



Solubility and Leaching of Radionuclides in Site Decommissioning Management Plan (SDMP) Soil and Ponded Wastes

Pacific Northwest National Laboratory

**U.S. Nuclear Regulatory Commission
Office of Nuclear Regulatory Research
Washington, DC 20555-0001**



Solubility and Leaching of Radionuclides in Site Decommissioning Management Plan (SDMP) Soil and Ponded Wastes

Manuscript Completed: May 2003

Date Published: June 2003

Prepared by

A.R. Felmy, V.L. LeGore, S.A. Hartley

Pacific Northwest National Laboratory

P.O. Box 999

Richland, WA 99352

P. Reed, NRC Project Manager

Prepared for

Division of Systems Analysis and Regulatory Effectiveness

Office of Nuclear Regulatory Research

U.S. Nuclear Regulatory Commission

Washington, DC 20555-0001

NRC Job Code W6409



ABSTRACT

Samples of disposed wastes from one former and two current U.S. Nuclear Regulatory Commission Site Decommissioning Management Plan Sites, labeled Sites D, E, and F, were studied to determine 1) the key radionuclides and their concentrations present in the waste, 2) the solubility limits and solubility limiting phases for these radionuclides, 3) the rate of attainment of solubility equilibrium, 4) the observed leaching rate for radionuclides that may or may not be solubility controlled, and 5) identify, if possible, the potential for radiocolloid formation. To achieve these goals, batch studies were conducted over ranges of solution pH values (2–12), solid to solution ratio, and particle size. In addition, flow-through column studies were conducted of selected samples to help verify the mechanisms and predictive relations identified in the batch experiments. The results show that the major radionuclides present in the wastes varied widely between the three sites.

At all three sites, comparisons of filtered and unfiltered analyses of samples from either flow-through columns or well waters did not show any evidence of radiocolloids. At Site F, certain well samples contained very high concentrations of iron oxide particles. However, these particles did not show any clear evidence of high radionuclide content.

Maximum dissolved concentrations (solubility limits) and radionuclide-leaching rates have been calculated for use in performance assessment calculations at all three sites. Observed Th concentrations at Site D were quite low; the maximum Th solubility was 3.2×10^{-8} M. U solubilities at Site D, 1.6×10^{-5} M, were the highest observed at any of the sites. The leaching rates at Site D for Th and U were calculated to be 3.1×10^{-9} g U/hr and 1.4×10^{-6} g U/hr, respectively. At Site E the Th solubilities and leach rates were also quite low, 3.16×10^{-9} M, and 1.5×10^{-10} g Th/hr, respectively. The solubilities and leach rates for U at Site E were also quite low, 3.16×10^{-9} M and 1.6×10^{-10} g U/hr, respectively. At Site F, the principal radionuclides retained in the soil were Cs-137 and Ra-226. The maximum observed solubilities for these radionuclides were 1.8×10^{-14} M and 8.5×10^{-12} M respectively. Maximum leach rates were 1.5×10^{-17} g/hr and 2.2×10^{-13} g/hr for Cs-137 and Ra-226 at Site F.

Statistical analysis of the observed solubilities was hampered by the generally very low solubilities (at or below the analytical detection limit) found for the radionuclides. Only the following means and standard deviations, assuming a normal distribution, were calculated:

Site D – U (8.9×10^{-6} M \pm 6.9×10^{-6})

Site F – Cs-137 (1.6×10^{-14} M \pm 2.4×10^{-15}), Ra-226 (3.0×10^{-12} M \pm 3.9×10^{-12}).

CONTENTS

ABSTRACT	iii
EXECUTIVE SUMMARY	ix
ABBREVIATIONS	xi
1. INTRODUCTION	1
2. SITE SAMPLING AND SAMPLE SELECTION.....	3
3. METHODS AND MATERIALS.....	7
3.1 Chemical Analysis Procedures	7
3.2 Radiological Analysis	7
3.3 Solubility and Batch Studies.....	8
3.4 Column Studies.....	9
3.5 Radiocolloids	9
4. RESULTS AND DISCUSSION	11
4.1 Chemical Analysis	11
4.2 Radiological Analysis.....	17
4.2.1 Site D	17
4.2.2 Site E.....	19
4.2.3 Site F	22
4.3 Solubility, and Leaching Studies	26
4.3.1 Site D	26
4.3.2 Site E.....	31
4.3.3 Site F	35
4.4 Calculations of Solubility Limits and Leaching Rates	40
4.4.1 Site D	41
4.4.2 Site E.....	41
4.4.3 Site F	42
4.5 Radiocolloids	42
4.6. Statistical Analysis.....	43
5. REFERENCES	45

APPENDIX

A TABLES OF EXPERIMENTAL DATA.....	A-1
------------------------------------	-----

FIGURES

3-1. Schematic of Column Apparatus.....	10
4-1. Alpha Spectra of Highest Activity Site D Sample. Th-232 and Daughters Present Only at Very Low Levels.....	19
4-2. Alpha Spectra of Sample K3 from Site E.....	22
4-3. Gamma Spectra of Soil Samples at Site F. a) Soil 2S, b) Soil 5S, and c) Soil 6S.	24
4-4. Total (T) Th Concentrations (moles/l) in Site D Solubility Studies.....	28
4-5. Total (T) U Concentrations (moles/l) in Site D Solubility Studies.	29
4-6. Total (T) U Concentrations (moles/l) in Site D Batch Leaching Studies.....	30
4-7. Total (T) Thorium and U Concentrations (moles/l) in Site D Column Studies.	30
4-8. Total (T) Th Solubilities (moles/l) in Site E Sample K2.....	32
4-9. Th-232 Daughters Solubilized in the Solubility Studies of Site E Sample K2.	32
4-10. Cs-137 Activities in Site F Soil Sample Solubility Studies.	36
4-11. Measured Radium-226 and Bismuth-214 Activities and Uncertainties for all Solubility, Batch Leaching, and Column Samples Between pH Values of 5 to 10 from Site F.	40
4-12. Statistically Simulated Distribution of Uranium Concentration at Site D Using Only the Mean and Standard Deviation of the Four Column Data Points.	44

TABLES

2-1. Description of Site Sampling and Well Locations at Site E.....	3
2-2. Description of Soil Sample Locations at Site F.....	4
4-1. Chemical Composition of Samples at Sites E (see Table 2-1) and D.	12
4-2. Chemical Composition with Depth for Core 46 (Location G) at Site E.	13
4-3. Chemical Analysis of Water and Well Samples at Site E (see Table 2-1).....	14
4-4a. Calculated Aqueous U(VI) Species in Surface and Well Waters at Site E.	15
4-4b. Calculated Aqueous U(VI) Species in Surface and Well Waters at Site E.....	15
4-5. Chemical Analysis of Soils and Sediments Site F. (2 sheets).....	15
4-6. Inorganic Chemical Analysis of Well and Surface Waters at the Site F.....	16
4-7. Volatile Organic Carbon Analysis of the Water Samples at the Site F (ug/l).....	17
4-8. Radiological Analysis of the Highest Activity Soil Sample at Site D.	18
4-9a. Radiological Analysis (Gamma Spectroscopy) of Wastes (Samples K1-K5) at Site E.	20
4-9b. Radiological Analysis (Gamma Spectroscopy) of Wastes (Core 46) and Plant Material at Site E.....	21
4-10. Radiological Analysis of Wastes at Site E.	21
4-11. Radiological Analysis of Soil and Vegetative Samples at Site F (pCi/g).	25
4-12. Radiological Analysis of the Water Samples at Site F (pCi/L).....	25
4-13. Calculated Aqueous Ni and U(VI) Species in Well Waters at Site F.	26
4-14. Measured pH Values in Batch Leaching Studies at Site D as a Function of Time.	27
4-15. Thorium Concentrations in Batch Leaching Studies of Site D Sample in the Absence of CO ₂	27
4-16. Chemical Analysis of Batch Leaching Studies for Samples from Site E.....	34
4-17. Chemical Analysis of Column Studies for Site E Samples.....	35

4-18. Ra-226 and Daughter Activities in Site F Solubility Studies.	37
4-19. Ra-226 and Daughter Activities in Site F Batch Leaching Studies.	38
4-20. The pH Values in Site F Batch Leaching Studies.	39
4-21. Radionuclide Concentrations in Site F Column Studies.	39
4-22. Summary of Solubility and Leaching Rate Calculations at Each Site.	42
4-23. Filtered and Unfiltered Thorium and Uranium Concentrations in Column Studies.	43

EXECUTIVE SUMMARY

Each year the U.S. Nuclear Regulatory Commission (NRC) receives requests to discontinue Site Decommissioning Management Plan (SDMP) Sites that involve the use of radioactive materials. However, the termination of some licenses and the possible release of the site for unrestricted or other uses are sometimes nonroutine owing to the level, volume, or complex nature of the radiological contamination. In such cases, a clearer scientific understanding of the nature, both physical and chemical, of the radiological contamination is required to make informed judgments as to the level of site remediation that may be required. As part of such an overall effort, this report summarizes the findings from solubility, batch, and soil/waste column studies conducted on wastes from one former and two current NRC Site Decommissioning Management Plan (SDMP) Sites. These studies were designed to determine 1) the key radionuclides and their concentrations present in the waste, 2) the solubility limits and solubility limiting phases for these radionuclides, 3) the rate of attainment of solubility equilibrium, 4) the observed leaching rate for radionuclides that may or may not be solubility controlled, and 5) identify, if possible, the potential for radiocolloid formation.

The results show that the major radionuclides present in the wastes varied widely between the different sites depending upon the specific application and the disposal practices. At two of the sites where radioactive slags or depleted U were disposed, the dominant radionuclides were Th and U with their associated daughter products. At Site D, U and associated daughters were the dominant radionuclides present. Th was present at only very low concentrations. At Site E, the samples contain depleted U and no solubility-controlling phase was present. Adsorption or ion exchange processes appear to control the leachable U concentrations in these samples. At Site E, Th and associated daughters were the dominant radionuclides. Th daughters were in secular equilibrium with the parent Th-232 in all samples. Analysis of data from solubility studies indicated that aqueous Th concentrations are solubility controlled, most likely by amorphous ThO₂(am). ThO₂(am) sets upper limits on the dissolved Th concentrations.

At the third site, Site F, several different radionuclides were present owing to the wide range of manufacturing activities conducted at the site. These varied activities resulted in the release of several different radionuclides including: H-3, Sr-90, Cs-137, Ni-63, and Ra-226. H-3 and Sr-90 were the dominant radionuclides found in the groundwater and Cs-137 and Ra-226 (with associated daughters) were the dominant radionuclides found in the soil samples. Ni-63 was present at relatively low activity (< 12 pCi/g) in the soil samples.

Comparisons of filtered and unfiltered analyses of effluent samples from flow-through columns from Site D did not show any evidence for the presence of radiocolloids, nor did analysis of filtered and unfiltered well water samples at Sites E and F. Maximum dissolved concentrations (solubility limits) and radionuclide-leaching rates have been determined for use in performance assessment calculations for all three sites.

Statistical analysis of the solubility and leaching data was hampered by low solubilities for the majority of the radionuclides found at the sites. Only limited statistical analysis was possible for U at Site D and for Cs-137 and Ra-226 at Site F.

These results provide experimental evidence on the nature of the contamination present at these sites and the range of conditions under which the radionuclides are likely to be either soluble and mobile in the groundwater or insoluble and immobile. Such results will likely assist in the evaluation of effective remediation strategies for these sites.

ABBREVIATIONS

Ac	actinium
Al	aluminum
(am)	amorphous
AS	alpha spectroscopy
Bi	bismuth
(c)	crystalline
Ca	calcium
Ci/ml	curies per milliliter
DMG	Dimethylglyoxime
Fe	iron
g	gram
GC	gas chromatography
GM	Gieger-Müller
IC	ion chromatograph
ICP	inductively coupled plasma spectroscopy
ICP-MS	inductively coupled plasma mass spectrometry
keV	one thousand electron volts
KP	kinetic phosphorescence
LSC	liquid scintillation counting
m	meter
mg	magnesium
mg/l	milligrams per liter
ml	milliliter
Mo	molybdenum
MS	mass spectrometry
Nb	niobium
NRC	U.S. Nuclear Regulatory Commission
ORISE	Oak Ridge Institute for Science and Education
Pb	lead
pCi/g	picocuries per gram

pH	negative log of the activity of H ⁺
PNNL	Pacific Northwest National Laboratory
ppm	parts per million
Ra	radium
Rn	radon
SDMP	Site Decommissioning Management Plan
Si	silicon
Ta	tantalum
Th	thorium
U	uranium
VOC	volatile organic compound
XRF	x-ray fluorescence
Zr	zirconium

1. INTRODUCTION

The U.S. Nuclear Regulatory Commission (NRC) has identified 25 SDMP materials facilities that are undergoing non-routine decommissioning (NRC 2002). All of these sites require some degree of remediation before sites can be released for unrestricted use. As a result, the NRC is currently in the process of conducting performance assessments of these sites to better ascertain the potential for radionuclides solubilization, leaching, or migration offsite. As part of this overall effort, the Pacific Northwest National Laboratory (PNNL) was contracted to obtain selected samples from different Site Decommissioning Management Plan (SDMP) sites and conduct batch and flow-through column leaching studies of these wastes to determine the radionuclides present in the waste, the maximum leachable concentrations (solubility limits) for important radionuclides, the time required for radionuclides to reach solubility equilibrium, the overall radionuclide leaching rates, and, if possible, identify the potential impact of colloids in transporting radionuclides.

This report presents detailed results of PNNL studies on one former and two current SDMP soil or ponded waste sites labeled Sites D, E, and F.

The waste at Site D primarily consists of DU mixed with soil and other material. The facility at Site E was used to smelt Mg/Th metal alloys from 1958 to about 1970. The Mg was recovered and used for underground cathode protection. The Th containing slag was broken up, crushed, and disposed (sluiced) into a 5-acre retention pond adjacent to a creek (no name creek). The disposal site occupies approximately 10 acres and is comprised of an upgradient freshwater pond, a 5-acre retention pond, and an old grass covered reserve pond. Previous site surveys show approximately 2 million ft³ of radioactive soil/sludge with >50pCi/g radioactivity. The site has been extensively sampled and contour plots of radioactivity levels have been determined and were shown to the sampling team by site personnel.

The principal radionuclides released at Site F were H-3, Sr-90, Cs-137, and Ra-226. The site is adjacent to a river, which has periodically flooded and redistributed the radionuclides. The groundwater gradient is generally from the site toward the river. There is also an old, mostly filled-in barge canal than ran between the main buildings at the site and the river. This canal served as a partial disposal basin during site operations. One of the sampling sites, designated S6, is located in the old canal and is labeled "East Lagoon" on previous maps of the site. There are an extensive number of sampling wells that have been drilled at the site. The sampling team utilized a subset of these wells to obtain current groundwater samples.

The following sections of this report describe site sampling and sample selection, chemical analysis, radiological analysis, solubility and leaching studies, and investigations of radiocolloids.

2. SITE SAMPLING AND SAMPLE SELECTION

The Oak Ridge Institute for Science and Education (ORISE) collected samples from Site D. PNNL received five samples. All samples consisted of a fine brown clay material with a consistent total U concentration (reported by ORISE)¹ varying from 14 to 39 pCi/g. A total of 18 samples from Site E were collected by PNNL and NRC staff on September 14 and 15, 1998. These samples consisted of five surface slag/sludge samples (depth 0–2’), six samples from a previously collected core (0–20’), four samples of pond/pore water, two stream samples, and one sample of plant material. In addition, staff collected four well samples from A&M Engineering and Environmental Services, Inc.² from locations up gradient and down gradient of the retention pond. The slag/sludge samples collected within the retention pond were from the locations identified as “hot spots” on the licensee map of site contamination. The sampling team verified the location of these hot spots using a Gieger-Müller (GM) counter. Table 2-1 presents a summary of the collected samples.

