ca	868	558	494	486	468	505	526
V	<0.10	<0.10	<0.1	<0.1	<0.1	<0.1	<0.1
Cr	<0.06	<0.06	<0.06	ND	<0.06	<0.06	<0.06
Mn	1.94	12.6	36.2	67.2	69.2	49.8	29.2
Fe	9.6	12.3	46.4	93.9 ^(c)	155	202	226
Co	0.22	0.46	0.94	2.1	2.6	3.20	3.48
Ni	0.24	0.44	1.35	3.1	4.0	5.1	5.75
Cu	0.12	0.10	0.07	0.08	0.05	0.07	0.08
Zn	0.56	1.02	2.17	4.70	6.02	7.83	9.36
As	<0.10	<0.1	<0.1	ND	<0.1	<0.1	<0.10
Se	0.60	1.06	0.78	ND	0.20	0.19	0.21
Sr	15.2	30.2	25.2	16.2	10.1	8.3	7.5
Mo	0.07	<0.06	<0.06	<0.06 ^(c)	<0.06	<0.06	<0.06
Cd	<0.02	<0.02	0.024	ND	0.07	0.11	0.07
Sb	0.6	<0.5	<0.5	<0.5	<0.5	0.50	<0.5
Ba	0.16	0.10	0.09	0.09	0.08	0.09	0.08
La	7.7	5.14	4.4	4.10	4.2	4.4	4.5
Pb	<0.04	<0.04	<0.04	ND	<0.04	<0.04	<0.04
U	0.19	0.09	0.04	ND	0.05	0.02	0.002
pH (units)	7.49	7.30	7.16	6.77	6.23	5.02	4.68
Eh (mv)	+211	+268	+161	+150	+234	+369	+404
Radionuclides (cps/ml)							
⁵¹ Cr	DL ^(b)	DL	DL	DL	DL	DL	DL
⁵⁴ Mn	1.349	8.943	29.166	55.543	62.805	43.316	24.912
⁵⁹ Fe	DL	0.005	0.061	0.122	0.155	0.164	0.209
⁷³ As	DL	DL	DL	DL	DL	DL	DL
⁷⁵ Se	0.302	0.498	0.457	0.726	0.783	0.767	0.849
^{110m} Ag	DL	DL	DL	DL	DL	DL	DL
¹⁰⁹ Cd	0.100	0.132	0.724	1.169	1.870	2.338	2.734
²¹⁰ Pb	DL	DL	DL	DL	DL	DL	DL

(a) ND - not determined.

(b) DL - activity was below detection limit as determined by PEAK SEARCH® Nuclear Data, Inc., Schaumburg, IL 60196, December 22, 1978 version.

(c) Analysis reported was obtained on ICP but atomic absorption/graphite furnace is preferred method.

TABLE B.4. Chemical Composition of Vacuum Extractor Columns 15-18 Effluent (mg/l) at Selected Cumulative Pore Volumes

Constituent	Cumulative Pore Volume					
	0.47	1.85	2.36	2.87	3.33	3.85
Li	0.26	0.43	0.86	1.70	0.97	0.66
B	0.04	0.03	0.06	0.48	0.38	0.23
HCO ₃ /CO ₃	ND ^(a)	ND	ND	ND	ND	ND
NO ₃	43.8	26.2	ND	ND	ND	20.0
F	2.4	3.4	ND	ND	ND	6.4
Na	123	466	425	382	342	259
Mg	281	310	306	504	1,080	1,040
Al	<0.3	<0.3	0.44	0.92	0.76	<0.3
Si	18.1	15.3	14.3	15.4	16.0	14.3
P	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SO ₄	2,300	3,340	3,820	4,820	6,660	6,120
Cl	380	360	316	242	146	92
K	71	76	62	77	113	142
Ca	877	841	820	759	576	494
V	<0.10	<0.10	ND	ND	ND	<0.1
Cr	<0.06	<0.06	0.06 ^(c)	ND	ND	<0.06
Mn	0.12	0.28	0.22	1.23	0.54	1.18
Fe	0.14	0.09	0.11 ^(c)	0.87 ^(c)	0.38 ^(c)	2.12
Co	<0.1	<0.1	<0.05	0.1	0.09	0.05
Ni	<0.2	<0.2	<0.1	<0.1	<0.1	<0.1
Cu	<0.05	<0.05	0.03 ^(c)	0.08 ^(c)	<0.03 ^(c)	<0.03
Zn	0.57	0.32	0.18	0.25	0.24	0.44
As	<0.10	<0.10	ND	ND	ND	<0.10
Se	1.92	0.60	ND	ND	ND	0.28
Sr	15.0	15.4	15.2	18.2	25.3	24.2
Mo	0.45	0.09	<0.05 ^(c)	<0.05 ^(c)	<0.05 ^(c)	<0.06
Cd	<0.02	<0.02	ND	ND	ND	<0.02
Sb	<0.5	<0.5	<0.3	<0.3	<0.3	0.26
Ba	0.21	0.15	0.14	0.14	0.11	0.08
La	7.2	7.0	0.5	0.5	0.4	4.3
Pb	<0.04	<0.04	ND	ND	ND	<0.04
U	0.06	0.14	ND	ND	ND	0.04
pH (units)	7.58	7.62	7.69	7.57	7.52	7.51
En (mv)	+434	+409	401	+324	+373	+270
Radionuclides (cps/ml)						
⁵¹ Cr	DL ^(c)	DL	0.008	DL	DL	DL
⁵⁴ Mn	0.013	0.125	0.082	0.698	0.203	0.700
⁵⁹ Fe	DL	DL	DL	DL	0.009	0.008
⁷³ As	DL	DL	DL	DL	DL	DL
⁷⁵ Se	0.310	0.261	0.441	0.490	0.457	0.384
^{110m} Ag	DL	DL	DL	DL	DL	DL
¹⁰⁹ Cd	DL	DL	DL	DL	0.021	0.026
²¹⁰ Pb	DL	DL	DL	DL	DL	DL

(a) ND - not determined.

(b) DL - activity was below detection limit as determined by PEAK SEARCH[®] Nuclear Data, Inc., Schaumburg, IL 60196, December 22, 1978 version.

(c) Analysis reported was obtained on ICP but atomic absorption/graphite furnace is preferred method.

TABLE B.5. Chemical Composition of Vacuum Extractor Columns 19-21 Effluent (mg/l) at Selected Cumulative Pore Volumes

Constituent	Cumulative Pore Volume					
	0.13	1.29	1.66	2.00	2.40	3.09
Li	0.27	0.22	0.42	0.49	0.77	0.86
B	0.02	0.02	0.04	<0.04	<0.04	0.04
HCO ₃ /CO ₃	ND ^(a)	ND	ND	ND	ND	ND
NO ₃	7.5	17.6	ND	ND	ND	20.0
F	2.8	2.4	ND	ND	ND	3.6
Na	113	216	321	388	439	398
Mg	303	271	278	260	293	389
Al	<0.3	<0.3	<0.15	0.23	0.21	<0.15
Si	16.3	15.4	14.6	13.7	14.2	14.7
P	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SO ₄	2660	2980	2960	3200	3580	4360
Cl	600	400	316	290	218	130
K	68	66	62	59	63	78
Ca	945	813	809	734	765	820
V	<0.10	<0.10	ND	ND	ND	<0.10
Cr	<0.06	<0.06	<0.06 ^(c)	<0.1 ^(c)	<0.1 ^(c)	<0.06
Mn	0.09	0.11	0.12	0.10	0.11	0.68
Fe	0.31	0.12	0.10 ^(c)	0.06 ^(c)	0.06 ^(c)	2.34
Co	<0.05	<0.05	<0.05	<0.05	<0.05	0.05
Ni	<0.10	<0.10	<0.10	<0.10	<0.10	0.10
Cu	<0.03	<0.03	0.04	<0.04	<0.04	<0.04
Zn	0.90	0.23	0.24	0.16	<0.15	0.30
As	<0.10	<0.10	ND	ND	ND	<0.1
Se	2.60	<0.02	ND	ND	ND	0.29
Sr	16.2	14.3	14.5	13.3	14.3	17.4
Mo	0.50	0.22	0.20 ^(c)	<0.05 ^(c)	<0.05 ^(c)	<0.06
Cd	<0.02	<0.02	<0.02 ^(c)	<0.02 ^(c)	<0.02 ^(c)	0.02
Sb	<0.3	<0.30	<0.3	<0.3	<0.3	0.14
Ba	0.22	0.16	0.20	0.14	0.13	0.11
La	7.7	6.8	0.4	0.40	0.41	6.8
Pb	<0.04	<0.04	ND	ND	ND	<0.04
U	0.07	0.13	ND	ND	ND	0.10
pH (units)	7.72	7.68	7.70	7.66	7.68	7.49
Eh(mv)	+445	+420	+387	+404	+370	+265
Radionuclides (cps/ml) ^(b)						
⁵¹ Cr	DL	DL	DL	DL	DL	DL
⁵⁴ Mn	DL	DL	0.017	DL	DL	0.474
⁵⁹ Fe	DL	DL	DL	DL	DL	DL
⁷³ As	DL	DL	DL	DL	DL	DL
⁷⁵ Se	DL	DL	0.163	0.114	0.188	0.245
^{110m} Ag	DL	DL	DL	DL	DL	DL
¹⁰⁹ Cd	DL	DL	DL	DL	DL	DL
²¹⁰ Pb	DL	DL	DL	DL	DL	DL

(a) ND - not determined.

(b) DL - activity was below detection limit as determined by PEAK SEARCH® Nuclear Data, Inc., Schaumburg, IL 60196, December 22, 1978 version.

(c) Analysis reported was obtained on ICP but atomic absorption/graphite furnace is preferred method.

TABLE B.6. Chemical Composition of Vacuum Extractor Columns 22-23 Effluent (mg/l) at Selected Pore Volumes

Constituent	Cumulative Pore Volume					
	0.25	1.56	0.87	1.19	1.48	2.11
Li	0.24	0.34	0.29	0.35	0.24	0.43
B	0.08 ^(a)	0.04	0.05	<0.04	0.05	0.06
HCO ₃ /CO ₃	ND	ND	ND	ND	ND	ND
NO ₃	38.8	ND	ND	ND	15.0	21.2
F	2.0	ND	ND	ND	2.4	2.8
Na	107	102	118	180	273	455
Mg	244	247	244	263	262	282
Al	<0.3	0.38	0.44	<0.3	<0.3	<0.3
Si	20.5	18.4	17.1	16.5	15.4	14.6
P	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SO ₄	2480	2100	2280	2540	2980	3520
Cl	440	334	316	322	380	280
K	65	58	60	64	69	73
Ca	758	762	744	791	764	772
V	<0.10	ND	ND	ND	ND	<0.1
Cr	0.07	<0.1 ^(c)	<0.1 ^(c)	<0.1 ^(c)	0.12	<0.06
Mn	0.08	0.08	0.09	0.09	0.13	0.12
Fe	<0.1	0.10 ^(c)	0.07 ^(c)	0.26 ^(c)	0.36	<0.1
Co	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Ni	<0.1	<0.1	<0.1	0.19	<0.10	<0.10
Cu	<0.04	<0.04 ^(c)	<0.04 ^(c)	<0.04 ^(c)	<0.04	<0.04
Zn	0.25	0.28	0.21	0.37	0.14	0.10
As	<0.10	ND	ND	ND	<0.10	<0.10
Se	1.40	ND	ND	ND	0.02	0.08
Sr	13.0	12.9	12.7	13.9	13.7	14.3
Mo	0.53	0.51 ^(c)	0.40 ^(c)	0.51 ^(c)	0.17	0.06
Cd	<0.02	<0.02	<0.02 ^(c)	<0.02	<0.02	<0.02
Sb	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Ba	0.19	0.18	0.16	0.34	0.14	0.13
La	6.32	0.41	0.43	0.37	6.4	6.44
Pb	<0.04	ND	ND	ND	<0.04	<0.04
U	0.06	ND	ND	ND	0.11	0.10
pH (units)	7.88	7.70	7.61	7.68	7.65	7.68
Eh (mv)	+427	+393	+409	+367	+376	+349
<u>Radionuclides (cps/ml)</u>						
⁵¹ Cr	DL ^(b)	DL	DL	DL	DL	DL
⁵⁴ Mn	DL	DL	DL	DL	DL	0.026
⁵⁹ Fe	DL	DL	DL	DL	DL	DL
⁷³ As	DL	DL	DL	DL	DL	DL
⁷⁵ Se	DL	DL	DL	DL	DL	0.073
^{110m} Ag	DL	DL	DL	DL	DL	DL
¹⁰⁹ Cd	DL	DL	DL	DL	DL	DL
²¹⁰ Pb	DL	DL	DL	DL-L	DL	DL

(a) ND - not determined.

(b) DL - activity was below detection limit as determined by PEAK SEARCH[®] Nuclear Data, Inc., Schaumburg, IL 60196, December 22, 1978 version.

(c) Analysis reported was obtained on ICP but atomic absorption/graphite furnace is preferred method.

TABLE B.7. Chemical Composition of Vacuum Extractor Column 24 Effluent (mg/l) at Selected Pore Volumes

Constituent	Cumulative Pore Volume				
	0.29	0.55	0.81	1.07	1.34
Li	0.19	0.30	0.30	0.36	0.22
B	0.04	0.05	0.04	0.06	0.05
HCO ₃ /CO ₃	ND ^(a)	ND	ND	ND	ND
NO ₃	32.4	ND	ND	ND	8.8
F	1.8	ND	ND	ND	2.2
Na	96	108	106	133	188
Mg	232	243	229	238	261
Al	<0.3	<0.3	0.41	0.46	<0.3
Si	18.3	17.8	15.7	17.0	15.8
P	<0.5	<0.5	<0.5	<0.5	<0.5
SO ₄	2300	2220	2160	2280	2780
Cl	440	334	316	304	380
K	60	60	55	59	70
Ca	729	747	693	724	787
V	<0.1	ND	ND	ND	<0.10
Cr	<0.06	<0.06 ^(c)	<0.06 ^(c)	<0.06 ^(c)	0.11
Mn	0.08	0.08	0.11	0.09	0.11
Fe	<0.1	<0.1 ^(c)	0.12 ^(c)	<0.10 ^(c)	<0.1
Co	<0.05	<0.05	<0.05	<0.05	<0.05
Ni	<0.1	<0.1	<0.1	<0.1	<0.1
Cu	<0.04	<0.04 ^(c)	<0.04 ^(c)	<0.04 ^(c)	<0.04
Zn	0.16	0.17	0.29	<0.15	0.24
As	<0.10	ND	ND	ND	<0.1
Se	1.20	ND	ND	ND	<0.02
Sr	12.5	12.7	11.8	12.3	13.8
Mo	0.49	0.46 ^(c)	0.44 ^(c)	0.36 ^(c)	0.25
Cd	<0.02	<0.02 ^(c)	<0.02 ^(c)	<0.01 ^(c)	<0.02
Sb	<0.3	<0.3	<0.3	<0.3	<0.3
Ba	0.17	0.16	0.15	0.15	0.15
La	6.1	0.4	0.4	0.5	6.5
Pb	<0.04	ND	ND	ND	<0.04
U	0.08	ND	ND	ND	0.10
pH (units)	7.65	7.82	7.63	7.80	7.70
Eh (mv)	+415	+372	+387	+371	+359
Radionuclides (cps/ml)					
⁵¹ Cr	DL ^(b)	DL	DL	DL	DL
⁵⁴ Mn	DL	DL	DL	DL	DL
⁵⁹ Fe	DL	DL	DL	DL	DL
⁷³ As	DL	DL	DL	DL	DL
⁷⁵ Se	DL	DL	DL	DL	0.006
^{110m} Ag	DL	DL	DL	DL	DL
¹⁰⁹ Cd	DL	DL	DL	DL	DL
²¹⁰ Pb	DL	DL	DL	DL	DL