Table 2-1. Description of Site Sampling and Well Locations at Site E.			
Sampling Location	Material Collected	Sampling Notes	Sample Labels
Site A	Pond water	Small pond next to peninsula	KW-1
Site B	Surface material	Whitish coloration	K1 and K1 rock
Site C	Slag/sludge, pore water, and plant material collected	Depth 18 in. pH 9.5, edge of hot spot	K2, KW-2, marsh grass
Site D	Slag/sludge and pore water collected	Depth 18in. pH 9.7	K3, KW-3
Site E	Outlet from freshwater pond	pH 8.7	KWP-1
Site F	Large pond in “retention pond”	pH 8.8	KW-4
Site G	Surface material	Approximate location of core 46 and hot spot near fence line	K4
Site H	Surface material	Gathered from highest GM reading at bare spot in reserve pond	K5 and K5 rock
Site I	Stream sample at weir	pH 8.9	KWP-2
Site P10	Well sample (WD = 8.44 ft)	pH(6.72-6.83)	P-10
Site MWD-4	Well sample (WD = 8.53 ft)	pH(6.80-6.83)	MWD-4
Site MWD-5	Well sample (WD = 11.94 ft)	pH(8.41-8.49)	MWD-5
Site MWD-8	Well sample (WD = 5.29 ft)	pH(7.67-7.74)	MWD-8

¹Personal communication from Wade Adams (ORISE).

² A&M Engineering and Environmental Services, Inc., Tulsa, Oklahoma.

At Site F, soil and water samples were collected on June 4, 2002. A total of seven soil samples, eight water samples, and one vegetative sample were collected. In addition, aliquots of the water samples were filtered in the field to obtain information on the dissolved versus particulate fraction. Measurements of the pH, Eh (redox potential), and conductivity were also made at the time of sampling whenever possible. A brief description of the samples is given in Tables 2-2 and 2-3.

Table 2-2. Description of Soil Sample Locations at Site F.		
Sample Designation	Location	Sampling Notes
S1	Northwest corner of plastics machine shop	--
S2	Adjacent to 8 x 8 block building	2000 uR/hr – top of grass, 2600 uR/hr at soil level
S3	Old garage site	1000 uR/hr beta/gamma, 300 uR/hr beta
S4	Under main building loading dock	500 uR/hr beta/gamma, 200 uR/hr beta
S5	Southwest corner of lacquer storage site, same as State of PA site	2500 uR/hr beta/gamma, 800 uR/hr beta
S6	East Lagoon	In dug hole contacting water
S7	Near licensee well 5, at outfall	--
V1	Same as S5	Strawberries

Table 2-3. Water Samples Collected at Site F.		
Sample Designation	Location	Sampling Notes
1L	East Lagoon, dug hole	pH = 6.4 Conductivity = 493 uS Eh (uncorrected) = -25mV Eh (corrected) = 166 mV
2L	East Lagoon, surface water	pH = 7.4 Conductivity = 412 uS Eh (uncorrected) = 210mV Eh (corrected) = 401 mV
3GW	Licensee Well A	pH = 7.7 Conductivity = 273 uS Eh (uncorrected) = 270mV Eh (corrected) = 461 mV
4GW	Licensee Well 3	pH = 6.35 Eh (uncorrected) = 317.5mV Eh (corrected) = 509 mV
5RW	River water	pH = 7.33 Eh (uncorrected) = 273mV Eh (corrected) = 464 mV
6GW	Well M4	pH = 5.64 Eh (uncorrected) = 137.4mV Eh (corrected) = 329 mV Large amounts of red iron oxide present in sample
7GW	Well M10	pH = 6.44 Eh (uncorrected) = 71.5mV Eh (corrected) = 263 mV Large amounts of red iron oxide present in sample
8GW	Well G	pH ~6 (pH paper) Eh (uncorrected) = 284.2mV Eh (corrected) = 476 mV
(a) Corrected Eh corresponds to the field Eh meter reading adjusted versus the normal hydrogen electrode (NHE).		

3. METHODS AND MATERIALS

The following discussion provides more details on the analysis procedures and sample preparation for the solubility, batch, and column studies.

3.1 Chemical Analysis Procedures

The pH measurements were performed using a combination glass electrode (Ross) calibrated with buffers at pH 4, 7, and 10. Conductivity was measured with a Pharmacia Biotech[®] conductivity meter and compared to KCl standards with a range concentration, of 0.001 M to 1.0 M. The Eh was measured with a Bradley James[®] Eh electrode. Anion analysis was performed using a Dionex DX6004 Chromatographic System[®]. Inorganic carbon analysis was performed using a Dohrman Model D-89[®]. Alkalinity titrations were performed using a Denver Instrument[®] 295 titrator, titrated to a pH 4.5 end point (method 403 in *Standard Methods for the Examination of Water and Wastewater* [Clesceri et al. 1999]). Analysis of cations was performed using an inductively coupled plasma (ICP) unit. High-purity calibration standards were used to calibrate and verify calibration (EPA Method 6010 B). A volatile organic carbon (VOC) analysis was performed by Severn Trent Services³ using gas chromatography (GC)/mass spectrometry (MS).

Total chemical analysis of solid materials was performed by energy dispersive x-ray fluorescence (XRF) with low (parts per million [ppm]) detection limits for most elements from Al to Ce. Chemical analysis of solutions was performed by ICP analysis, except for samples with low concentrations of Th, U, or Nb, which were determined by inductively coupled plasma mass spectrometry (ICP-MS). Surface area analysis was conducted using a Micrometrics Model 2010 Brunauer-Emmett-Teller[®] analyzer.

All analysis was performed under guidelines provided in PNNL Quality Assurance good practices procedures: ICPMS (PNNL-AGC-415), ICP (PNNL-AGG-ICP-AES); IC (EPA Method 300, *The Determination of Inorganic Anions in Water by Ion Chromatography*); and XRF (use of NBS standard reference materials).

3.2 Radiological Analysis

Gamma spectroscopy analysis of solid and solution samples was conducted using a high-efficiency intrinsic germanium detector calibrated over the energy range 60 to 2000 keV. The following energy peaks were used to determine the radionuclide concentrations: Ac-228, 911 keV; Bi-212, 727 keV; Pb-212, 239 keV; Ra-226, 186 keV; Bi-214, 609 keV; Pb-214, 352 keV; Th-234, 62.3 keV. All analyses were performed on duplicate or triplicate samples.

Selected samples were also submitted for analysis of isotopic ratios by alpha spectroscopy (AS) (Th) and kinetic phosphorescence (KP) (U). To separate the U, the samples were dissolved in HCl and passed through anion exchange columns. The columns were washed with concentrated

³ Severn Trent Services, St. Louis, Missouri.

HCl, then 6M HCl + NH₄I. U was then eluted with dilute nitric acid. Th samples required extra fusions with KOH and K₂S₂O₇ to assure all of the thorium minerals had dissolved. The Th from the fusion solutions was collected on NdF₃, then fumed with sulfuric acid to eliminate the fluoride. The Nd (with Th) was re-precipitated with strong base to separate the sulfate and then dissolved in nitric acid. Th was then separated on a nitrate anion exchange column. The product solution was then measured for Th by AS.

In the case of samples from Site F, samples for H-3 were analyzed by distillation followed by liquid scintillation counting (LSC) and samples for Sr-90 were analyzed by ion exchange, elution, and LSC. Selected samples for Ra-226 were analyzed by BaSO₄ precipitation, separation onto membrane filters and subsequent counting by AS.

Ni-63 was determined in the soil samples by first treating the material with concentrated HNO₃ to destroy the organics, evaporation to dryness, followed by redissolution in HCl. Dimethylglyoxime (DMG) is then added to the sample to precipitate Ni(DMG)₂, which is then extracted into methylene chloride. The Ni (DMG)₂ destroyed by HNO₃ and the Ni-63 dissolved into dilute HCl. This procedure should eliminate all other beta emitters. Ni-63 is then determined using LSC.

3.3 Solubility and Batch Studies

Solubility studies were conducted for equilibration times extending from 32 days to a maximum of 275 days at either 1:30 or 1:10 soil to solution ratios. Solubility studies were conducted either in an atmosphere chamber under an atmosphere of ultrapure argon or on the bench top over a broad range of pH values extending from approximately 1 to 12 depending upon the specific samples examined. Batch studies were conducted both in an atmospheric chamber in the absence of CO₂ and on the bench top where CO₂ was allowed into the samples. The bench-top studies were conducted as both “long-term” and “short-term” experiments. In the long-term studies the samples were kept lightly capped but there was no forced equilibration with atmospheric CO₂. In the short-term studies the samples were vigorously bubbled with air over a three-day period to ensure the equilibration with atmospheric CO₂. The introduction of CO₂ is potentially important owing to the possible formation of either Th(IV) carbonate complexes (Felmy et al. 1997) or U carbonate complexes (Grenthe et al. 1992). All of the batch studies were conducted at the “natural” pH of the sample, which varied with reaction time, and conditions, as the samples dissolved. No pH adjustments were made by adding acid or base. All of the batch and solubility suspensions were prepared in the following manner. For each site sample a solid/solution suspension was prepared by placing approximately 1 gram of material in 30 ml of deionized water in each 50-ml centrifuge tube. Approximately 24 such suspensions were prepared for each sample in the solubility studies. Each sample was independently adjusted to a different pH value within the prescribed range using reagent grade HCl or NaOH. The batch samples were prepared in the same manner but only two suspensions (duplicates) were prepared for each site sample. All suspensions were then placed on an orbital shaker and shaken until sampling. Sampling of the solubility and batch suspensions consisted of pH measurements followed by centrifugation at 2000 x g for 7 to 10 min. A sample of the supernatant was then filtered through an Amicon CentriCon-30[®] type filter with effective 30,000-molecular-weight cutoff and average pore diameter of 3.6 nm. The membrane were pretreated by washing with

pH-adjusted deionized water (to the approximate pH of the sample) followed by filtration of a 0.5 ml to 1.0 ml aliquot of sample to saturate any adsorption sites. This first aliquot of the sample was then discarded. This pretreatment process was then followed by filtration of approximately 5 ml of sample. Approximately 1 ml of this sample was then withdrawn and acidified for ICP or ICP-MS and radiological analysis. The remaining unacidified sample was retained for anion analysis by IC.

3.4 Column Studies

Flow-through column experiments for determining the impact of flow rate on leaching behavior were conducted using 32-ml Savelex[®] Teflon[®] columns (see Figure 3-1) connected to 3M modular infusion pumps operating at a flow rate of 0.1 or 1.0 ml/hr. Each 32-ml column was then packed with 30 to 40 g of soil material depending upon the exact particle size. The final solution volume in each column (pore volume) was then approximately 16 to 17 mls. Porous frits were placed at the top and bottom of each column to prevent any fine suspended material from passing through the column. The solutions entered the columns through the bottom and passed out the top into a sealed collection bottle. Samples from the collection bottle were taken, pH measurements made, and filtered as described for solubility and batch studies. Filtrates were split into acidified and unacidified aliquots for analysis by ICP or ICP-MS and IC, respectively. Radiological analysis was also performed on an acidified sample. Column experiments were continued for times extending to 72 days depending upon the sample.

3.5 Radiocolloids

The potential for radiocolloid transport was assessed by comparisons between filtered and unfiltered well water and column samples. The filters used to separate the particles from solutions were Amicon CentriCon-30[®] type filter with effective 30,000-molecular-weight cutoff and average pore diameter of 3.6 nm. The use of filters with such a small pore size means that any suspended or colloidal material will be removed (with the possible exception of extremely small nanoparticles). The difference between filtered and unfiltered analysis will therefore represent a maximum potential for radiocolloid migration because a wide range of colloidal or suspended particles would be removed by filtration. The designation “soil” represents soil or slag material depending upon the specific sample. The pH port, which was present on only a few columns, was not used. All pH measurements were made in the sample-collecting vessel.

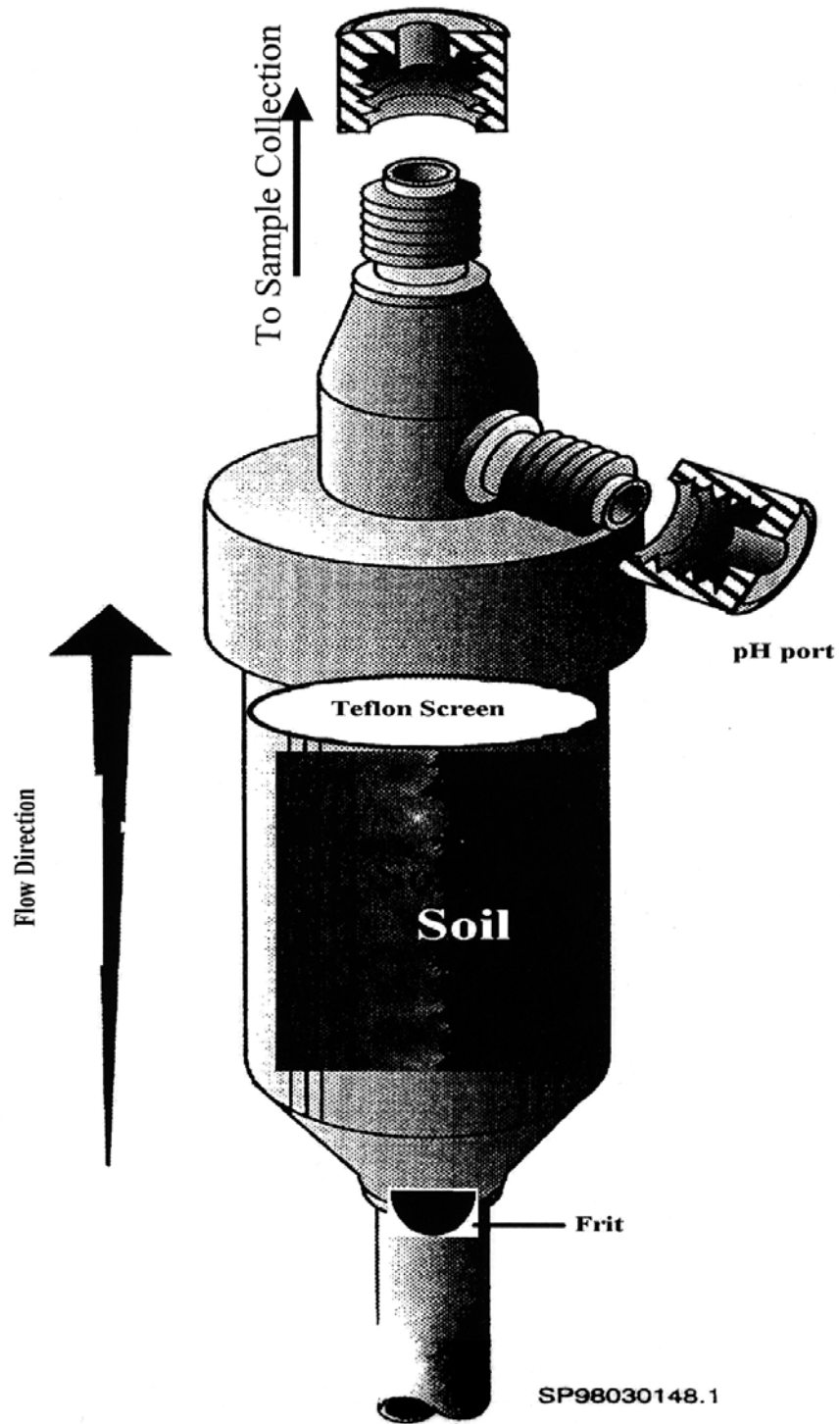


Figure 3- 1. Schematic of Column Apparatus.

4. RESULTS AND DISCUSSION

4.1 Chemical Analysis

The total chemical analysis of the highest activity soil sample at Site D (see Table 4-1, last column) shows a bulk composition dominated by Al, Si, and Ca characteristic of alumino-silicate minerals or calcium alumino-silicate minerals with significant amounts of Fe. The element in highest concentration with radioactive isotopes is U.

The total chemical analysis of the solid materials collected at Site E (Table 4-1) shows that the principal constituent is Mg (as high as 36% by weight) with lesser amounts of Si, Al, Mn, Ca, and Fe. The high Mg apparently resulting from the disposal of Mg/Th alloy slags. The total chemical analysis also shows significant concentrations of Th (as high as 1600ppm) but total U was undetectable by XRF (detection limit ~ 10ppm). These same trends are evident in core 46 (Table 4-2), except there is less Mg and Th in the upper section of core 46 and more Al and Si than in the samples from the retention pond. The higher Al and Si readings are indicative of a higher alumina-silicate mineral content (more natural sediment proportions).

Chemical analysis of the pore waters within the retention pond (sampling Site C, sample KW-2, and Site D, sample KW-3) showed exceptionally high pH values (pH 9.5 – 9.7) (Table 4-3). Such high pH readings are indicative of chemical equilibrium with brucite ($\text{Mg}(\text{OH})_2(\text{c})$). These high pH readings indicate that the Th present on the site is most likely very insoluble (Felmy et al. 1991), either as hydrous thorium oxide or crystalline thoranite ($\text{ThO}_2(\text{c})$). This is supported by the chemical analysis of the collected water samples (Table 4-3), which show Th concentrations at or below the analytical detection limit (~0.2ug/l). The dissolved U concentrations in all samples were also quite low, either at or below the analytical detection limit (~ 0.2ug/l). It is also interesting to note that there is apparently some naturally occurring U in the drainage of no-name creek since detectable U was found in the outlet from the freshwater pond (sample KWP-1). No other radionuclides, with the exception of 5pCi/ml of ^{210}Pb in the sample from the up-gradient freshwater pond, were present at concentrations >1pCi/ml in any water sample taken at the site, data not shown.

The well water analysis shown in Table 4-3 for Site E was used as input for geochemical modeling calculations using the MINTEQ-A2 equilibrium model (Allison et al. 1991). These results, for U (Table 4-4a), using the original MINTEQ-A2 database, show that the predominant aqueous species in solution should be anionic uranium-carbonate complexes. However, there have been considerable changes in the available thermodynamic data for aqueous complexes published since the compilation of the MINTEQ-A2 database. These efforts include the extensive NEA review of the thermodynamics of U (Grenthe et al. 1992) and the work on mixed metal-uranyl-carbonates (Kalmykov and Choppin 2000). The authors have therefore revised the thermodynamic data for aqueous complexes of uranium in the MINTEQ-A2 database with these more recent data. The results (Table 4-4b) show quite a dramatic difference in the computed aqueous speciation. Most significantly, the aqueous species of U are now dominated by a neutral ($\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$) complex. How such differences in chemistry affect the migration of U(VI) species in groundwater is still unknown.

Element (ppm)	Sample K1	Sample K2	Sample K3	Sample K4	Sample K5	Site D Highest Activity Sample
Al	31800±3000	28400±3500	19500±3300	38500±4100	33800±3700	56100±6200
Si	98800±7100	92200±6900	38200±3200	125600±9200	16500±12000	258000±1,000
K	4380±310	860±80	340±40	6390±460	7150±510	20000±1400
Ca	8330±520	13390±950	3120±230	24800±1800	10360±740	13970±1000
Mg	194900	300400	364300	157600	164800	--
Ba	2307±121	4990±250	3550±180	6620±340	3410±180	--
Mn	21600±1519	10060±710	8190±580	8550±610	4050±290	460±71
Tl	1650±120	1790±1300	1230±90	3370±240	2670±190	--
Fe	11200±7800	26300±1900	17500±1200	51600±3600	15700±1100	42700±3000
Ni	382±31	125±14	118±13	206±20	66.4±9.5	608±52
Cu	508±38	260±21	450±33	665±50	163±14	177±20
Zn	2418±179	1790±130	2230±160	1710±120	1114±79	241±22
Pb	128±12	128±12	78.1±8.1	186±16	90.9±8.9	--
Cr	324±24	<20	<17	157±16	<17	--
As	104±9	<23	<22	<27	<21	--
Se	5.56±2.14	11.6±2.9	13.9±2.9	10.8±3.3	<4.5±2.3	<5.5±5.5
P	910±470	1730±550	1920±460	<1300	2400±530	--
S	<300	1400±260	1500±250	<480	<400	--
Rb	20±2.1	<3	<2.8	24.8±2.9	38.1±3.4	100.9±9.1
U	<5	<5.3	<4.8	<7.5	<6.8	65.2±8.5
Sr	40.3±3.3	48.1±4.2	22.9±2.5	119±9	84.5±6.5	118.4±9.4
Y	25±2.5	59.6±4.8	61.2±4.8	60±5	44.2±3.8	31±3.9
Nb	5.9±1.5	4.1±2	<3.6	7±2.2	6.8±1.8	75.6±6.5
Mo	25±4.3	<14	<12	<13	<9.4	21.5±4.1
Zr	2923±205	7160±500	6200±430	5460±380	2740±190	--
Th	513±37	1290±92	1600±110	1277±91	632±46	28±10
Hg	--	--	--	--	--	<7.3±7.3
Br	--	--	--	--	--	<5.7±5.7
Ga	--	--	--	--	--	21.4±5.7

Element (ppm)	Depth (1-2 ft)	Depth (2-3 ft)	Depth (4-5 ft)	Depth (5-6 ft)	Depth (6-9 ft)
Al	52500±4800	41900±4400	34000±4100	49000±5500	59400±6500
Si	303000±21000	147000±11000	70300±5400	46000±4000	37900±3600
K	15100±1100	8190±590	4020±300	2500±200	1630±150
Ca	8620±620	24200±1700	21700±1500	13450±960	14100±1000
Mg	25800	173170	258000	291000	286000
Ba	1128±63	5680±290	7650±390	6140±310	4910±250
Mn	1031±88	8340±600	15300±1100	28700±2000	43100±3000
Tl	3800±270	3360±240	3180±230	3040±220	2800±200
Fe	23000±1600	33100±2300	57600±4000	32000±2300	40000±2800
Ni	82±11	110±14	247±24	210±23	387±37
Cu	119±11	503±38	686±51	1088±80	1520±110
Zn	244±19	1430±100	2330±170	3480±250	4560±320
Pb	47.8±6.2	159±14	175±16	661±50	1269±93
Cr	58±9.6	91±13	170±18	374±32	649±51
As	<20	<25	<31	<44	<55
Se	<3.2	12.1±3.1	19.9±4.1	28±5.8	34.7±7.2
P	1860±620	2840±700	1880±670	1500±690	<1600
S	<400	840±260	1330±290	<700	<860
Rb	75.6±5.8	37.7±3.5	<4.4	<5.6	<6.6
U	<7.3	<7.3	<7.2	<9.4	<11
Sr	94.7±7.1	124.6±9.3	114.1±8.7	86.4±7.3	77.2±7.1
Y	36.3±3.2	62.8±5.1	82.6±6.4	126.9±9.9	158±12
Nb	9.2±1.6	7.1±2	5.5±2.3	8.6±3.6	11.8±4.1
Mo	<5.4	<13	<15	<24	<28
Zr	910±64	5980±420	8200±570	13220±930	17700±1200
Th	104.3±9.7	1177±84	2010±140	3480±250	4500±320

Table 4-3. Chemical Analysis of Water and Well Samples at Site E (see Table 2-1).

	KWP-1	P-10	KWP-2	KW-1	KW-2	KW-3	MWD-4	MWD-5	MWD-8	KW-4
pH	8.7	7.29	8.9	8.3	9.5	9.7	7.04	8.15	7.62	8.8
Na	11	21	11	52	14	39	48	44	31	34
K	4.2	0.8	7.2	128	12	18	34	190	200	67
Ca	30	39	35	127	3.2	4.5	110	63	58	23
Mg	4.3	11	6.3	288	88	55	59	35	110	180
Cl	6	19	10	310	40	53	290	410	450	310
F	0.3	0.53	0.3	4	1.6	0.9	0.64	2.3	2.5	4
IC	18	42.9	22.4	89.5	54.1	60	40.8	15.8	59.8	61.7
SO ₄	35	4.6	12	230	20	14	69	11	4.8	73
Th (ug/l)	<0.2 [.02]	<0.2 [.02]	<0.2 [.02]	<0.2 [.02]	<0.2 [.02]	<0.2 [.02]	<0.2 [.02]	<0.2 [.02]	<0.2 [.02]	<0.2 [.02]
U (ug/l)	0.24 [.079]	0.86 [.28]	0.36 [.12]	0.92 [.30]	<0.2 [.066]	<0.2 [.066]	1.14 [.38]	0.1 [.033]	0.14 [.046]	<0.2 [.066]

(a) Concentrations in mg/l, pH in units. Inorganic carbon (IC) in mg/l as C. Numbers in brackets are in pCi/l.

Three soil samples with the highest radiological activity at Site F were selected for chemical analysis (Table 4-5). The results showed that the soils were predominately aluminosilicates with significant amounts of Ca and Fe. The Fe most likely being present as an oxide/hydroxide. In contrast to the other sites, no detectable concentrations of Th or U were found in these high activity soils. This absence of Th and U is a direct consequence of the differing manufacturing activities at the Site F.

Chemical analysis of the water samples (see Table 4-6) show that the waters are predominately calcium bicarbonate-sulfate waters with near circumneutral pH values. The measured redox potentials varied widely among the samples and were correlated with the dissolved Fe concentration. The lower the redox potential (Eh), the higher the concentration of dissolved Fe. The high-dissolved Fe being most likely present as ferrous Fe (Fe(II)). Detectable concentrations of VOC compounds (see Table 4-7) were also found in two of the water samples that exhibited reducing conditions, samples 6GW and 7GW, suggesting a link between disposal of solvents or other organic containing solutions and the onset of reducing conditions. The VOC results are lower than the earlier analysis based upon the 1996 Monserco study (Monserco 1996). The only other water sample with high Fe and reducing conditions was the single sample taken from the hole dug in the East Lagoon (sample 1L). This sample exhibited the lowest redox potential and the highest dissolved iron content, but no detectable VOCs were found. The reason for the lower redox potential is obvious from the physical setting. Sample 1L was taken from the bottom of the marshy lagoon where the soils undoubtedly contained a high-organic content resulting from vegetative decay.

Sample	$\text{UO}_2(\text{OH})_3^-$	$\text{UO}_2\text{CO}_3(\text{aq})$	$\text{UO}_2(\text{CO}_3)_2^{2-}$	$\text{UO}_2(\text{CO}_3)_3^{4-}$
KWP-1	1.8	--	26.5	71.5
P-10	--	2.6	76.5	20.9
KWP-2	1.2	--	15.8	83.0
KW-1	--	--	5.1	94.9
MWD-4	--	4.4	76.4	19.2
MWD-5	--	--	42.3	56.2
MWD-8	--	--	35.0	64.6

(a) Use of the U(VI) thermodynamic data in Allison et al. (1991). All values in percent of total soluble U.

Sample	$\text{UO}_2(\text{CO}_3)_2^{2-}$	$\text{UO}_2(\text{CO}_3)_3^{4-}$	$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$
KWP-1	2.2	5.8	92.0
P-10	13.9	3.8	81.9
KWP-2	--	4.7	94.4
KW-1	--	6.5	93.1
MWD-4	8.3	2.1	89.1
MWD-5	3.9	5.2	90.9
MWD-8	5.4	10.0	84.5

(a) Use of more recent thermodynamic data (see text). All values in percent of total soluble U.

Element (ppm)	Sample S2	Sample S5	Sample S6
Al	52300±3900	43300±3300	65400±4800
Si	243000±17000	269000±19000	207000±15000
K	14400±1000	11800±840	13720±960
Ca	41800±2900	10820±770	10060±720
Mg	9080	5640	6360
Ba	374±28	379±33	434±32
Mn	1341±99	885±67	133±24
Tl	4870±340	5370±390	7110±510
Fe	26200±1800	25100±1800	24500±1700
Ni	40±6	23±5	120±10
Cu	45±5	76±7	507±36
Zn	1004±71	823±58	666±47
Pb	124±10	181±13	239±17

Cr	75±7	124±10	741±52
As	12±2	7±2	7±2
P	2560±420	2120±320	5610±480
S	1760±170	1510±160	8640±640
Rb	64±5	57±4	85±6
U	<5 (1.6)	<4 (1.3)	<9 (3.0)
Sr	92±7	95±7	125±9
Y	25±2	26±2	36±3
Nb	9±1	12±1	18±2
Mo	<2	3±1	8±1
Zr	281±14	293±15	216±11
Th	<7 (.77)	<5 (.55)	<13 (1.3)
Pb	139±8	194±10	253±13
Cd	140	150	68
(a) Numbers in parenthesis are in pCi/g.			

	1L	2L	3GW	4GW	5RW	6GW	7GW	8GW
pH(units)	6.4	7.4	7.7	6.35	7.33	5.64	6.44	6
Eh(mv)	166	401	461	509	464	329	263	476
Na	6	17	10	10	15	6	5	12
K	6	11	3	2	2	4	8	2
Ca	67	51	27	38	22	43	53	31
Mg	3	3	6	7	5	4	10	7
Cl	13	24	26	22	23	3	3	18
F	0.49	0.10	0.04	0.05	0.07	0.10	0.05	0.39
IC ^(b)	36	50	17	21	17	<10	45	26
Alkalinity (mg/l C)	34	43	17	24	14	7	40	22
SO ₄	67	13	24	24	21	119	35	23
Mn	0.30	--	3.78	-	0.29	4.09	1.07	1.33
Sr	0.23	0.14	0.14	0.45	0.10	0.23	0.25	0.50
Zn	0.19	0.15	--	--	--	0.24	--	--
Fe	30.8	--	--	--	0.36	4.35	4.33	--
U (ug/l)	0.232 [.076]	0.191 [.063]	<0.05	<0.01	0.068 [.022]	<0.05	<0.01	<0.01
(a) All values are mg/l, unless denoted otherwise. Numbers in brackets are in pCi/l.								
(b) Inorganic carbon (mg/l as C).								

Table 4-7. Volatile Organic Carbon Analysis of the Water Samples at the Site F (ug/l).			
Organic	4GW	6GW	7GW
1, 1 Dichloroethane	3.0	.27 (1.3)	.76 (3.2)
Cis-1, 2 Dichloroethene	2.3	.26	.65 (0.8)
1, 1, 1 Trichloroethane	4.8	--	.48
Trichloroethene	.31	--	.62 (0.8)
Tetrachloroethene	--	- (0.2)	1.1 (1.8)
(a) Values in parenthesis were taken from Monserco (1996).			

4.2 Radiological Analysis

Radiological analyses of site materials yield the isotopic composition of the radioactive elements. Such analyses are important not only for more detailed analyses of possible health effects but also because the relative ratios of the various isotopes yields important information on isotopic separation processes that may have occurred at the site. This information is key to understanding the site history, waste disposal practices, and migration fate of each isotope at the site.