(a) ND - not determined.

(b) DL - activity was below detection limit as determined by PEAK SEARCH[®] Nuclear Data, Inc., Schaumburg, IL 60196, December 22, 1978 version.

(c) Analysis reported was obtained on ICP but atomic absorption/graphite furnace is preferred method.

TABLE B.8. Chemical Composition of Vacuum Extractor Columns 7, 13 and 14 Effluent at Selected Cumulative Pore Volumes

	Column 7 Cumulative Pore Volume											
	1.55	2.24	3.33	4.48	5.78	7.05	8.61	10.19	11.48	12.83	14.35	15.67
pH	7.85	7.86	7.71	7.70	6.90	5.39	4.06	3.84	3.79	3.78	3.76	3.70
Eh	+420	ND ^(b)	+402	+423	+154	+363	+480	+485	+481	+503	+451	+463
²¹⁰ Pb	DL ^(a)	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL
²²⁸ Ra	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL

	Column 13 Cumulative Pore Volume							
	0.32	0.92	1.32	1.70	2.21	2.72	3.14	3.57
pH	7.69	7.58	7.23	7.46	6.36	7.16	6.98	5.44
Eh	+377	+383	+174	+278	+272	+281	+255	ND
²¹⁰ Pb	DL	DL	DL	DL	DL	DL	DL	DL
²²⁸ Ra	DL	DL	DL	DL	DL	DL	DL	DL

	Column 14 Cumulative Pore Volumes		
	0.33	0.63	0.86
pH	7.64	7.67	6.80
Eh	+409	+411	+291
²¹⁰ Pb	DL	DL	DL
²²⁸ Ra	DL	DL	DL

(a) DL - activity was below detection limit as determined by PEAK SEARCH® Nuclear Data Inc., Schaumburg, IL, 60196, December 22, 1978 version.

(b) ND - not determined.

APPENDIX C

RADIONUCLIDE DISTRIBUTION RETAINED ON THE SEDIMENTS

TABLE C.1. Radionuclide Distribution in Vacuum Extractor Column Sediments at End of Experiment (cpm/g)

<u>Depth (mm)</u>	<u>⁵¹Cr</u>	<u>⁵⁴Mn</u>	<u>⁵⁹Fe</u>	<u>⁷³As</u>	<u>⁷⁵Se</u>	<u>^{110m}Ag</u>	<u>¹⁰⁹Cd</u>	<u>²¹⁰Pb</u>
<u>Columns 1-6 Mixed</u>								
0 - 18.1	2,433	12,473	3,636	66,167	30,902	27,526	2,023	277,952
18.1 - 36.2	2,324	11,852	1,962	7,478	1,888	1,426	2,682	8,526
36.2 - 54.2	2,154	10,764	1,171	354	223	DL	1,933	1,148
54.2 - 72.3	2,598	9,962	438	DL	84	DL	1,920	467
72.3 - 90.4	1,218	9,216	249	DL	143	DL	1,869	94
90.4 - 108.5	258	7,634	215	DL	123	DL	1,589	DL
<u>Columns 8-12 Mixed</u>								
0 - 18.1	66	6,568	369	DL	34.7	DL	1,348	19
18.1 - 36.2	18	6,660	265	DL	23.0	DL	1,873	DL
36.2 - 54.2	22	6,744	278	DL	44.1	DL	1,997	DL
54.2 - 72.3	DL ^(a)	7,594	304	DL	80.7	DL	2,659	DL
72.3 - 90.4	DL	7,010	156	DL	104.8	DL	3,084	DL
90.4 - 108.5	DL	7,424	274	DL	133.5	DL	3,304	DL
<u>Columns 15-18 Mixed</u>								
0 - 36.2	DL	18,174	60	DL	40.8	DL	1,811	DL
36.2 - 72.3	DL	14,698	15.2	DL	92.2	DL	734	DL
72.3 - 108.5	DL	5,006	DL	DL	121.3	DL	46	DL
<u>Columns 19-21 Mixed</u>								
0 - 36.2	DL	313	DL	DL	40	1.5	12	DL
36.2 - 72.3	DL	2.8	DL	DL	79	DL	DL	DL
72.3 - 108.5	DL	DL	DL	DL	336	DL	DL	DL
<u>Columns 22-23 Mixed</u>								
0 - 36.2	DL	9.7	DL	DL	51	DL	3.6	DL
36.2 - 72.3	DL	DL	DL	DL	28	DL	DL	1.2
72.3 - 108.5	DL	DL	DL	DL	60	DL	DL	DL
<u>Column 24</u>								
0 - 54.2	DL	2.3	DL	DL	5.7	DL	0.6	DL
54.2 - 108.5	DL	DL	DL	DL	6.8	DL	DL	DL

(a) DL - radioactivity below detection limit for PEAK SEARCH® isotope separation scheme.

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TABLE C.2. Radionuclide Distribution in Vacuum Extractor
Column Sediments at End of Experiment (cpm/g)

<u>Depth (mm)</u>	<u>^{210}Pb</u>	<u>^{228}Ra</u>
<u>Column 7</u>		
0 - 18.1	2,285,114	DL (a)
18.1 - 36.2	20,108	DL
36.2 - 54.2	5,636	DL
54.2 - 72.3	2,770	12.6
72.3 - 90.4	2,022	33.6
90.4 - 108.5	673	42.9
<u>Column 13</u>		
0 - 36.2	113	2.5
36.2 - 72.3	14	23.4
72.3 - 108.5	30	19.8
<u>Column 14</u>		
0 - 36.2	119	DL
36.2 - 72.3	4	25.6
72.3 - 108.5	5	29.7

(a) DL - radioactivity below detection limit.

APPENDIX D

SEMI-SELECTIVE EXTRACTION DATA

TABLE D.1. Volume of Extractant (mls) and Weight Data (g) Actually Used in Semi-Selective Extraction Scheme

Step	Sediment Sample								
	Columns 1-6						Columns 8-12		
	55-65	45-55	35-45	25-35	15-25	0-15	32-62	22-32	0-12
1	100	100	100	100	100	100	100	100	100
2	100	100	100	100	100	100	100	100	100
3	200	200	200	200	200	200	150	200	200
4	150	150	200	200	200	200	150	150	150
5	120	120	150	150	150	150	150	120	120
Starting Weight	5.000	5.000	5.004	4.999	5.005	4.995	5.005	5.000	5.000
Residual Weight	4.459	4.399	ND	ND	ND	ND	4.561	4.639	4.621
Weight Loss	0.541	0.601	---	---	---	---	0.444	0.361	0.379

Step	Sediment Sample						
	Columns 15-18	Columns 19-23	Column 7			Columns 13-14	Clay Liner
	0-62	0-62	51-61	31-41	0-31	0-62	Original
1	100	100	100	100	100	100	100
2	100	100	100	100	100	100	100
3	150	150	150	150	150	150	150
4	150	150	150	150	150	150	150
5	150	150	150	150	150	150	150
Starting Weight	5.003	4.995	4.999	5.000	5.004	5.003	5.000
Residual Weight	4.343	4.5310	4.302	4.332	4.471	4.651	4.515
Weight Loss	0.660	0.464	0.697	0.668	0.533	0.352	0.485

**TABLE D.2. ICP Analyses of Extract Solutions From Vacuum Extractor Columns
Shown in Figure 2 (mg/l)**

Element	Step	Depth (mm)										
		Columns 1-6					Columns 8-12			Columns 13-18	Columns 19-23	
		0-18,1	18,1-36,2	36,2-54,2	54,2-72,3	72,3-90,4	90,4-108,5	108,5-162,7	162,7-180,8	198,9-217,0	217,0-325,5	325,5-542,5
Al	1	22,3	28,4	19,3	23,6	19,7	12,1	18,5	4,9	3,5	<0,3	<0,3
	2	11,1	3,3	9,3	9,8	15,2	8,9	5,3	6,5	3,7	1,9	1,2
	3	1,9	1,4	2,2	5,0	6,8	5,1	2,4	3,8	4,0	2,2	2,8
	4	19	20	23	33	42	29	39	30	25	34	31
	5	80	84	82	92	112	78	48	86	89	65	64
Si	1	1,7	2,5	1,7	2,5	2,0	2,5	2,8	1,7	1,6	1,2	1,4
	2	0,9	0,6	1,6	1,8	2,3	2,1	1,1	1,3	1,1	1,0	0,6
	3	0,9	1,0	1,9	3,2	3,6	3,3	1,0	1,1	1,2	3,5	2,3
	4	4,4	1,2	2,0	10,9	15	11	17	13	12	18	19
	5	42	43	42	44	46	40	26	45	38	30	36
Ca	1	39,3	61,4	132	191	168	168	185	120	117	141	189
	2	12,2	3,7	17	18	35	20	19	58	44	23	19
	3	1,7	1,2	3,2	5,4	6,0	4,6	8,2	12,4	7,7	10,4	15,4
	4	0,2	0,2	0,0	0,0	0,3	0,0	0,8	0,1	0,0	0,0	0,1
	5	1,6	1,2	1,3	1,6	1,2	1,9	0,6	0,5	0,4	0,9	1,1
Mn	1	1,0	1,3	1,2	1,0	0,7	0,4	1,6	1,0	1,1	2,7	0,06
	2	0,4	0,1	0,2	0,1	0,2	0,1	0,2	0,6	0,5	0,5	0,08
	3	0,05	0,02	0,04	0,06	0,06	0,06	0,14	0,24	0,09	0,11	0,26
	4	0,06	0,08	0,11	0,14	0,22	0,18	0,32	0,34	0,37	0,74	0,31
	5	0,42	0,43	0,50	0,52	0,58	0,36	0,28	0,58	0,50	0,63	0,37
Fe	1	18,0	21,3	12,0	6,1	2,6	4,7	10,9	1,5	0,4	0,1	<0,05
	2	12,7	8,4	10,7	6,0	3,6	3,5	3,2	4,8	1,9	1,1	0,8
	3	12,0	10,0	16,0	13,4	10,0	5,6	12,2	17,0	11,4	5,4	6,2
	4	75	85	88	69	68	46	96	84	84	76	83
	5	146	148	136	140	154	66	78	148	154	90	102
Zn	1	1,0	0,8	0,7	0,6	0,6	0,6	1,0	0,9	1,0	0,6	0,3
	2	0,6	0,4	0,5	0,5	0,4	0,4	0,5	0,7	0,6	0,6	0,5
	3	0,3	0,3	0,3	0,3	0,3	0,3	0,3	0,3	0,2	0,1	0,5
	4	0,3	0,2	<0,2	0,3	0,3	0,3	0,5	0,4	0,5	0,5	0,5
	5	0,5	0,5	0,5	0,5	0,6	0,5	0,4	0,6	0,6	0,5	0,5
Sr	1	0,33	0,54	0,98	1,30	1,10	1,10	1,60	1,00	1,10	1,40	3,40
	2	0,12	0,04	0,19	0,17	0,31	0,21	0,21	0,58	0,47	0,34	0,31
	3	0,02	0,01	0,04	0,05	0,06	0,07	0,06	0,09	0,07	0,17	0,22
	4	<0,02	<0,02	<0,02	0,02	0,05	0,05	0,08	0,07	0,08	0,09	0,07
	5	0,06	0,07	0,05	0,07	0,08	0,08	0,05	0,11	0,11	0,11	0,08
Be	1	<0,02	0,34	0,16	0,20	0,10	0,14	0,12	<0,02	0,03	0,08	0,13
	2	0,09	0,11	0,24	0,21	0,23	0,24	0,12	0,16	0,14	0,12	0,08
	3	0,04	0,06	0,11	0,12	0,14	0,12	0,02	0,02	0,05	0,09	0,06
	4	0,04	0,04	0,04	0,04	0,13	0,06	0,19	0,11	0,13	0,12	0,13
	5	0,34	0,26	0,28	0,30	0,34	0,42	0,12	0,28	0,30	0,20	0,21

TABLE D.3. ICP Analyses of Extract Solutions From Vacuum Extractor Columns
Shown in Figure 3 (mg/l)

Element	Step	Depth (mm)			
		Column 7			Columns 13-14
		0-18.1	36.2-54.2	54.2-108.5	108.5-325.5
Al	1	20.0	14.8	39.0	<0.3
	2	14.7	11.2	8.1	3.5
	3	1.8	1.7	1.8	2.9
	4	19	30	35	40
	5	64	62	76	65
Si	1	0.7	0.8	1.0	0.7
	2	0.3	0.6	0.7	0.9
	3	1.6	1.6	1.6	4.4
	4	5.6	11	15	22
	5	38	34	40	36
Ca	1	106	91.5	173	112
	2	57	38	26	61
	3	6.2	7.2	7.2	10.0
	4	0.8	0.0	0.4	0.2
	5	0.6	0.2	1.1	0.5
Mn	1	1.6	0.9	2.1	1.5
	2	1.0	0.7	0.4	1.0
	3	0.09	0.09	0.09	0.44
	4	0.11	0.24	0.20	0.54
	5	0.32	0.28	0.32	0.35
Fe	1	12.5	8.4	13.3	0.1
	2	15.6	13.1	5.3	1.7
	3	6.4	5.0	5.0	6.2
	4	61	131	100	110
	5	115	110	112	92
Zn	1	0.8	0.6	0.9	0.6
	2	0.6	0.6	0.5	0.7
	3	0.3	0.3	0.3	0.13
	4	0.3	0.3	0.4	0.57
	5	0.5	0.4	0.4	0.48
Sr	1	0.78	0.62	1.40	1.60
	2	0.22	0.31	0.46	0.96
	3	0.07	0.10	0.10	0.22
	4	0.06	0.07	0.05	0.11
	5	0.09	0.07	0.04	0.08
Ba	1	<0.02	<0.02	0.09	<0.02
	2	0.02	0.03	0.07	0.16
	3	0.04	0.09	0.09	0.14
	4	0.07	0.06	0.12	0.14
	5	0.32	0.24	0.21	0.20