4.2.1 Site D

Radiological analysis of the highest activity Site D sample (Table 4-8 and Figure 4-1) showed principally total U (by KP) and the first U-238 daughter (Th-234). Other daughter products of the U-238 decay chain may be detectable (see Th-230 peak in Figure 4-1) but present only at very low levels. Thus, this sample indicates that U was very cleanly separated from its daughters at some time in the past and only the U ended up getting mixed with the waste. This is in agreement with the site characterization, which shows that much of the U originates from depleted uranium disposed at the site. There were no signs of natural Th-232 or its daughters in this sample.

Table 4-8. Radiological Analysis of the Highest Activity Soil Sample at Site D.		
Nuclide	Gamma Spectroscopy	AS/KP
Th-Series (3)	--	
232-Th	--	1±0.2
228-Ac	--	-
228-Th	--	2±0.4
224-Ra	--	-
212-Pb	--	-
212-Bi	--	-
238-U Series (20)	--	23±0.5
238-U	--	--
234-Th	30±10	--
234-U	--	--
230-Th	--	1±0.2
226-Ra	--	--
214-Pb	--	--
214-Bi	--	--
235-U Series	--	--
235-U	--	--

(a) Gamma spectroscopy analyses represent the average of three subsamples of each slag. AS/KP represent Th isotopic analysis by AS and total U by KP. All values in pCi/g.

(b) Uranium values are close to detection limit and because of interferences are hard to quantify with the counting system. Values in parenthesis are calculated from the XRF data for thorium and uranium assuming all of the Th is Th-232 (1.1×10^{-7} Ci/g) and all of the U is U-238 (3.3×10^{-7} Ci/g).

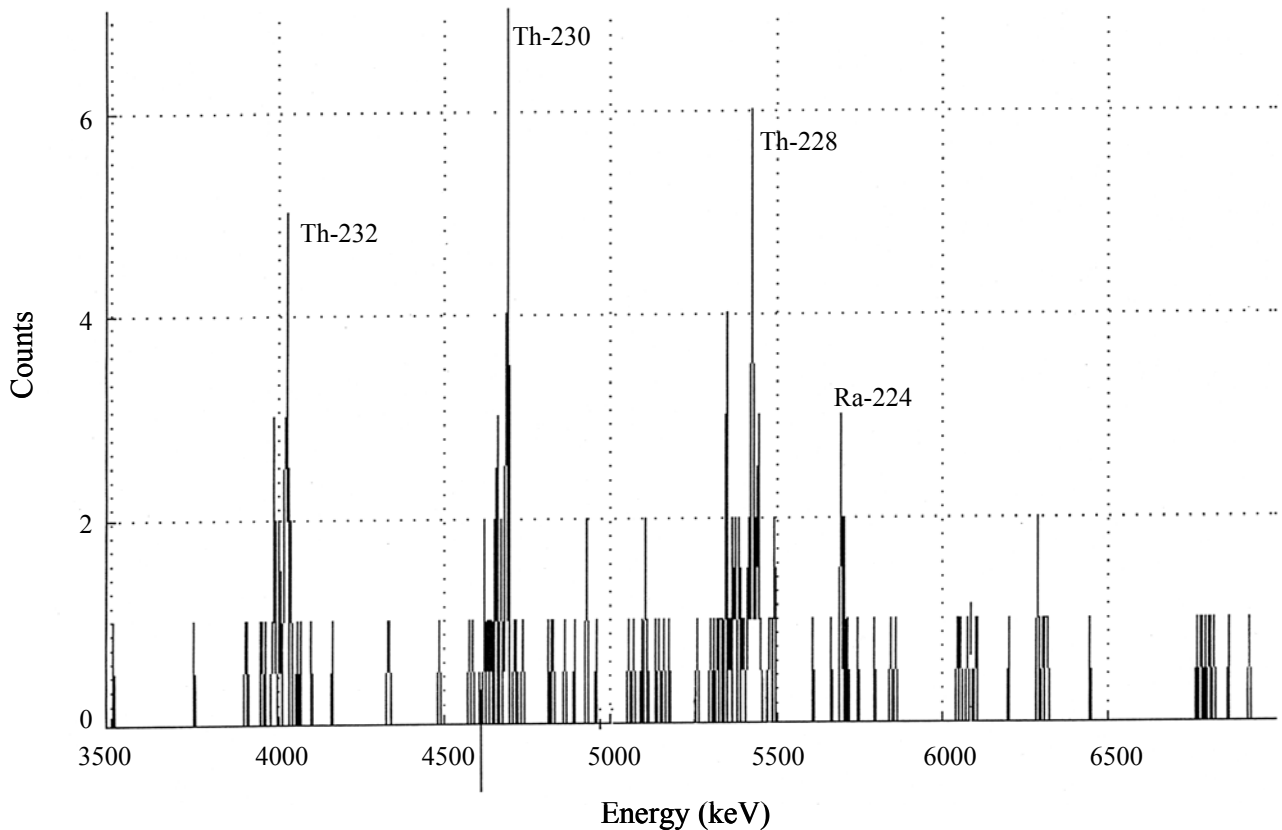


Figure 4-1. Alpha Spectra of Highest Activity Site D Sample. Th-232 and Daughters Present Only at Very Low Levels.

4.2.2 Site E

The radiological analysis of the solid materials at the Site E by gamma spectroscopy (Tables 4-9a and 4-9b) and AS and KP (Table 4-10) show that the ^{232}Th daughters appear to be in secular equilibrium. The single analysis of ^{232}Th by AS also indicates that the ^{232}Th is in secular equilibrium with the ^{228}Th daughter (Figure 4-2). However, the AS analysis of ^{232}Th for sample K3 is less than half the analysis of the daughters by gamma spectroscopy. This is most likely the result of sample heterogeneity combined with a small sample size ($\sim 0.1\text{g}$) for the AS analysis. As expected all ^{238}U daughters detectable by gamma spectroscopy are near background levels owing to the low concentrations of U in the samples. Interestingly the AS of these samples shows significant concentrations of the ^{238}U daughter ^{230}Th . Apparently natural ^{238}U was present in the materials at one time. The U being removed in processing the Mg/Th alloy. The insoluble Th daughter remained in the waste.

Radiological analysis of the deep core obtained by Site E staff showed fairly uniform distribution of radiological components with depth. It is also interesting to note that the sample of plant material (grasses) collected near the K2 "hot spot" contained very low levels of ^{232}Th daughters. It is possible that even these low values could have been the result of small amounts of inorganic

waste associated with this material. There does not appear to be any indication of a bio-concentration effect, at least in this vegetative sample.

In the case of the surface and well waters at Site E, radiological analysis of all of the samples collected at the site did not reveal the presence of any radionuclides at activities greater than 1 pCi/l. This analysis included all of the Th-232 daughters. Apparently, the daughters of Th-232 are retained in the insoluble $\text{ThO}_2(\text{am})$ as will be indicated later in the section on solubilities.

Table 4-9a. Radiological Analysis (Gamma Spectroscopy) of Wastes (Samples K1-K5) at Site E.

Nuclide	K1	K2	K3	K4	K5
232-Th Series	--	--	--	--	--
228-Ac	--	108±3	96±3	187±0.5	39±1
212-Bi	--	--	111±3	--	46±1
212-Pb	43±2	115±4	106±4	199±0.7	47±2
224-Ra	42±1	--	107±2	201±0.5	48±1
228-Th	37±5	129±22	101±32	--	31±5
238-U Series	--	--	--	--	--
226-Ra	2±0.2	1±0.5	3±0.8	1±0.3	3±0.3
214-Bi	--	3±1	3±0.3	1±0.2	2±1
214-Pb	1±0.05	3±0.2	3±0.6	1±0.05	2±0.08
234-Th	8±3	--	--	--	--
(a) Values in pCi/g.					

Nuclide	(2-3) ft	(4-5) ft	(5-6) ft	(6-9) ft	Plant Material
232-Th Series	--	--	--	--	--
228-Ac	81±2	96±2	151±4	--	6±0.2
212-Bi	--	110±3	176±5	--	8±0.4
212-Pb	87±4	104±4	169±6	194±8	7±0.3
224-Ra		107±2	180±3	197±6	7±0.4
228-Th	83±6	105±34	161±15	221±13	--
238-U Series	--	--	--	--	--
226-Ra	6±1	4±0.6	7±1	10±0.6	2±0.3
214-Bi	--	5±0.3	7±0.4	8±0.2	<1
214-Pb	--	5±0.7	8±0.2	9±0.3	<1
234-Th	--	--	--	--	--

(a) Values in pCi/g.

Nuclide	K3 (Sample 1)
232-Th Series	--
232-Th	36±2
228-Th	39±3
238-U Series	<1
238-U	--
234-U	--
230-Th	66±3

(a) Values in pCi/g.
 (b) Thorium isotopes were analyzed by AS and uranium by KP.

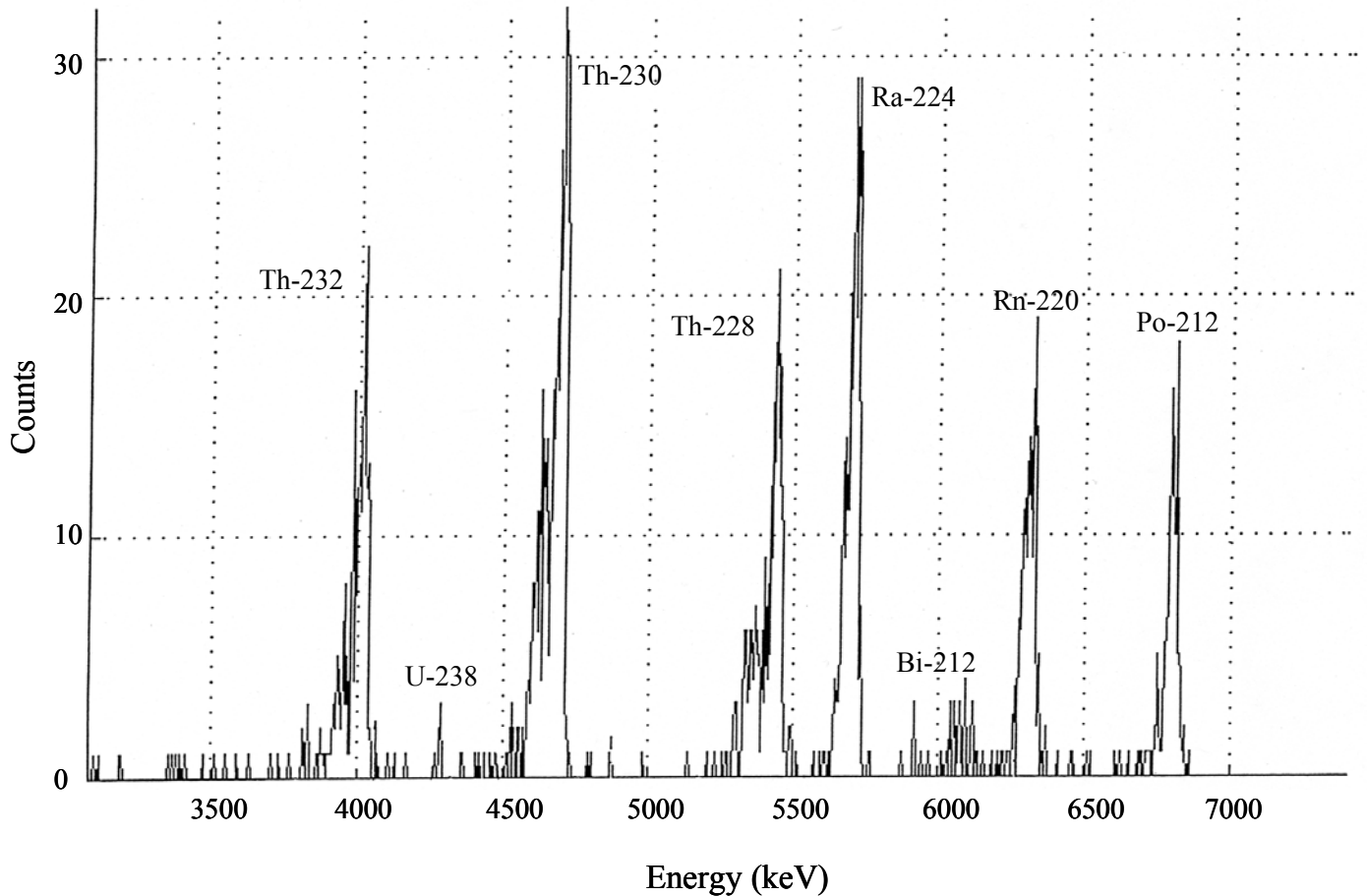


Figure 4-2. Alpha Spectra of Sample K3 from Site E.

4.2.3 Site F

Radiological analysis of the soils and vegetative samples collected at Site F (see Table 4-11 and Figure 4-3) show that the dominant radionuclides are Cs-137 and Ra-226 with associated daughters (Bi-214), along with small amounts of Ni-63. Am-241 was detected only in the soil sample from the East Lagoon (6S) and possibly at site 4S, although the concentrations are close to the detection limits. Also of note is that Ra-226 was found in the vegetative sample (strawberries) collected at the site. Therefore, the possibility of vegetative uptake of radionuclides does exist. A far more exhaustive study than that conducted here, including complete washing of samples to remove any accumulated dust, would be required to verify this concern/issue. The concentrations of H-3 and Sr-90 were very low in the solid materials. Certainly, the small concentrations of H-3 could be due to small amounts of adsorbed water. In contrast to the results for the soils, the radionuclides found in the water samples were H-3, Sr-90, and one sample with Ra-226 and Ni-63 (see Table 4-12). So the Cs-137, though present in high concentration in the soils, is apparently in a nonleachable fraction. When the H-3 and Sr-90 analyses are compared against the earlier Monserco (1996) data for the same wells (see the

values in parenthesis in Table 4-12), it is apparent that the concentrations in the groundwater have decreased significantly. The results in this study are based upon filtered samples, so the Sr-90 values are soluble concentrations. It is not clear from earlier reports if some fraction of particulate matter might have been included in the reported measurements. Several of these wells had very high concentrations of particulates (predominately iron oxides), which could have adsorbed some of the Sr-90. However, only very low concentrations of Sr-90 were found in the soil samples, which supports the conclusion that the Sr-90 is principally in solution. The single sample with detectable Ra-226 was found in the hole dug in the mud at the bottom of the East Lagoon (1L). It is not entirely clear why the Ra-226 is the highest in this sample. The associated soil (sample 6S, Table 4-11) does not contain a high concentration of Ra-226. It is possible that the Ra-226 is related to the reducing conditions that exist in the sample and the high dissolved Fe content. Reducing conditions could have resulted in the dissolution of iron oxides and the release of Ra^{2+} into solution. The presence of the high concentrations of Fe^{2+} could have then prevented removal via ion exchange or other processes. In any event, the measured Ra-226 concentrations are consistent with estimates of Ra-226 in the well samples (10-100 pCi/L) provided by site personnel based upon total alpha analysis. It is not clear if there is any dissolved Am-241 in the water samples, since results are all at or very close to the analytical detection limits.

Geochemical modeling of the well water analysis shown in Table 4-6 and Table 4-11 shows that the Ni is present primarily as the uncomplexed Ni^{2+} ion and U is present either as anionic uranium carbonate complexes or as the neutral $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ (aq) complex (Table 4-13). If present as a cationic species, the Ni may be less mobile than if complexed and present as an anion.

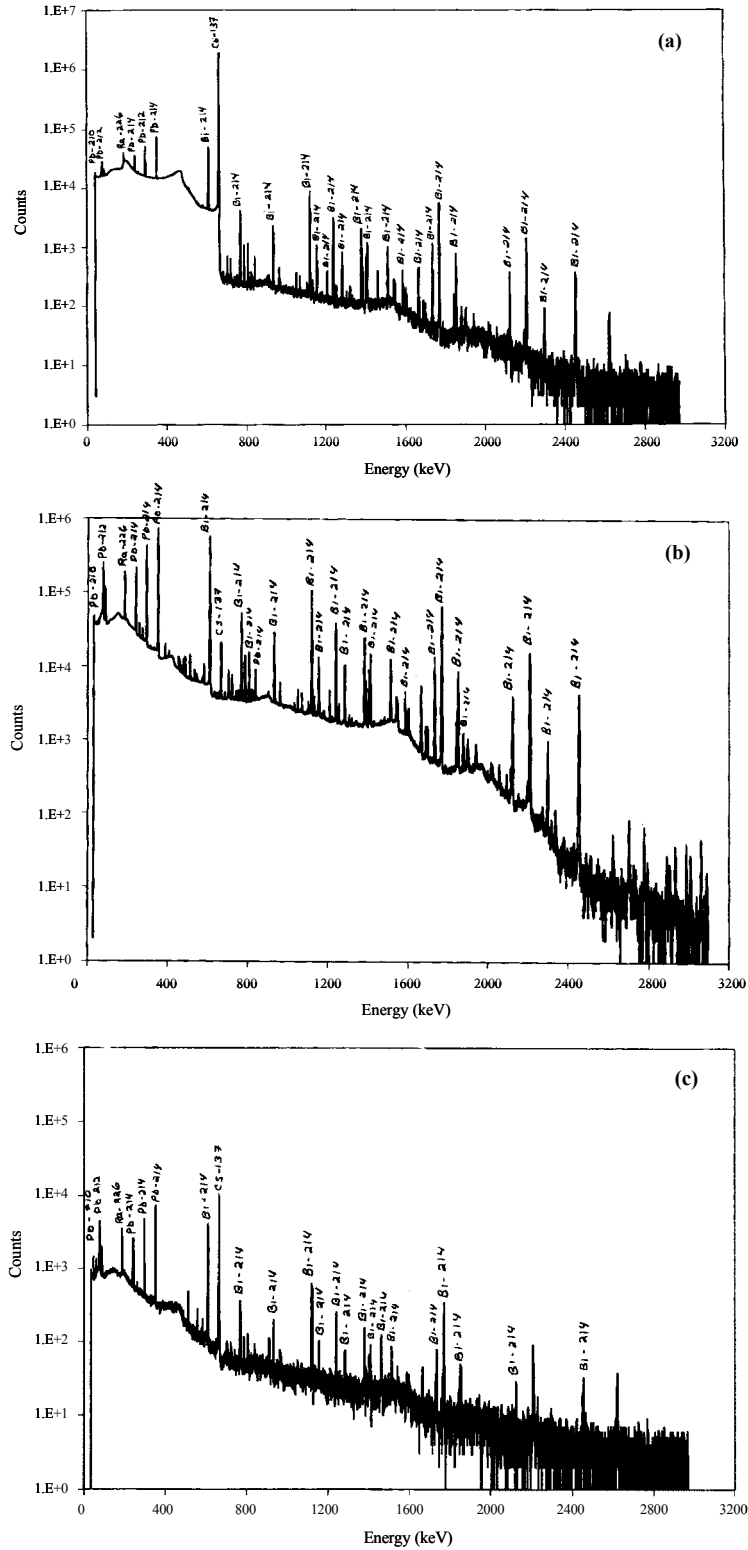


Figure 4-3. Gamma Spectra of Soil Samples at Site F. a) Soil 2S, b) Soil 5S, and c) Soil 6S.

	1S	2S	3S	4S	5S	6S	7S	V1
²²⁶ Ra	133±3	244±5	21±0.4	112±2	4600±90	61±1	69±1	8±0.2
H-3	9±0.3	69±1	18±0.5	10±0.3	5±0.2	125±4	13±0.4	14±0.7
¹³⁷ Cs	3±0.1	5920±180	2500±100	25±1	4±0.4	89±4	23±0.7	<9
⁹⁰ Sr	0.3±0.04	0.8±0.08	12.1±1.2	16.7±3.3	8.7±0.9	2.8±0.3	0.5±0.05	3.6±0.1
²³² Th	<0.5	<2	0.8±0.2	<0.6	<4	2±0.2	1±0.1	<31
²⁴¹ Am	<3	<10	<5	3±0.5	<10	5±0.6	<3	<70
⁶³ Ni	0.7±0.05	.38±0.04	1.6±0.06	1.2±0.06	--	12±0.02	3.4±0.1	--

	1L	2L	3GW	4GW	5RW	6GW	6GW Rust	7GW	7GW Rust	8GW
²²⁶ Ra	37±7	ND	<14	<15	<13	<8	6±0.6	<8	<2	<8
H-3	3120±250	1630±230	3040±240	18,000±700	ND	4440±270 (12,702)		7690±380 (49,200)		603±200 (1280)
¹³⁷ Cs	<90	<100	<80	<70	<70	<70	1.4±0.4	<70	<0.9	<100
⁹⁰ Sr	<20	<20	<20	490±108	<20	890±160 (3823)		8630±1200 (89,000)		<20 (6)
²⁴¹ Am	<0.2	0.21±0.07	<0.5	<0.3	<0.3	0.52±0.16	<7	<0.2	<8	<0.2
⁶³ Ni	40 ± 4	6 ± 4	7 ± 4	10 ± 4	5 ± 4	19 ± 4	-	7 ± 4	-	1 ± 3

ND = Not determined, insufficient sample for AS.
(a) The term "Rust" indicates the reddish precipitate present in the well samples that were removed by filtration and counted. Values in parenthesis are average values from Monserco (1996).

Table 4-13. Calculated Aqueous Ni and U(VI) Species in Well Waters at Site F.								
	1L	2L	3GW	4GW	5RW	6GW	7GW	8GW
Ni ²⁺	79.9	53.7	68.6	87.9	--	80.2	77.8	90.0
NiSO ₄ (aq)	4.8	--	1.8	2.2	--	9.2	2.5	2.2
NiHCO ₃ ⁺	14.5	22.9	11.0	9.3	--	10.5	18.7	7.5
NiCO ₃ (aq)	--	10.8	10.5	--	--	--	--	--
Ni(CO ₃) ₂ ²⁻	--	11.8	7.7	--	--	--	--	--
UO ₂ CO ₃ (aq)	20.0	--	--	--	--	--	--	--
UO ₂ (CO ₃) ₂ ²⁻	39.5	6.3	--	--	20.0	--	--	--
UO ₂ (CO ₃) ₃ ⁴⁻	--	2.7	--	--	11.0	--	--	--
Ca ₂ UO ₂ (CO ₃) ₃ (aq)	39.3	90.9	--	--	68.6	--	--	--
(a) All values in percent of total soluble nickel or uranium. Only samples with detectable nickel or uranium were included.								

4.3 Solubility, and Leaching Studies

4.3.1 Site D

The pH values for the “long-term” samples exposed to CO₂ (see Table 4-14) show very similar values to those in the absence of CO₂, indicating that the light capping of these samples prevented influx of sufficient CO₂ to equilibrate the solutions, with the possible exception of the longest-term (45 day) samples. However, the “short-term” studies with vigorous bubbling did show lower pH values more typical of equilibration with atmospheric CO₂. The pH values in the column experiments (see Table 4-14) are also in line with this trend.

4.3.1.1 Thorium

The total Th concentrations in the Site D sample (see Table 4-1) were very low relative to the other sites sampled. This very low Th concentration is reflected in very low observed Th solubilities (see Figure 4-4), which seldom exceeded 10⁻⁸M even at very low pH values. This result agrees with the batch leaching data that shows maximum Th concentrations of 10^{-7.5}M (see Table 4-15). Finally, all dissolved Th concentrations in the batch studies in the presence of CO₂ and in the column studies were at or below the analytical detection limit of approximately 10^{-8.5}M (data not shown).

Table 4-14. Measured pH Values in Batch Leaching Studies at Site D as a Function of Time.

Leaching Time	Batch Study No CO ₂	Batch Study CO ₂ – “Long Term”	Batch Study CO ₂ – “Short Term”	Column Experiments
2 hr	8.57	8.88	--	--
6 hr	8.57	--	--	--
.75 days	--	--	8.06	--
3 days	8.53	8.56	8.13	--
5 days	--	--	--	8.23
7 days	8.81	8.50	--	--
8 days	--	--	--	8.21
14 days	--	8.34	--	--
30 days	--	--	--	8.43
45 days	--	8.22	--	--
78 days	--	--	--	8.29

Table 4-15. Thorium Concentrations in Batch Leaching Studies of Site D Sample in the Absence of CO₂.

Leaching Time	-log [Th]
2 hr	-8.29
6 hr	< -8.50
3 days	-7.45
7 days	< -8.50
15 days	< -8.50
37 days	-7.54

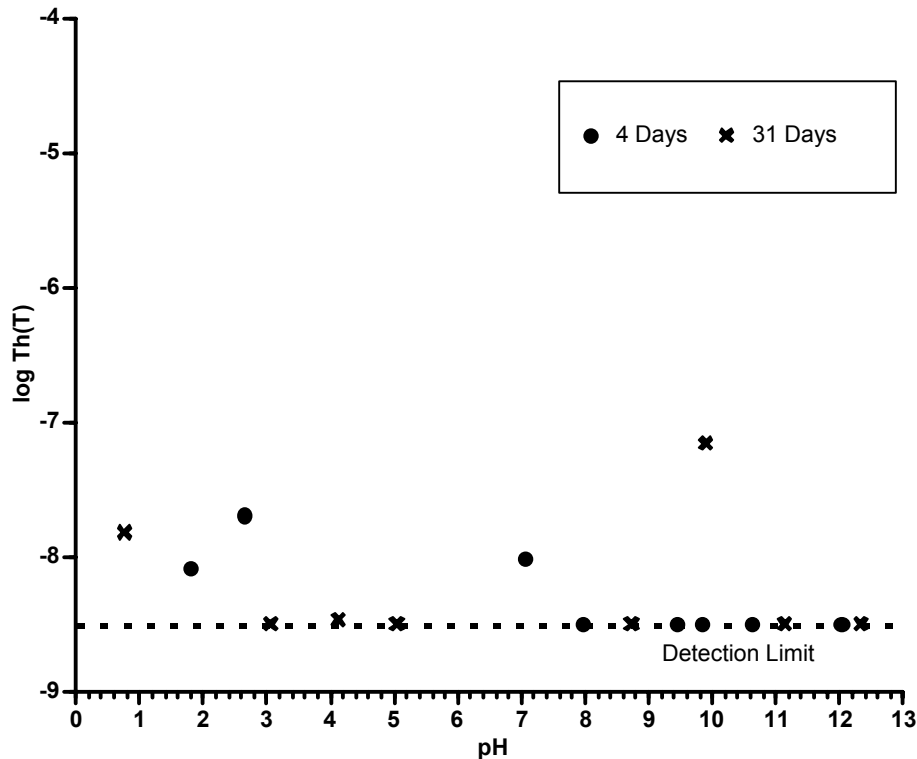


Figure 4-4. Total (T) Th Concentrations (moles/l) in Site D Solubility Studies.

4.3.1.2 Uranium

The total U concentration in the Site D sample (see Table 4-1) is significantly different than that at Site E. The Site D process resulted in the conversion of depleted UF_6 to depleted U_3O_8 . This difference in chemical form results in quite different observed U solubilities (see Figure 4-5). The U in Site D samples is relatively easily solubilized by acid with essentially 100% of the U soluble at low pH values. The observed U concentrations in solution also do not appear to correspond to any known solubility controlling solid phase for a U(VI) solid. The dramatically reduced soluble U concentrations over the pH range 3 to 5 seem to correspond more to adsorption edges for U(VI) on aluminum oxide or silica oxide surfaces (McKinley et al. 1995) than to expected solubility trends. This is also reasonable given the clayey nature of Site D samples. The observed U concentrations in the batch leaching studies (see Figure 4-6) were similar both in the presence and absence of CO_2 and show very similar trends to the solubility studies at the same pH values. This is expected. Site D samples were all a fine clayey soil. These studies therefore closely mimic the solubility studies except that no pH adjustments were made in the batch studies. However, the results for the column studies were dramatically different (see Figure 4-7). These data show very high dissolved U concentrations. These increases in concentration are clearly related to the much higher solid/solution ratio in the column studies as opposed to the solubility or batch studies. This dependence on solid/solution ratio is a clear indication that the U in Site D samples is highly reactive and not controlled by solubility phenomena. It appears likely that the observed U concentrations in solution are controlled by adsorption or ion exchange processes on the soil minerals.

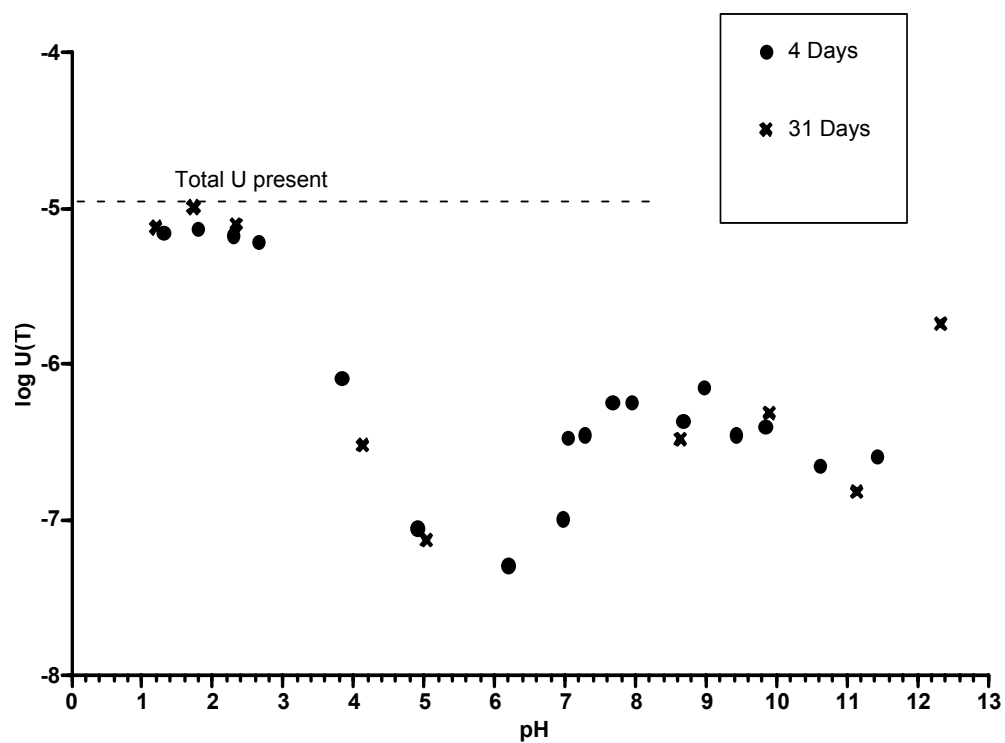


Figure 4-5. Total (T) U Concentrations (moles/l) in Site D Solubility Studies.

The dashed line labeled “Total U present” represents the U concentration in solution if all of the U in the sample dissolved.