TABLE D.4. ICP Analyses of Extract Solutions From Original Morton Ranch Clay Liner (mg/l)

<u>Element</u>	<u>Step</u>	
Al	1	<0.3
	2	1.9
	3	1.6
	4	35.0
	5	63.0
Si	1	0.7
	2	1.3
	3	2.4
	4	22
	5	33
Ca	1	96
	2	72
	3	16.6
	4	0
	5	0.8
Mn	1	0.02
	2	0.10
	3	0.07
	4	0.30
	5	0.30
Fe	1	<0.05
	2	1.3
	3	3.6
	4	96.0
	5	95.0
Zn	1	<0.4
	2	0.5
	3	0.3
	4	0.4
	5	0.4
Sr	1	1.50
	2	1.20
	3	0.23
	4	0.04
	5	0.06
Ba	1	<0.02
	2	0.18
	3	0.08
	4	0.10
	5	0.22

TABLE D.5. XRF Analyses of Vacuum Extractor System 1 Sediments Before and After Selective Extraction

Element	Units	Type	Depth (mm)											
			Columns 1-4				Columns 5-12				Column 13-18		Column 19-23	
			0-18,1	18,1-36,2	36,2-54,2	54,2-72,3	72,3-90,4	90,4-108,5	108,5-162,7	162,7-180,8	198,9-217,0	217,0-325,5	325,5-542,5	
Al	%	B	6.22	6.42	6.04	6.03	7.03	6.92	6.32	6.85	6.32	6.42	6.28	
		A	5.67	5.75	5.88	5.71	7.42	7.00	7.04	7.06	6.64	6.74	6.83	
Si	%	B	32.3	31.7	32.1	31.4	31.6	32.6	31.4	31.8	31.6	32.4	30.8	
		A	31.1	32.3	34.1	35.0	34.5	35.1	32.1	32.9	34.0	39.8	30.8	
P	%	B	<0.41	<0.36	<0.37	<0.39	<0.36	<0.37	<0.36	<0.35	<0.39	<0.36	<0.37	
		A	<0.39	<0.35	<0.38	<0.34	<0.40	<0.37	<0.36	<0.35	<0.35	<0.35	<0.38	
S	%	B	<0.17	<0.15	0.33	0.39	0.52	0.36	0.40	0.40	0.31	0.45	0.24	
		A	<0.16	<0.15	<0.15	<0.15	<0.16	<0.15	<0.14	0.16	<0.15	<0.15	<0.15	
Cl	%	B	<0.09	<0.09	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	
		A	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	
K	%	B	1.71	1.76	1.73	1.70	1.73	1.81	1.71	1.81	1.75	1.77	1.77	
		A	1.71	1.75	1.68	1.71	1.74	1.67	1.71	1.68	1.70	1.76	1.67	
Ca	%	B	0.13	0.64	0.41	0.33	0.54	0.39	0.56	0.55	0.58	0.64	0.60	
		A	0.07	0.07	0.07	0.07	0.07	0.12	0.09	0.13	0.16	0.17	0.08	
Ti	%	B	0.34	0.34	0.33	0.34	0.34	0.35	0.35	0.35	0.34	0.34	0.34	
		A	0.34	0.34	0.34	0.37	0.37	0.38	0.37	0.36	0.37	0.36	0.35	
Fe	%	B	2.78	2.74	2.68	2.71	2.74	2.80	2.90	2.87	2.97	2.86	2.65	
		A	1.68	2.01	1.50	1.49	1.78	1.77	2.01	2.00	1.90	2.16	2.00	
V	ppm	B	147	86	141	109	57	91	62	98	54	100	62	
		A	58	86	80	54	80	83	94	70	58	107	56	
Cr	ppm	B	72	54	97	69	75	73	54	56	66	45	60	
		A	53	63	80	34	98	57	60	54	60	75	68	
Mn	ppm	B	168	140	162	159	176	196	175	193	219	332	151	
		A	93	95	76	69	86	71	100	107	110	167	107	
Co	ppm	B	<30	<30	<31	<30	<30	<31	<31	<31	<31	<30	<30	
		A	<23	<25	<22	<22	<24	<24	<25	<25	<24	<25	<25	
Ni	ppm	B	16.4	28.5	18.2	23.5	22.1	24.7	29.9	28.1	41.0	43.0	50.0	
		A	14.3	17.0	16.8	11.3	15.4	18.6	18.3	19.6	20.4	27.9	19.3	
Cu	ppm	B	18.8	22.7	18.8	26.6	37.8	37.1	25.9	23.4	24.3	23.6	23.6	
		A	13.2	15.5	11.5	16.6	26.1	25.0	13.1	18.0	16.9	21.8	19.9	
Zn	ppm	B	62.3	72.9	52.9	59.7	67.5	88.3	83.2	81.1	110.5	96.5	88.8	
		A	35.6	43.0	30.4	33.9	42.5	43.0	56.2	56.0	63.7	69.0	55.9	
Ga	ppm	B	13.8	13.0	13.4	14.5	14.8	13.7	14.5	13.4	14.7	13.2	14.3	
		A	11.9	13.1	10.8	10.9	12.3	11.5	13.7	13.1	13.1	12.8	12.9	
Hg	ppm	B	44.5	<4.4	<4.5	<4.4	<4.6	<4.6	<4.6	<4.5	<4.5	<4.5	<4.5	
		A	<5.9	<4.0	<3.8	<3.9	<4.1	<4.0	<4.0	<4.0	<4.2	<4.0	<4.0	
Sa	ppm	B	3.1	<0.8	2.5	<0.8	2.2	2.7	0.84	0.98	2.3	1.1	2.11	
		A	1.5	<0.8	<0.8	1.3	1.1	1.8	1.2	1.6	<0.8	1.5	<0.8	
Pb	ppm	B	13.2	17.5	15.6	25.2	22.6	19.6	18.1	20.1	17.1	20.4	17.2	
		A	8.9	8.0	7.3	10.7	8.1	11.8	11.6	12.2	11.6	13.3	13.0	
As	ppm	B	11.4	6.2	5.2	4.5	4.0	5.1	5.4	5.6	6.2	3.8	6.7	
		A	4.3	4.0	4.8	4.2	5.2	3.0	5.0	2.9	4.1	4.1	3.5	
Br	ppm	B	<0.7	<0.7	<0.7	<0.7	<0.7	<0.8	<0.8	<0.8	<0.8	<0.8	<0.7	
		A	<0.7	<0.7	<0.7	<1.0	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	
Rb	ppm	B	89.2	92.6	92.0	91.2	91.9	94.5	95.6	94.3	95.2	94.6	91.7	
		A	84.0	89.7	82.7	81.4	89.4	84.2	93.3	90.1	87.5	91.3	89.4	
Sr	ppm	B	49.8	114.0	62.2	66.4	76.3	75.0	84.6	83.0	90.0	120.1	130.0	
		A	36.3	38.8	37.4	33.1	39.5	37.2	41.4	43.2	43.7	54.8	41.0	
U	ppm	B	13.6	7.6	22.8	47.3	65.5	68.8	29.5	16.8	9.2	4.2	3.3	
		A	5.0	9.4	8.2	8.6	12.6	22.2	8.0	13.5	1.2	11.6	11.5	
Y	ppm	B	26.2	27.3	26.0	28.8	29.0	29.9	32.9	31.0	28.2	27.0	27.6	
		A	18.1	19.3	19.0	18.5	19.4	20.7	22.7	22.3	20.7	22.5	20.9	
Zr	ppm	B	297	297	314	317	314	333	317	316	320	303	316	
		A	270	270	310	348	264	318	299	281	282	306	281	
Nb	ppm	B	13.8	15.2	14.0	13.9	14.3	14.4	14.1	15.3	15.3	13.9	14.7	
		A	14.4	14.1	13.1	14.6	15.2	14.5	15.6	14.0	14.3	13.5	15.0	
Mo	ppm	B	4.6	4.7	4.5	6.8	4.8	5.5	5.7	5.6	6.4	3.6	5.0	
		A	3.7	4.3	5.1	5.8	4.3	4.1	4.9	4.3	4.3	4.5	4.0	
Ag	ppm	B	23.7	<5.8	25.7	21.2	31.1	16.0	21.4	32.8	39.6	10.4	<6.1	
		A	5.6	<6.1	<5.9	<6.4	<5.4	10.5	<6.5	<5.7	14.5	7.6	<5.6	
Sn	ppm	B	<5.5	<6.5	<7.0	<7.6	<7.7	<6.0	<7.9	<8.9	<7.6	<6.1	<6.8	
		A	<6.1	<7.0	<6.7	<7.2	<6.6	<7.2	<7.6	<6.3	<7.4	<7.8	<6.9	
Sb	ppm	B	9.0	13.2	16.0	<6.5	<6.4	<6.5	<6.6	<6.5	<6.4	10.0	<7.7	
		A	8.3	<7.9	<6.1	<6.0	<7.4	11.8	<6.4	7.9	<6.2	9.2	<6.1	
Te	ppm	B	<5.7	<7.0	<7.5	<7.6	<6.2	<6.3	<6.8	<6.7	<6.0	<7.0	<7.4	
		A	<7.0	<7.5	<7.3	<7.7	<7.2	<7.7	<6.3	<7.0	<6.1	<6.3	<7.5	
Ce	ppm	B	7.5	49.2	49.5	10.3	<11	14.8	<11	15.6	11.4	10.6	49.4	
		A	<8.6	9.5	8.8	49.3	49.2	12.8	49.9	<8.6	49.7	<11	49.2	
Ba	ppm	B	300	300	340	570	546	575	573	581	534	548	539	
		A	531	520	550	557	561	560	543	560	579	547	617	
La	ppm	B	40.6	39.7	41.9	46.7	30.6	48.4	37.6	51.1	32.9	45	42.2	
		A	40.8	34.2	26.6	30.1	32.0	27.6	41.1	40.6	32.0	46	36.2	
Ce	ppm	B	77.3	67.5	63.5	80.2	64.5	76.4	91	82	83.2	88.6	67.4	
		A	46.2	59.1	55.0	46.3	55.8	57.8	36.1	68	60.1	57.7	63.7	
Nd	ppm	B	34.3	36	50	32	39	48	<24	<25	29	23.8	29	
		A	27.5	<21	54	22	25	33	23	36	<23	33	<21	