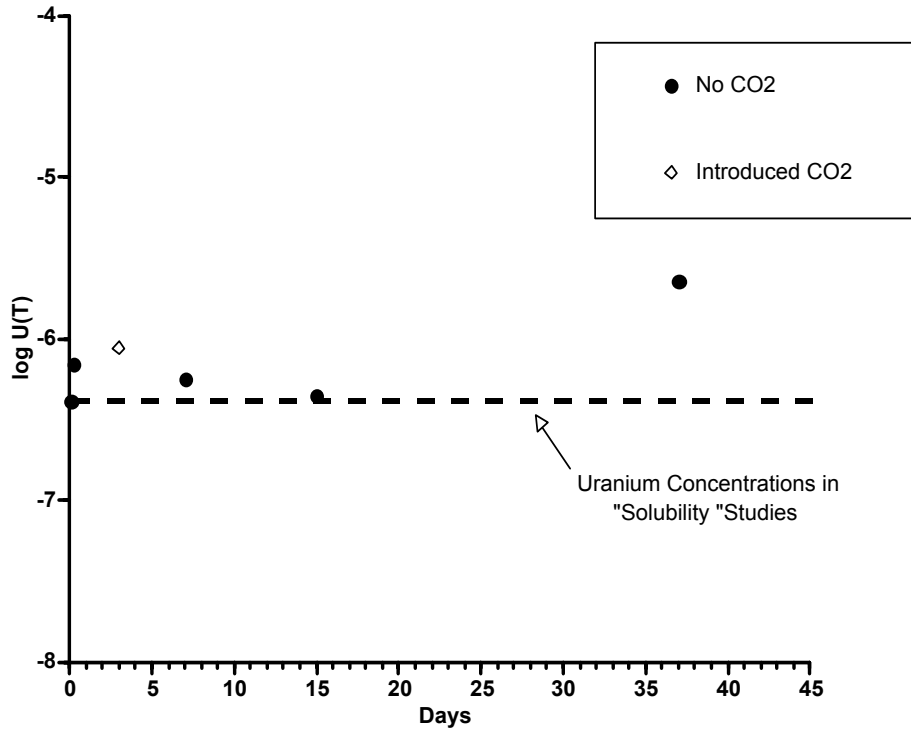


Figure 4-6. Total (T) U Concentrations (moles/l) in Site D Batch Leaching Studies.

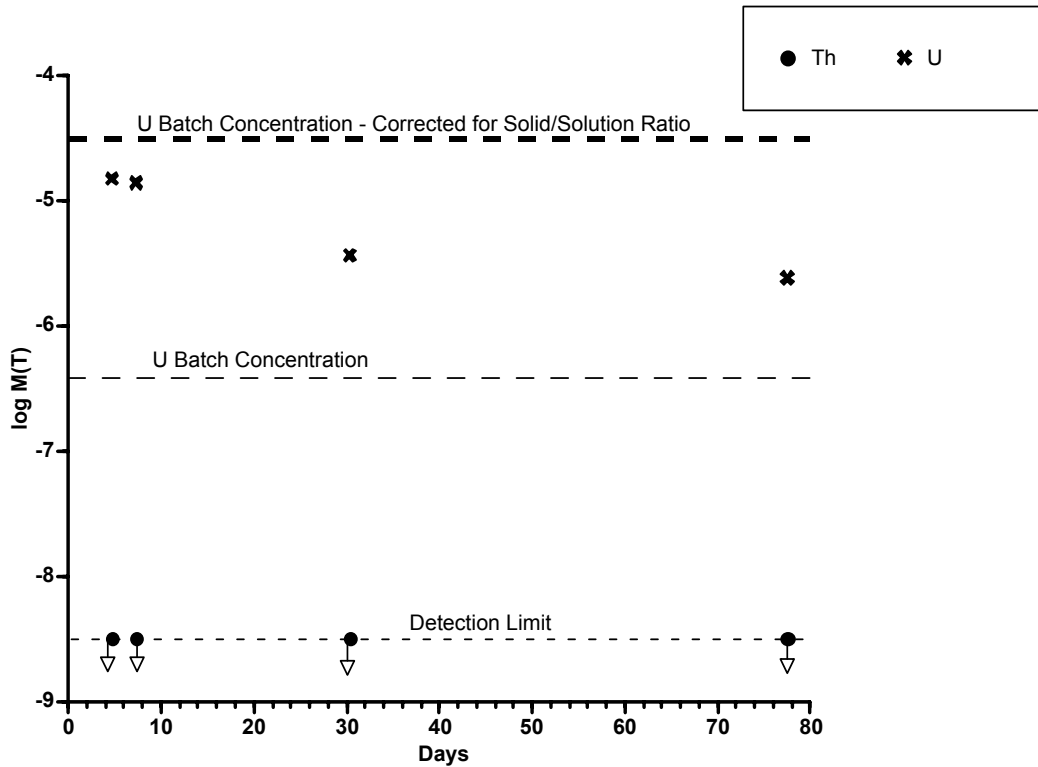


Figure 4-7. Total (T) Thorium and U Concentrations (moles/l) in Site D Column Studies.

M represents either Th or U. The dashed line labeled “U Batch Concentration – Corrected for

Solid/Solution Ratio” represents the soluble U in the batch experiments multiplied by the higher solid/solution ratio in the column experiments.

4.3.1.3 Other Radionuclides

The radiological analysis of the solubility and column data did not show significant concentrations of any Th-232 or U-238 daughter. Bi-212 and Pb-212 were detected in a few samples, but the concentrations were so low and the uncertainty of the analysis so high that any quantification of concentration was impossible. Such low concentrations are consistent with the radiological analysis of the solid Site D sample, shown in Table 4-1.

4.3.2 Site E

The solubility of one of the highest activity samples (K2) from the freshwater pond was studied over a range of pH values (1-12) to help identify the solubility controlling phases for the radionuclides. The results of these studies for Th (see Figure 4-8) show the Th solubilities are apparently being controlled by hydrous thorium oxide. This fact explains the very low (i.e., undetectable) dissolved Th concentrations in the retention pond even though significant Th exists in the solid phase. Also of interest are the observed amounts of ^{232}Th daughters that were solubilized in these solubility experiments (Figure 4-9). The amounts of released daughters quite closely follow the hydrous thorium oxide solubility curve. At low pH where the hydrous thorium oxide dissolves, the daughter concentrations increase rapidly. At higher pH there were no measurable daughters in solution. Given the differences in chemical behavior between the daughters (Pb, Bi, and Ra isotopes) it seems highly unlikely that isotopes of these elements would coincidentally follow the hydrous thorium oxide solubility curve. Apparently the daughter products from the decay of ^{232}Th are trapped inside the insoluble thorium oxide particles and are only released when this parent thorium compound dissolves. This hypothesis would also explain the absence of daughters in the water samples at the site. The solubility data for U (data not shown) show only very low dissolved U even at the lowest pH values, owing to the very small concentrations of U in the samples.

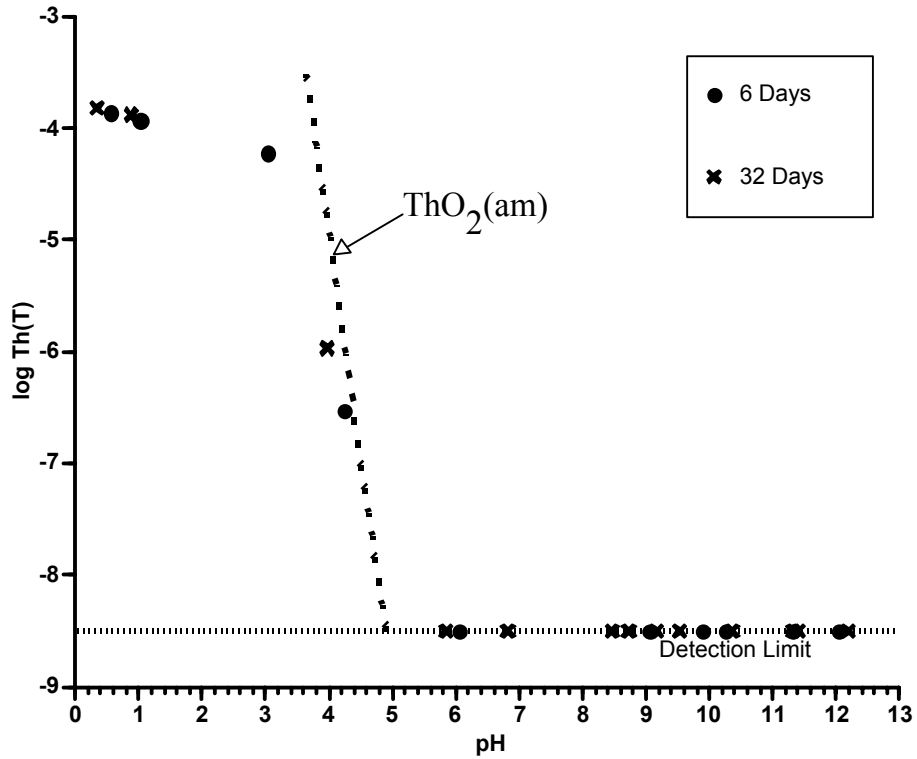


Figure 4-8. Total (T) Th Solubilities (moles/l) in Site E Sample K2.

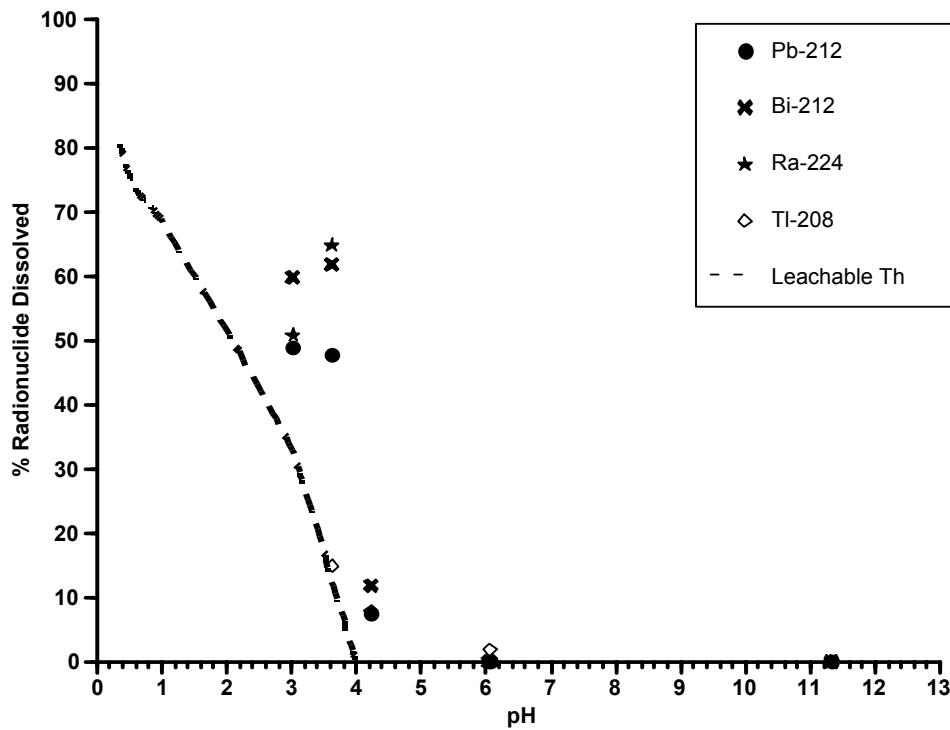


Figure 4-9. Th-232 Daughters Solubilized in the Solubility Studies of Site E Sample K2.

Batch leaching and column studies were also conducted on the two samples from the “hot spot”

(K2 and K3). The batch studies were conducted in contact with atmospheric CO₂. These studies therefore monitor not only the observed changes in elemental and radionuclide concentrations with time, but also allow the introduction of CO₂. This introduction of CO₂ is especially important given the fact that aqueous carbonate complexes are potentially strong enough to solubilize the hydrous thorium oxide (Felmy et al. 1997) and potentially liberate any ²³²Th daughters entrained in the solids. The effect of carbonate was not evaluated in the previously described solubility studies. The solubility studies focused on the identification of solubility controlling phases and on the effects of changes in pH. The column studies focused on the effects of water flow on radionuclide solubility and leaching. As water flows through the waste, the more soluble Mg and Ca compounds are leached from the waste and the pH decreases. The batch leaching and column studies therefore provide information on the response of the waste to changes in environmental factors (i.e., introduced water and infiltrating atmospheric gases).

The results of the batch leaching studies (see Table 4-16) show initially high pH values that decrease as CO₂ is introduced over time. The introduced CO₂ is evident in the increasing inorganic carbon concentrations. It is important to note that the dramatic decrease in Ca concentration in the 35-day sampling of the batch studies corresponds to the appearance of a “white precipitate” or coating on the sample container, presumably containing some calcite (CaCO₃). The precipitate began as a white floc and continued to increase with time, eventually effectively cementing together many of the remaining waste particles. The introduction of CO₂ therefore results in decreases in pH and transformation of the waste material from what appears to be predominant hydroxide compounds to predominantly carbonate compounds. Interestingly, this increase in carbonate content has not solubilized any of the Th or other radionuclides in the waste, as all radionuclide concentrations remained at or below the detection limits.

The results of the column studies (see Table 4-17) show different but predictable trends. The solution flowing through the column does not allow the carbonate content to build up as was seen in the batch tests. In fact, the carbonate content actually decreases during the column studies. This suppresses the formation and precipitation of carbonate containing solids. The major elements therefore follow a somewhat more predictable trend of initial dissolution followed by washout in the column. The pH values decrease with time as more and more of the initial basic solid components of the waste are removed in the column effluent. However, the radionuclides present in the column effluent remain at the detection limit. This is also expected from the solubility studies at the corresponding pH values.

Table 4-16. Chemical Analysis of Batch Leaching Studies for Samples from Site E.				
Sample	pH (units)	Ca (mg/l)	Mg (mg/l)	Inorganic Carbon (mg/l as C)
K2				
2 hr	9.96	2.2	14	--
6 hr	10.13	33	32	--
3 days	9.96	94	83	--
7 days	9.93	82	130	92
14 days	9.87	88	195	146
35 days	9.56	1.9	318	199
99 days	9.30	0.73	150	--
K3				
2 hr	9.96	0.64	19	--
6 hr	10.14	34	41	--
3 days	9.95	4.6*	73	--
7 days	9.97	4.4*	120	109
14 days	9.88	110	160	148
35 days	9.61	1.5	280	183
99 days	9.19	0.64	190	--

Table 4-17. Chemical Analysis of Column Studies for Site E Samples.					
Sample	pH (units)	Ca (mg/l)	Mg (mg/l)	Cl (mg/l)	Inorganic Carbon (mg/l as C)
K2					
0.72 (5 days)	9.46	110	120	50	64
2.60 (11 days)	9.47	7.8	89	34	62
6.11 (24 days)	9.21	83	80	4.5	48
24.9 (66 days)	8.53	1.5	34	--	--
K3					
1.05 (5 days)	9.14	6.9	58	55	47
2.87 (11 days)	9.12	73	84	46	40
6.27 (24 days)	8.92	5.3	52	15	38
24.8 (66 days)	8.83	1.1	37	--	--
(a) Numbers in the left-hand column represent cumulative pore volumes of solution through the column. Numbers in parenthesis represent the actual time of leaching.					

4.3.3 Site F

Three of the soil samples obtained at Site F were examined in the initial solubility studies. These samples include soil sample 2, which had the highest concentration of Cs-137, soil sample 5, which had the highest concentration of Ra-226, and soil sample 6, which was taken from the bottom of the East Lagoon. This latter sample was selected since it was the only sample where the soils were in direct contact with the analyzed water.

The only radionuclides detected in the solubility studies were Cs-137 and Ra-226 with associated daughters. This fact is expected from the solids characterization data (see Table 4-10) which shows very low, or no detectable concentrations, of H-3, Sr-90, Th-232, and Am-241. The addition of significant amounts of solution to these samples in the solubility studies only results in a further dilution of these already low values. As a result, only the results for Cs-137 and Ra-226 have meaning.

The solubility data for Cs-137 in these samples (see Figure 4-10) shows a consistent trend for all samples. At pH values greater than four, all samples show Cs-137 concentrations in solution that were at or near the analytical detection limit. Cs-137 in detectable concentration was evident only under the most acidic conditions when significant dissolution of the soils was occurring as a result of added acid. As expected, the Cs-137 concentrations in the acid region were directly correlated with the total Cs-137 present in the soil (see Table 4-11). The absence of Cs-137 from solution in the solubility studies at pH values near those found at the site is also in agreement with the absence of Cs-137 from the groundwater (Table 4-12).

The solubility data for Ra-226 and/or its daughter Bi-214, is provided in Table 4-18. These analyses were done primarily by gamma spectroscopy. This fact, combined with the small

amounts of solution available for analysis, means that the analytical detection limits are higher than for the groundwater. The limited analysis done by AS is, in general, good agreement with the gamma spectroscopy results except for the lower-activity samples. In the lower-activity samples, the gamma spectroscopy appears to overestimate the Ra-226 owing to the high associated uncertainty. The results do show significant increases in Ra-226 or Bi-214 in solution in the more acid pH region. In fact, if the observed Ra-226 concentrations in the solubility studies are corrected for the solid/solution ratio in the experiments (a factor of 30 or 10) it can be seen that the Ra-226 is essentially 100% removed from the solids under the most acidic conditions. This is in contrast to the results for Cs-137 where only a fraction of the Cs was removed even under the most acid conditions. Clearly, the Ra-226 is in a different chemical form in the soils than the Cs-137. At pH values near those found at the site, the observed solubilities of Ra-226 are greatly reduced over their acid values and are close to the detection limits. The low observed concentrations are in at least qualitative agreement with the low observed concentration of Ra-226 found in the groundwater at the site (Table 4-12).

The results for the batch leaching studies (Table 4-19) are also consistent with the solubility results in that the Cs-137 concentrations are at or below the detection limit (~ 0.1 pCi/ml) in all samples and the Ra-226 or Bi-214 concentrations (Table 4-19) are similar to the results of the solubility studies at the same pH values. The pH values in the batch studies were all found to be in the range 7 to 9 (Table 4-20).

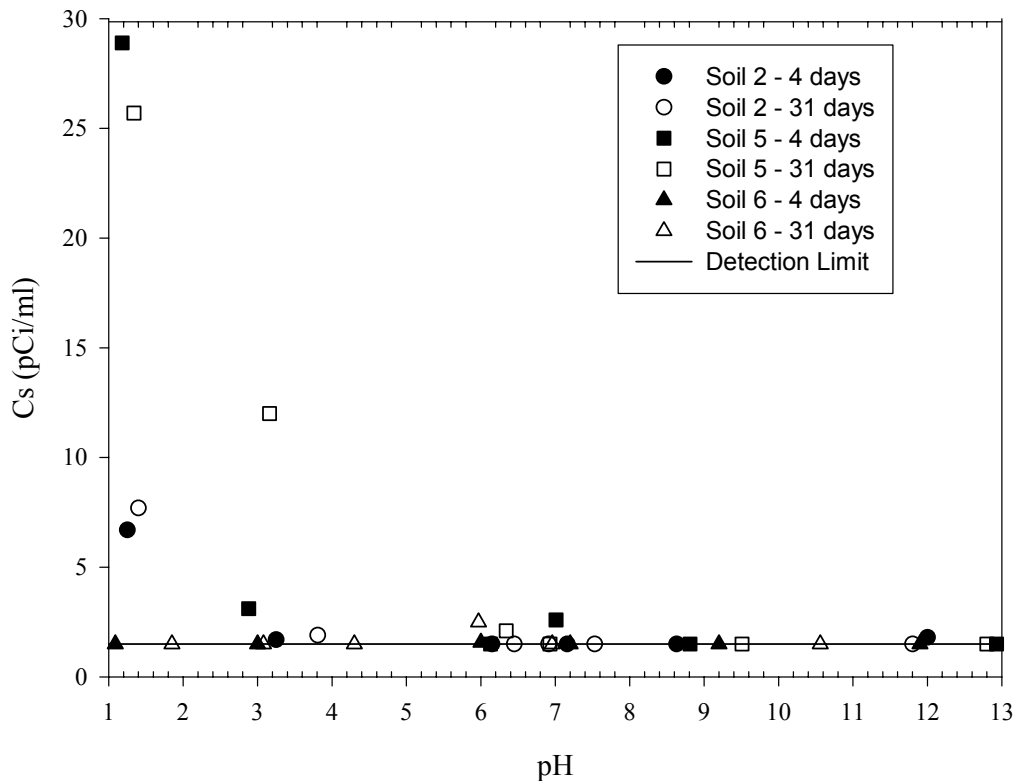


Figure 4-10. Cs-137 Activities in Site F Soil Sample Solubility Studies.

Table 4-18. Ra-226 and Daughter Activities in Site F Solubility Studies.						
Sample	pH (units)	Bi-214	Ra-226	pH (units)	Bi-214	Ra-226
--	--	31 days	--	--	--	--
Soil 2 - 30:1	1.40	9.3 ± 1.8	15.9 ± 4.4 (11 ± 0.2)	--	--	--
--	3.81	11.0 ± 4.5	10.2 ± 6.3	--	--	--
--	6.45	4.9 ± 1.5	4.9 ± 3.0	--	--	--
--	6.91	4.5 ± 1.5	--	--	--	--
--	7.53	3.3 ± 1.3	--	--	--	--
--	11.79	6.6 ± 4.4	--	--	--	--
--	--	4 days	--	--	32 days	--
Soil 2 - 10:1	1.55	60 ± 16	32 ± 7	1.94	20 ± 7	30 ± 5 (31 ± 0.62)
--	5.62	9.8 ± 5.6	--	6.01	6.0 ± 1.7	--
--	7.29	4.1 ± 1.4	--	6.88	8.7 ± 4.7	--
--	9.95	7.0 ± 6.4	--	8.01	4.6 ± 3.5	--
--	--	4 days	--	--	32 days	--
Soil 3 -10:1	2.06	9.7 ± 6.0	--	3.83	11.0 ± 4	- (1.4 ± .07)
--	6.03	6.8 ± 3.4	--	6.29	6.0 ± 4.1	-
--	7.17	6.3 ± 6.0	--	7.22	6.1 ± 1.5	10.9 ± 4.3
--	9.58	2.2 ± 1.3	--	8.11	3.6 ± 1.1	--
--	--	31 days	--	--	--	--
Soil 5 – 30:1	1.34	325 ± 59	298 ± 13 (290 ± 5.8)	--	--	--
--	3.16	38 ± 11	146 ± 7.3	--	--	--
--	6.34	11 ± 7.5	--	--	--	--
--	6.93	7.0 ± 2.4	--	--	--	--
--	9.51	4.9 ± 4.2	--	--	--	--
--	12.80	13 ± 7.5	--	--	--	--
--	--	31 days	--	--	--	--
Soil 6 – 30:1	1.85	12 ± 7.1	14 ± 4.4 (0.52 ± .04)	--	--	--
--	4.32	4.6 ± 1.8	--	--	--	--
--	5.97	14 ± 5.5	--	--	--	--
--	6.96	7.1 ± 3.9	--	--	--	--
--	10.56	2.1 ± 1.2	--	--	--	--

(a) All values in pCi/ml. analysis by gamma spectroscopy. Values in parenthesis were determined by AS.

Table 4-19. Ra-226 and Daughter Activities in Site F Batch Leaching Studies.		
Sample	Bi-214	Ra-226
Soil 2 – 30:1	--	--
2 hr	8.1 ± 3.8	--
6 hr	3.2 ± 0.8	--
3 days	4.3 ± 3.0	--
7 days	4.2 ± 1.5	--
14 days	5.9 ± 4.6	--
36 days	7.2 ± 4.5	--
Soil 2 - 10:1	--	--
2 hr	--	--
6 hr	4.0 ± 1.3	--
3 days	19 ± 10	--
7 days	14 ± 6.4	--
14 days	8.1 ± 3.9	--
35 days	--	--
Soil 3 - 10:1	--	--
2 hr	5.4 ± 1.3	--
6 hr	10 ± 5.3	--
3 days	3.9 ± 1.5	--
7 days	9.8 ± 5.5	--
14 days	--	--
35 days	--	--
Soil 5 – 30:1	--	--
2 hr	5.6 ± 2.6	--
6 hr	4.7 ± 1.4	--
3 days	6.1 ± 1.3	--
7 days	5.7 ± 3.3	--
14 days	6.5 ± 1.4	--
36 days	5.0 ± 1.6	--
Soil 6 – 30:1	--	--
2 hr	4.6 ± 3.3	--
6 hr	11 ± 5.7	--
3 days	8.8 ± 5.4	--
7 days	6.5 ± 5.3	--
14 days	11 ± 4.3	--
36 days	3.4 ± 1.3	--
(a) All values in pCi/ml. Data are shown for two different solution to solid ratios (30:1 and 10:1). Analysis via gamma spectroscopy.		

Leaching Time	Soil 2 – 30:1	Soil 2 – 10:1	Soil 3 – 10:1	Soil 5 – 30:1	Soil 6 – 30:1
2 hr	7.63	7.77	7.71	7.26	7.39
6 hr	7.53	7.78	7.90	7.40	7.44
3 days	7.84	8.02	7.98	7.75	6.72
7 days	7.92	7.77	7.62	7.91	7.18
14 days	--	7.78	7.78	--	--
15 days	8.01	--	--	7.81	7.01
35 days	--	7.80	7.80	--	--
36 days	8.07	--	--	8.05	7.72

Also, as was true in the solubility studies, the concentrations of the other potential radionuclides (H-3, Sr-90, Th-232, and Am-241) were at or below the detection limits as a result of their initially very low values in the soil materials.

The results from the column studies (see Table 4-21) show very similar trends to the solubility and batch experiments. Cs-137 concentrations are at or below the detection limits and Ra-226 is also very near the detection limits for the gamma spectroscopy. The AS measurements of Ra-226 are significantly lower than the gamma spectroscopy measurements for two of the soil columns. Again, this is consistent with the solubility results and indicates that the gamma spectroscopy values should be treated as upper limits. Further evidence for this conclusion comes from a statistical analysis that includes all of the solubility data for Ra-226 and Bi-214 in the solubility studies, batch leaching studies, and columns studies (Figure 4-11). These results show that if the lower limits of the error bars are accepted from the gamma spectroscopy analysis of these samples, then almost half of the analysis could be either at zero or show negative concentrations. The analysis of Ra-226 by AS also shows low concentrations (the three circled points in Figure 4-11) but have very much smaller associated errors and therefore appear to be more reliable.

Sample	Pore Volumes	Cs-137	Ra-226	Sr-90
Soil 2 – fast column	14.18	--	3.2 ± 1.1	--
Soil 2 – slow column ^(a)	6.04	0.21 ± 0.06	0.10 ± 0.02	< .02
“	11.80	--	3.9 ± 1.0	--
Soil 5 – fast column	11.25	0.20 ± 0.06	-	--
Soil 5 – slow column ^(a)	3.37	<.2	1.9 ± 0.2	0.14 ± 0.01
“	8.18	0.15 ± 0.04	3.9 ± 2.1	--
Soil 6 – fast column	13.20	--	8.2 ± 1.5	--
Soil 6 – slow column ^(a)	3.16	<.2	0.02 ± 0.006	<.04
“	7.76	0.18 ± 0.05	6.8 ± 1.2	--

(a) The designation “fast column” refers to a flow rate of 1ml/hr. The designation “slow column” refers to a flow

rate of 0.1ml/hr. All values in pCi/ml. The asterisk designation refers to analysis of Ra-226 via AS.

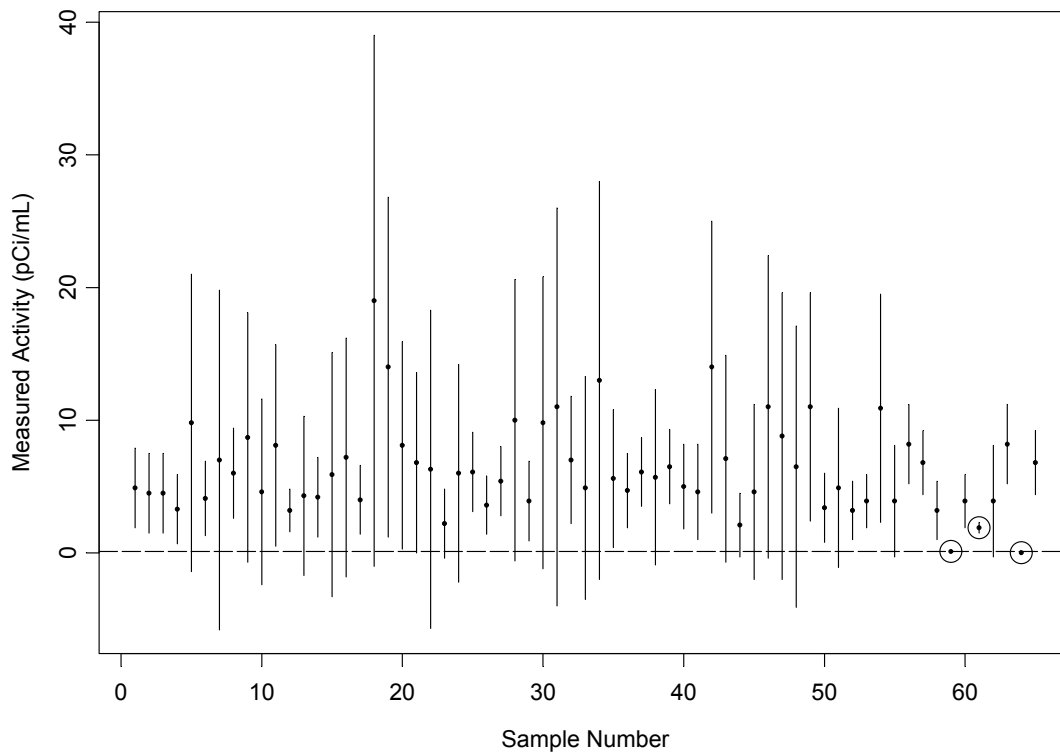


Figure 4-11. Measured Radium-226 and Bismuth-214 Activities and Uncertainties for all Solubility, Batch Leaching, and Column Samples Between pH Values of 5 to 10 from Site F.

This pH range covers the entire range of values found at the site. All analysis is by gamma spectroscopy, except the three circled points that were determined by AS.

4.4 Calculations of Solubility Limits and Leaching Rates

This section presents calculations of the equilibration mass transfer (leaching) rates of Th and U from samples at Sites D and E. Leaching rates for radionuclides at Site F were performed only for Cs-137 and Ra-226 because the other radionuclides were either soluble (H-3 and Sr-90) or the measured concentrations were at or near the analytical detection limits (Ni-63, Am-241). For the radionuclides, these *leaching* rates were calculated using the highest observed dissolved concentration at the shortest equilibration time. This yielded the highest mass transfer rate for equilibration that can be calculated from the data. It is certainly possible that a higher transfer rate could have been calculated if samples were taken at earlier times (earliest times were 2 hr for batch data). Nevertheless, all of the samples reached equilibrium or at least steady state concentrations extremely rapidly since so little mass needed to be transferred to reach the steady state concentration. These calculations numerically demonstrate this fact.