B = Sediment content before selective extraction.

A = Sediment content after selective extraction (step 6 residue(s)).

TABLE D.6. XRF Analyses of Vacuum Extractor System 2 and Original Morton Ranch Clay Liner Sediments Before and After Selective Extraction

Element	Units	Type	Depth (mm)				Original Morton Ranch Clay Liner
			Column 7			Columns 13-14	
			0-18.1	36.2-54.2	54.2-108.5	108.5-325.5	
Al	%	B	6.00	6.10	5.77	6.38	6.42
		A	6.17	5.64	6.34	6.87	6.51
Si	%	B	29.7	30.9	30.2	31.4	31.70
		A	33.6	32.1	33.3	35.5	33.2
P	%	B	<0.40	<0.35	<0.31	<0.35	<0.36
		A	<0.39	<0.39	<0.36	<0.38	<0.38
S	%	B	0.75	0.93	0.68	0.42	<0.15
		A	<0.15	<0.16	0.25	<0.15	<0.15
Cl	%	B	<0.08	<0.08	<0.07	<0.08	<0.08
		A	<0.08	<0.08	<0.08	<0.08	<0.08
K	%	B	1.71	1.67	1.63	1.76	1.76
		A	1.75	1.70	1.73	1.78	1.68
Ca	%	B	0.60	0.67	0.53	0.59	0.64
		A	0.09	0.14	0.09	0.12	0.13
Ti	%	B	0.35	0.34	0.33	0.35	0.34
		A	0.36	0.35	0.35	0.37	0.37
Fe	%	B	2.62	3.00	2.74	2.86	2.74
		A	1.72	1.82	1.87	1.97	1.91
V	ppm	B	174	194	109	87	86
		A	79	69	73	57	64
Cr	ppm	B	74	85	85	73	54
		A	46	51	54	68	63
Mn	ppm	B	181	157	154	212	140
		A	97	89	95	94	99
Co	ppm	B	<29	<31	<30	<31	<30
		A	<23	<24	<24	<25	<24

TABLE D.6. (contd)

Element	Units	Type	Depth (mm)				Original Morton Ranch Clay Liner
			Column 7			Columns 13-14	
			0-18.1	36.2-54.2	54.2-108.5	108.5-325.5	
Ni	ppm	B	17.9	20.0	21.9	33.8	28.5
		A	15.4	13.4	16.1	17.0	20.7
Cu	ppm	B	17.8	16.3	26.1	23.6	22.7
		A	13.3	12.9	14.6	13.9	14.3
Zn	ppm	B	55.3	55.7	60.3	84.8	72.9
		A	35.5	36.7	40.9	52.2	54.5
Ga	ppm	B	14.5	12.6	12.1	14.3	13.0
		A	12.8	13.0	11.7	13.5	13.4
Hg	ppm	B	<4.4	<4.4	<4.4	<4.5	<4.4
		A	<4.1	<4.0	<4.0	<4.2	<4.1
Se	ppm	B	4.4	1.5	2.9	1.4	<0.8
		A	1.4	<0.8	1.5	0.9	<0.8
Pb	ppm	B	10.4	13.1	21.5	17.1	17.5
		A	9.1	9.4	11.3	13.4	13.1
As	ppm	B	11.8	7.6	5.4	6.3	6.2
		A	3.7	5.0	4.2	3.5	3.8
Br	ppm	B	<0.7	<0.8	<0.8	<0.8	<0.7
		A	<0.7	<0.7	<0.7	<0.7	<0.7
Rb	ppm	B	88.2	89.8	92.5	94.6	92.6
		A	88.9	87.4	88.7	88.9	89.7
Sr	ppm	B	71.5	75.2	73.1	111.7	114.0
		A	42.5	40.6	38.8	41.1	43.2
U	ppm	B	15.3	16.1	47.4	16.0	7.6
		A	9.7	7.2	10.2	9.0	6.8
Y	ppm	B	24.3	26.1	28.2	29.5	27.3
		A	18.2	20.2	20.4	21.3	21.9
Zr	ppm	B	295	301	357	314	297
		A	268	269	286	283	285

TABLE D.6. (contd)

Element	Units	Type	Depth (mm)				Original Morton Ranch Clay Liner
			Column 7			Columns 13-14	
			0-18.1	36.2-54.2	54.2-108.5	108.5-325.5	
Nb	ppm	B	13.7	14.2	13.9	15.8	15.2
		A	14.3	13.6	14.5	15.0	15.9
Mo	ppm	B	3.7	4.3	6.7	5.9	4.7
		A	4.2	4.0	5.2	4.1	3.6
Ag	ppm	B	<6.0	<6.3	<11	<7.1	<5.8
		A	<5.5	<5.3	<5.8	6.0	31.1
Sn	ppm	B	<6.5	<7.5	<12	<8.2	<6.6
		A	<6.4	<6.1	<7.4	<6.6	<7.7
Sb	ppm	B	<7.2	<8.5	<14	<9.1	13.2
		A	<7.4	9.2	<8.7	11.6	<8.4
Te	ppm	B	<7.5	<8.6	<13	<9.0	<7.0
		A	<7.2	<6.6	<7.8	<7.2	<8.2
Cs	ppm	B	<8.1	11.4	<16	<10	<9.2
		A	11.1	<8.6	<10	13.2	<11
Ba	ppm	B	491	517	581	544	500
		A	519	556	571	550	546
La	ppm	B	32.6	48.6	41	50.3	39.7
		A	22.6	34.2	32.7	28.4	30.6
Ce	ppm	B	68.7	59.9	77	76.2	67.5
		A	62.2	55.1	52.1	57.2	64.5
Nd	ppm	B	20.6	29.0	<35	<24	36
		A	32.3	<18	32	34	39

B = Sediment content before selective extraction.

A = Sediment content after selective extraction (step 6 residuals).

TABLE D.7. Student's t-Statistics on Difference Between Original and Residual Sediment Content Vacuum Extractor System 1 (Columns 1-6, 8-12,15-24)

Element	$\bar{D}$	S	t	Significance
Al	-0.05	0.45	-0.36	not significant
Si	-1.64	1.52	-3.58	significant at 99% level
P	below detection limits			
S	0.19	0.11	5.43	significant at 99% level
Cl	below detection limits			
K	0.04	0.06	2.52	significant at 95% level
Ca	0.43	0.13	10.79	significant at 99% level
Ti	-0.02	0.01	-4.25	significant at 99% level
V	16.45	37.67	1.45	not significant
Cr	3.40	15.43	0.73	not significant
Mn	86.54	32.13	8.93	significant at 99% level
Fe	0.96	0.23	14.15	significant at 99% level
Co	below detection limits			
Ni	10.37	4.84	7.11	significant at 99% level
Cu	7.56	3.33	7.53	significant at 99% level
Zn	26.39	8.32	10.52	significant at 99% level
Ga	1.56	1.13	4.58	significant at 99% level
Hg	below detection limits			
Se	0.58	0.94	2.04	significant at 90% level
Pb	8.37	3.34	8.31	significant at 99% level
As	4.21	5.90	2.37	significant at 95% level
Br	below detection limits			
Rb	5.44	3.22	5.60	significant at 99% level
Sr	45.91	22.22	6.85	significant at 99% level
U	15.89	21.42	2.46	significant at 95% level
Y	8.16	1.72	15.76	significant at 99% level
Zr	19.55	22.77	2.85	significant at 95% level
Nb	-0.21	0.96	-0.72	not significant
Mo	0.72	0.88	2.72	significant at 95% level

TABLE D.7. (contd)

Element	$\bar{D}$	S	t	Significance
Ag	14.02	10.36	4.49	significant at 99% level
Sn	below detection limits			
Sb	1.32	2.96	1.48	not significant
Te	below detection limits			
Cs	below detection limits			
Ba	-9.00	34.00	-0.88	not significant
La	6.32	8.34	2.51	significant at 95% level
Ce	20.21	11.50	5.83	significant at 99% level
Nd	6.51	9.43	2.29	significant at 95% level

$\bar{D}$ = average difference in before vs. after extraction for each element.

S = standard deviation.

$t = \bar{D} \cdot \sqrt{n}/S$.

n = 11.

Note: 10 degrees of freedom.

Note: A negative D means that the concentration of the element is greater in the residual sediment than the pre-extraction sediment.

TABLE D.8. Student's t-Statistics on Difference Between Original and Residual Sediment Content of Vacuum Extractor System 2 (Columns 7, 13 and 14)

Element	$\bar{D}$	S	t	Significance
Al	-0.94	1.08	-1.75	not significant
Si	-3.08	1.32	-4.65	significant at 99% level
P	below detection limits			
S	0.52	0.22	4.81	significant at 99% level
Cl	below detection limits			
K	-0.05	0.04	-2.31	significant at 95% level
Ca	0.49	0.04	25.78	significant at 99% level
Ti	-0.02	0.01	-3.14	significant at 98% level
V	71.50	46.18	3.10	significant at 98% level
Cr	24.48	13.23	3.70	significant at 99% level
Mn	82.23	26.13	6.29	significant at 99% level
Fe	0.96	0.15	13.16	significant at 99% level
Co	below detection limits			
Ni	7.93	6.18	2.57	significant at 95% level
Cu	7.28	3.93	3.70	significant at 99% level
Zn	22.70	6.61	6.87	significant at 99% level
Ga	0.63	0.89	1.40	not significant
Hg	below detection limits			
Se	1.43	1.12	2.54	significant at 95% level
Pb	4.73	3.82	2.47	significant at 95% level
As	3.67	3.04	2.42	significant at 95% level
Br	below detection limits			
Rb	2.80	2.70	2.08	significant at 90% level
Sr	42.13	19.16	4.40	significant at 99% level
U	14.68	15.08	1.95	significant at 90% level
Y	7.00	1.17	11.98	significant at 99% level
Zr	40.25	20.61	3.91	significant at 99% level
Nb	0.05	0.75	0.13	not significant
Mo	0.80	1.09	1.47	not significant
Ag	below detection limits			

TABLE D.8. (contd)

Element	$\bar{D}$	S	t	Significance
Sn	below detection limits			
Sb	below detection limits			
Te	below detection limits			
Cs	below detection limits			
Ba	-15.75	21.98	-1.43	not significant
La	13.65	6.07	4.50	significant at 99% level
Ce	13.80	9.74	2.83	significant at 98% level
Nd	-9.43	9.16	-2.06	significant at 90% level

$\bar{D}$ = average difference in before vs. after extraction for each element.

S = standard deviation.

t = $\bar{D} \cdot \sqrt{n}/S$.

n = 4.

Degrees of freedom = 3.

Note: A negative D means that the concentration of the element, is greater in the residual sediment than the pre-extraction sediment.