4.4.1 Site D

Solubility was controlled for Th and not U. Th - data from the coarse batch study were used (Table 4-5). The highest solubility observed was $10^{-7.5}$ M Th after 3 days contact time. The solution volume was 30 ml. This yields the following:

- Maximum solubility = 3.2×10^{-8} M
- Leaching rate = 3.1×10^{-9} gTh/hr

U - data from the column study (Figure 4-5) were used to define a “solubility” limit owing to the high solid/solution ratio and U concentration. Data from the batch study (see Figure 4-4) were used to give a maximum leaching rate. The highest U concentration observed in the column study was $10^{-4.8}$ M U after 4.7 days of leaching and this was selected as the solubility limit. The leaching rate was calculated from the batch data at 2 hr of leaching (steady state already obtained). The solution volume was 30 ml and the specific surface area was $19 \text{ m}^2/\text{g}$. This yields the following:

- Maximum solubility = 1.6×10^{-5} M
- Leaching rate = 1.4×10^{-6} gU/hr. or 7.5×10^{-8} gU/m².hr⁴

4.4.2 Site E

The extremely insoluble nature of the radionuclide containing phases in Site E waste makes it possible to calculate only a maximum leach rate based upon the authors’ best estimate of the analytical detection limit for each nuclide. In the case of Th and U this detection limit is approximately $10^{-8.5}$ M. Although we cannot determine a time for dissolution from the batch or column data, it does appear from the solubility studies that the dissolved Th and U is in equilibrium with the solids by the first sampling period (6 days). The maximum leach rates can be calculated as follows:

$$10^{-8.5} \text{ M} = (3.16 \times 10^{-9} \text{ moles/l}) \times (0.03 \text{ L of solution}) = 9.5 \times 10^{-11} \text{ moles dissolved into the solution.}$$

This dissolution occurred in at most 6 days. This yields a leach rate of: 1.5×10^{-10} g Th/hr and 1.6×10^{-10} g U/hr. The rate for U being an obvious high maximum given the low to undetectable concentration of U in the waste. Those calculated “solubility limits” obviously are controlled by the analytical detection limits as opposed to physical processes.

⁴The leaching rates are calculated as follows:

$$(4 \times 10^{-7} \text{ moles U/l})(.031)(238 \text{ gU/mole}) / ((2 \text{ hrs.})(19 \text{ m}^2/\text{gsoil})(1 \text{ gsoil})) \\ = 7.5 \times 10^{-8} \text{ gU/m}^2 \cdot \text{hr.}$$

4.4.3 Site F

The principal radionuclides present in the soils at Site F were Cs-137 and Ra-226. The other radionuclides were either present mostly in the groundwater, H-3 and Sr-90, or were present in the soils at only very low concentration (Ni-63, Am-241, Th-232). In the latter case, the calculation of solubilities or leaching rates is either irrelevant or too low to be measurable.

In the case of Cs-137 and Ra-226 the best data for calculating maximum solubilities and leaching rates is the column data (Table 4-20) analyzed by AS. These data show the maximum leachable Cs-137 concentration was 0.21 pCi/ml (1.8×10^{-14} M) and the maximum Ra-226 concentration was 1.9 pCi/ml (8.5×10^{-12} M). Higher concentrations are reported by gamma spectroscopy but the uncertainties are too high for any definitive use (see Figure 4-10). Although these concentrations are probably not controlled by specific precipitation/dissolution reactions involving discrete solid phase, they do represent upper limits on the possible radionuclide concentration in solution. As such, in computer models such as RESRAD (Yu et al. 2000), their use as maximum “solubilities” has merit. Using these data, the maximum leaching rates would be 1.5×10^{-17} g Cs-137/hr and 2.2×10^{-13} g Ra-226/hr.

The solubility and leaching data from all three sites is summarized in Table 4-22.

Site	U		Th		Cs		Ra	
	Solubility Limit (g/cc)	Leaching Rate (pCi/yr)	Solubility Limit (g/cc)	Leaching Rate (pCi/yr)	Solubility Limit (g/cc)	Leaching Rate (pCi/yr)	Solubility Limit (g/cc)	Leaching Rate (pCi/yr)
Site D	7.4×10^{-9}	3.0	3.8×10^{-6}	4000	--	--	--	--
Site E	7.4×10^{-10}	0.1	7.6×10^{-10}	0.5	--	--	--	--
Site F	--	--	--	--	2.5×10^{-15}	10	1.9×10^{-12}	1900

4.5 Radiocolloids

The best evidence for the presence of radiocolloids is direct analysis of such particles in the groundwater at the site. Unfortunately, this was not possible for Site D since PNNL received only soil samples. In the absence of direct determination, analysis of filtered and unfiltered samples from flow-through column experiments are the only source of information on Site D radiocolloids.

In the case of Site D, comparison of filtered and unfiltered Th and U concentrations in the column studies (Table 4-23) showed high dissolved U concentrations that are identical with or without filtration. Thus, the uranium in Site D leachates appears to be present in the dissolved form.

Table 4-23. Filtered and Unfiltered Thorium and Uranium Concentrations in Column Studies.	
Analysis	Site D
Th - UF	$< 10^{-8.5} \text{M}$
Th - F	$< 10^{-8.5} \text{M}$
U - UF	$10^{-5.60} \text{M}$
U - F	$10^{-5.62} \text{M}$
UF = Unfiltered F = Filtered at Site D.	

In the case of Site E, no radionuclides at concentrations greater than 1 pCi/l were found in either filter or unfiltered samples at the site. Thus there was no evidence for radiocolloid migration at Site E.

At Site F, analysis of particulate material (labeled rust in Table 4-12) collected in the well water samples showed only very low activities indicating that the radionuclides in these wells were predominantly in solution. In addition, analysis of filtered and unfiltered column samples by LSC for total beta and alpha showed newly identical activities (data not shown). Thus, no clear evidence was found for radiocolloid migration at Site F.

4.6. Statistical Analysis

Statistical analysis of the solubility and leaching data proved very difficult at all three sites owing to the generally very low concentrations (at or below the detection limit).

In the case of Site D, all observed Th concentrations were at or below the detection limit so no statistical analysis of the Th data was possible. In the case of U, the concentrations were quite high but varied with solid-to-solution ratio. Therefore, the U did not appear to be solubility controlled and the best data that would be representative of the expected groundwater concentrations would be the column studies. However, there are only four data points in the column experiments (see Figure 4-7). With only four data points, there is no way to determine the uniqueness of the statistical distribution (normal, lognormal, etc.); therefore, there was insufficient information to refute the hypothesis that the data are normally distributed. If a normal distribution is assumed, the mean is $8.9 \times 10^{-6} \text{M}$ and the standard deviation is 6.9×10^{-6} . If an overall distribution of possible U concentrations is simulated using this mean and standard deviation, the resulting distribution is quite broad (Figure 4-12). This broad distribution is not supported by the solubility or batch leaching data which also indicate high U concentrations in solution. The broadness is solely statistical fact given the small number of data points from the column studies.

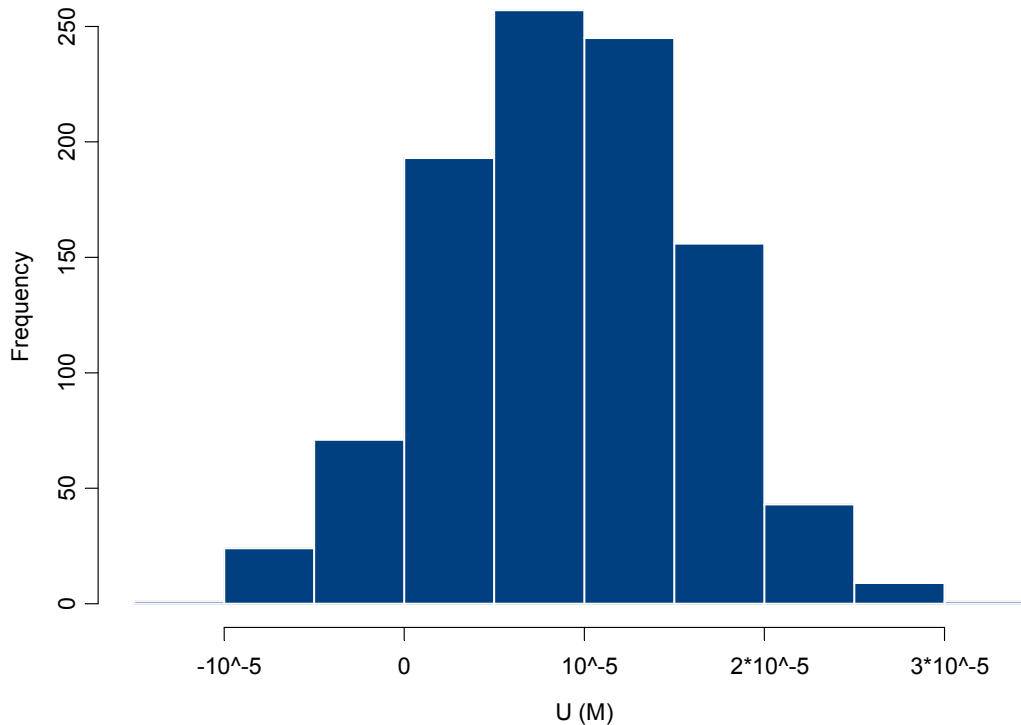


Figure 4-12. Statistically Simulated Distribution of Uranium Concentration at Site D Using Only the Mean and Standard Deviation of the Four Column Data Points.

In the case of Site E, Th was the only major radionuclide present in the waste material. However, the dissolved concentrations of Th never exceeded the analytical detection limit in any of the solubility or leaching studies. Therefore, no statistical analysis was possible.

In the case of Site F, the predominant radionuclides in the soils were Cs-137 and Ra-226. In the case of these radionuclides, most of the analytical data from the solubility and leaching experiments was at or below the analytical detection limit. The only really reliable data for statistical analysis was therefore the column data (Table 4-20) for Cs-137 and the AS analysis of Ra-226. Use of these data yielded a mean and standard deviation for Cs-137 of $1.6 \times 10^{-14} \text{ M} \pm 2.4 \times 10^{-15}$ and for Ra-226, $3.0 \times 10^{-12} \text{ M} \pm 3.9 \times 10^{-12}$. In the case of Ra-226, there are only three points (two quite low and one considerably higher). As a result, the standard deviation for Ra-226 is quite high and use of these results in performance assessment would also be questionable.

5. REFERENCES

- Allison, J.D., D.S. Brown, and K.J. Novo-Gradac. EPA/600/3-91/021, "MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems (Version 3)." U.S. Environmental Protection Agency, Environmental Research Laboratory: Athens, Georgia. 1991.
- Clesceri, L.S., A.E. Greenberg, and A.D. Eaton. *Standard Methods for the Examination of Water and Wastewater, 20th Edition*. American Public Health Association: Washington, D.C. 1999.
- Felmy, A.R., D. Rai, S.M. Sterner, M.J. Mason, N.J. Hess, and S.D. Conradson. "Thermodynamic Models for Highly Charged Aqueous Species: Solubility of Th(IV) Hydrated Oxide in Concentrated NaHCO₃ and Na₂CO₃ Solutions." *Journal of Solution Chemistry*. Vol. 26, No. 3, pp: 233-248. 1997.
- Felmy, A.R., D. Rai, and M.J. Mason. "The Solubility of Hydrated Thorium (IV) Oxide in Chloride Media: Development of an Aqueous Ion-interaction Model." *Radiochimica Acta*. Vol. 55, pp: 177-185. 1991.
- Grenthe, I., J. Fuger, R.J.M. Konings, R.J. LeMire, A.B. Muller, C. Nguyen-Trung and H. Wanner. *Chemical Thermodynamics of Uranium*. North Holland, Elsevier Science Publishers: Amsterdam, The Netherlands. 1992.
- Kalmykov, S.N. and G.R. Choppin. "Mixed Ca²⁺/UO₂²⁺/CO₃²⁻ Complex Formation at Different Ionic Strengths." *Radiochimica Acta*. Vol. 88, pp: 603-606. 2000.
- McKinley, J.P., J.M. Zachara, S.C. Smith, and G.D. Turner. "The Influence of Uranyl Hydrolysis and Multiple Site-Binding Reactions on Adsorption of U(VI) to Montmorillonite." *Clays and Clay Minerals*. Vol. 43, No. 5, pp: 586-598. 1995.
- Monserco (1996). Report No. Monserco196/NB/1821.
- U.S. Nuclear Regulatory Commission. (2002). "2002 ANNUAL UPDATE – STATUS OF DECOMMISSIONING PROGRAM", SECY-02-0169, U.S. Nuclear Regulatory Commission, Washington D.C. 20555-0001, September 18, 2002.
- Yu, C., D. LePoire, E. Gnanapragasam, J. Arnish, S. Kamboj, B.M. Biwer, J.-J. Cheng, and S.Y. Chen. "Probabilistic Modules for the RESRAD 6.0 and RESRAD-BUILD 3.0 Computer Codes." NUREG/CR-6697 (ANL/EAD/TM-98). U.S. Nuclear Regulatory Commission: Washington, D.C. 2000.

APPENDIX A

TABLES OF EXPERIMENTAL DATA.

Table A1. Data Supporting Figure 4-4.

pH	log Th 4 days	log Th 31 days
0.76	--	-7.82
1.79	-8.09	--
2.64	-7.69	--
3.06	--	-8.5
4.13	--	-8.47
5.04	--	-8.5
7.04	-8.01	--
7.95	-8.5	--
8.73	--	-8.5
9.43	-8.5	--
9.84	-8.5	--
9.9	--	-7.16
10.61	-8.5	--
11.14	--	-8.5
12.02	-8.5	--
12.33	--	-8.5

Table A2. Data Supporting Figure 4-5. (2 sheets)

pH	log U(T) 4 days	log U(T) 31 days
1.2	`	-5.12
1.3	-5.15	--
1.73	--	-4.99
1.79	-5.13	--
2.33	--	-5.1
2.28	-5.17	--
2.64	-5.21	--
3.83	-6.09	--
4.13	--	-6.52
4.9	-7.05	--
5.04	--	-7.13
6.19	-7.29	--
6.96	-6.99	--
7.04	-6.47	--
7.27	-6.45	--
7.67	-6.24	--

Table A2. Data Supporting Figure 4-5. (2 sheets)

pH	log U(T) 4 days	log U(T) 31 days
7.95	-6.24	--
8.64	--	-6.48
8.67	-6.36	--
8.96	-6.15	--
9.43	-6.45	--
9.84	-6.4	--
9.9	--	-6.31
10.61	-6.65	--
11.14	--	-6.82
11.42	-6.59	--
12.33	--	-5.74

Table A3. Data Supporting Figure 4-6.

Days	Log U(T) No CO2	log U(T) Short Term (CO2)
0.08	-6.39	--
0.25	-6.16	--
3	--	-6.06
7	-6.25	--
14	--	--
15	-6.35	--
37	-5.64	--

Table A4. Data Supporting Figure 4-7.

Days	log Th Log(moles/L)	log U Log(moles/L)
4.7	-8.5	-4.83
7.3	-8.5	-4.86
30.3	-8.5	-5.44
77.5	-8.5	-5.62

Table A5. Data Supporting Figure 4-8.

pH	log Th(T) 6 days	log Th(T) 32 days
0.34		-3.82
0.56	-3.86	
0.88		-3.88
1.02	-3.93	
3.02	-4.22	
3.97		-5.97
4.23	-6.53	
5.85		<-8.5
6.05	<-8.5	
6.82		<-8.5
8.46		<-8.5
8.73		<-8.5
9.06	<-8.5	
9.17		<-8.5
9.53		<-8.5
9.88	<-8.5	
10.26	<-8.5	
10.36		<-8.5
11.32	<-8.5	<-8.5
11.41		<-8.5
12.03	<-8.5	
12.19		<-8.5

Table A6. Data Supporting Figure 4-9.

pH	Pb-212	Bi-212	Ra-224	Tl-208
3.02	49	60	51	--
3.62	48	62	65	15
4.23	7.6	12	--	8
6.05	0.1	0.1	--	2
11.32	0.1	0.1	0.1	--