TABLE D.9. Radiocounting Data for Extract Solutions From Vacuum Extractor System 1 (pCi/ml)

Nuclide	Step	Depth (mm)										Columns 19-23
		Columns 1-5					Columns 6-12					
		0-18,1	18,1-36,2	36,2-54,2	54,2-72,3	72,3-90,4	90,4-108,5	108,5-162,7	162,7-180,8	180,8-217,9	217,9-325,5	
⁵¹ Cr	1	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL
	2	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL
	3	DL	DL	DL	62,9	DL	DL	DL	DL	DL	DL	DL
	4	96,2	136,4	97,1	71,8	149,2	DL	DL	DL	DL	DL	DL
	5	73,4	154,8	84,7	122,5	91,2	DL	DL	DL	DL	DL	DL
⁵⁴ Mn	1	525	629	586	456	295	121	275	159	144	276	1,3
	2	205	31,5	87	52	69	25	32	89	66	70	DL
	3	24,3	9,8	14	20	17	10	19	11	15	43	3,0
	4	23,3	24,6	22	28	28	23	30	39	35	60	2,3
	5	26,2	33,0	19	26	30	30	10	35	28	28	DL
⁵⁹ Fe	1	DL	DL	7	DL	DL	DL	21	DL	DL	34	DL
	2	DL	5	DL	DL	DL	DL	10	DL	DL	8	DL
	3	18	DL	12	DL	DL	DL	9	10	6	5	DL
	4	112	70	30	DL	DL	DL	12	11	3	0	DL
	5	80	45	7	5	DL	14	4	1	DL	24	DL
⁷⁵ As	1	25	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL
	2	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL
	3	52	9	DL	DL	DL	DL	DL	DL	DL	DL	DL
	4	3,303	208	11	DL	DL	DL	DL	DL	DL	DL	DL
	5	348	96	4	DL	DL	DL	DL	DL	DL	DL	DL
⁷⁹ Se	1	DL	DL	DL	DL	DL	DL	3	DL	DL	DL	DL
	2	DL	DL	DL	DL	DL	DL	DL	DL	7	DL	DL
	3	6	DL	DL	DL	DL	DL	DL	DL	0	9	DL
	4	315	10	0,4	DL	0,3	DL	1	DL	3	4	4
	5	11	2	DL	DL	DL	3	11	5	8	DL	DL
^{110m} Ag	1	757	47	DL	DL	DL	DL	DL	DL	DL	DL	DL
	2	315	10	DL	DL	DL	DL	DL	DL	DL	DL	DL
	3	30	0,7	DL	DL	DL	DL	DL	DL	DL	DL	DL
	4	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL
	5	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL	DL
¹⁰⁹ Cd	1	291	346	503	265	287	112	392	321	379	69	DL
	2	110	26	49	52	44	43	35	131	184	30	DL
	3	14	7	7	15	13	20	16	18	21	13	DL
	4	DL	17	16	15	10	8	21	15	27	DL	DL
	5	7	18	20	8	10	32	DL	30	27	DL	DL
²¹⁰ Pb	1	5,054	251	88	28	16	DL	6	DL	DL	DL	4
	2	1,674	33	13	8	5	DL	6	3	2	4	DL
	3	224	3	2	DL	DL	DL	DL	4	DL	DL	DL
	4	4,571	75	37	DL	DL	3	DL	2	12	DL	2
	5	18,087	496	23	11	DL	DL	DL	DL	4	DL	DL

DL - activity was below detection limit as determined by PEAK SEARCH® Nuclear Data, Inc., Schaumburg, IL 60196, December 22, 1978 version.

TABLE D.10. Radionuclide Data for Extract Solutions from Vacuum Extractor System 2 (pCi/ml)

Nuclide	Step	Depth (mm)			
		Column 7			Columns 13-14
		0-18.1	36.2-54.2	54.2-108.5	108.5-325.5
^{210}Pb	1	6,085	DL	167	DL
	2	5,308	11	30	DL
	3	145,471	4	14	DL
	4	14,304	85	25	22
	5	114,706	315	59	129
^{228}Ra	1	DL	DL	DL	DL
	2	DL	DL	DL	DL
	3	DL	DL	DL	DL
	4	DL	DL	DL	DL
	5	DL	DL	DL	DL

DL - activity was below detection limit as determined by PEAK SEARCH®
Nuclear Data, Inc., Schaumburg, IL 60196, December 22, 1978
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TABLE D.11. Radiocounting Data for Sediments From Vacuum Extractor System 1 and 2 (pCi/g)

		Depth (mm)										
Nuclide	Type	Columns 1-6						Columns 8-12			Columns 15-18	Columns 19-23
		0-18.1	18.1-36.2	36.2-54.2	54.2-72.3	72.3-90.4	90.4-108.5	108.5-162.7	162.7-180.8	198.9-217.0	217.0-325.5	325.5-542.2
⁵¹ Cr	B	4,584	5,810	3,487	4,669	1,826	317	DL	DL	DL	DL	DL
	A	233	463	267	672	313	261	DL	DL	DL	DL	DL
⁵⁴ Mn	B	8,816	8,376	8,211	7,609	6,274	6,437	5,020	5,428	5,401	9,828	42
	A	476	1,022	551	818	1,059	2,808	16	1,205	1,846	3,645	1,001
⁵⁹ Fe	B	3,605	2,604	1,134	435	218	213	382	388	323	76	DL
	A	486	550	132	62	66	108	DL	41	60	25	DL
⁷⁵ As	B	125,592	9,388	145	DL	DL	DL	DL	DL	DL	DL	DL
	A	15,220	2,961	41	DL	DL	DL	DL	DL	DL	DL	DL
⁷⁹ Se	B	8,226	370	43	21	34	48	11	20	35	29	26
	A	3,938	250	20	19	17	35	11	15	27	19	8
^{110m} Ag	B	12,631	673	DL	DL	DL	DL	DL	DL	DL	DL	DL
	A	7,091	278	DL	DL	DL	DL	DL	DL	DL	DL	DL
¹⁰⁹ Cd	B	11,048	6,043	6,606	6,194	4,910	5,690	6,122	7,029	9,065	2,328	DL
	A	285	572	388	534	704	1,897	251	1,448	3,107	827	779
²¹⁰ Pb	B	13,594	27,424	4,703	2,209	319	DL	DL	DL	DL	DL	45
	A	5,967	17,520	1,112	286	DL	DL	3,847	70	572	99	56

Depth (mm)					
		Column 7	Columns 13-14		
		0-18.1	36.2-54.2	54.2-108.5	108.5-325.5
²¹⁰ Pb	B	5,794,609	24,534	10,751	264
	A	955,762	18,971	4,262	1,453
²²⁸ Ra	B	DL	DL	DL	DL
	A	DL	DL	DL	DL

B = Sediment content before selective extraction.

A = Sediment content after selective extraction (step 6 residuals).

DL = activity was below detection limit as determined by PEAK SEARCH®

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16. ABSTRACT (200 words or less) We discuss progress on the development of laboratory tools to aid in the prediction of migration potential of contaminants present in acidic uranium mill tailings leachate. Further, empirical data on trace metal and radionuclide migration through a clay liner are presented. Acidic uranium mill tailings solution was percolated through a clay liner. These laboratory columns and subsequent sediment extraction data show: 1) As, Cr, Pb, Ag, Th and V migrate very slowly; 2) U, Cd, Ni, Zn, Fe, Mn and similar transition metals are initially immobilized during acid neutralization but later are remobilized as the tailings solution exhausts the clay liner's acid buffering capacity. Such metals remain immobilized as long as the effluent pH remains above a pH value of 4 to 4.5 but they become mobile once the effluent pH drops below this range; and 3) fractions of the Se and Mo present in the influent tailings solution are very mobile. Possible controlling mechanisms for the pH dependent immobilization-mobilization of the trace metals are discussed. Using several column lengths (from 4.5 to 65 cm) and pore volume residence times (from 0.8 to 40 days) we found no significant differences in contaminant migration rates or types and extent of controlling processes. Thus, we conclude that the laboratory results may be capable of extrapolation to actual disposal site conditions.			
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