This copy Replaces
34456 0349251 1

JUN 1 1990
DATE ISSUED

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0382870 3

ORNL/TM-10561

ornl

OAK RIDGE
NATIONAL
LABORATORY

MARTIN MARIETTA

Laboratory Measurement of Radionuclide Sorption in Solid Waste Storage Area 6 Soil/Groundwater Systems

H. A. Friedman
A. D. Kelmers

OAK RIDGE NATIONAL LABORATORY
CENTRAL RESEARCH LIBRARY
CIRCULATION SECTION
4500N ROOM 175
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this report, send in name with report and the library will arrange a loan.

OPERATED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

ORNL/TM-10561
Dist. Category UC- 512

Chemical Technology Division

LABORATORY MEASUREMENT OF RADIONUCLIDE SORPTION IN SOLID WASTE STORAGE AREA 6 SOIL/GROUNDWATER SYSTEMS

H. A. Friedman
A. D. Kelmers

June 1990

Prepared for the
DOE Office of Remedial Action Program Support

Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0382870 3

CONTENTS

	Page
ABSTRACT	1
1. INTRODUCTION	1
2. MATERIALS AND METHODS	2
2.1 SOILS AND GROUNDWATER	2
2.2 BATCH CONTACT METHODOLOGY	4
3. RESULTS	5
3.1 RADIONUCLIDE SORPTION ISOTHERMS	5
3.1.1 Cesium	6
3.1.2 Cobalt	6
3.1.3 Europium	8
3.1.4 Strontium	9
3.1.5 Uranium	11
3.2 COMPARISON OF SOILS	12
3.3 EFFECT OF pH	14
3.3.1 Europium	15
3.3.2 Uranium	16
3.4 EFFECT OF ORGANIC REAGENTS	17
4. DISCUSSION	18
4.1 SORPTION ISOTHERM TESTS	18
4.2 SCOUTING TESTS	19
4.3 RECOMMENDED SORPTION RATIO VALUES FOR MOBILITY MODELING	20
5. ACKNOWLEDGMENTS	21
6. REFERENCES	21

LABORATORY MEASUREMENT OF RADIONUCLIDE SORPTION IN SOLID WASTE STORAGE AREA 6 SOIL/GROUNDWATER SYSTEMS

H. A. Friedman
A. D. Kelmers

ABSTRACT

Batch contact sorption tests were completed to measure the sorption of several radionuclides in Oak Ridge National Laboratory's Solid Waste Storage Area 6 (SWSA-6) saturated zone soil/groundwater system at a pH of near neutral. In the linear region of the sorption isotherms, sorption ratios for cesium, cobalt, and europium were typically near the analytical detection limit of >3000 L/kg. Strontium and uranium sorption ratios were lower, ranging from 50 to 75 L/kg. The SWSA-6 soil had a high sorption capacity for these elements; and competition for sorption sites, as evidenced by decreased sorption ratios, was not observed in tests with cesium, cobalt, and europium. Minor competition effects were noted for strontium and uranium. Several SWSA-6 unsaturated zone soils were tested; the sorption was markedly reduced in the case of cesium and cobalt. Scouting tests were performed to explore the effects of pH on europium and uranium and the effects of added organic reagents on europium sorption. Provisional sorption ratio values are recommended for use in modeling the mobility of these radionuclides in the SWSA-6 saturated zone.

1. INTRODUCTION

The modeling of the migration of contaminants through low-level waste (LLW) sites conventionally involves the use of retardation factors to characterize the reduced mobility of the contaminants, relative to the groundwater flow rate, which results from sorption of the contaminants onto the soil (Lutton et al. 1982). The retardation factor, R_F (dimensionless), is derived from the expression

$$R_F = 1 + K_D(\rho/\theta) ,$$

where K_D = the experimentally measured sorption distribution coefficient (L/kg),

SWSA-6 trench (located at N 17,500, E 24,650). This sample may be representative of the SWSA-6 saturated zone soils; at least, it was taken from below the leached, unsaturated soil region. After the sample was received in the laboratory on February 10, 1986, the soil was air dried and then screened without crushing to obtain fine material for the sorption tests. Approximately 2 kg of the as-received material passed a 20-mesh screen. This -20-mesh soil fraction was homogenized in a V-blender and used in the sorption experiments. This soil is identified as "SWSA-6 soil," or simply "soil," in this report. Some of the +20-mesh material was used to stabilize the groundwater, as described later.

A few experiments were carried out with small samples of three well-characterized SWSA-6 soils received from S. Y. Lee (ORNL Environmental Sciences Division). These samples are identified in this report as "claystone," "sandstone," and "sandstone plus." The information received with the samples characterized them as follows: claystone, <2 mm; sandstone with manganese coatings, 2-5 mm; and sandstone with shale partings and clay films. These soils are further described in Lietzke and Lee (1986).

The groundwater used in the experiments was from an ~4.5-gal sample of water from well PS-8, which was received in the laboratory on February 10, 1986, in a 5-gal plastic bottle. As received, the groundwater pH was ~8.1. To stabilize the groundwater, about 1 to 2 kg of the +20-mesh soil material was added to the 5-gal bottle, and the soil and groundwater were occasionally mixed by shaking the bottle. The pH of samples of groundwater not stabilized by soil tended to drift upward with time. The presence of the soil components stabilized the groundwater pH at ~7.0 to 7.2 in tests conducted for various times at three water/soil ratios (Table 2.1). Presumably, calcite in the soil was replenishing dissolved CO_2 lost to the atmosphere. Groundwater samples for use in the experiments were withdrawn from the top of the solution in the 5-gal bottle after allowing the soil to settle overnight or longer.

was calculated from the respective element concentrations. The concentration of the element on the solids was calculated from the difference in the initial and after-contact concentration of the groundwater. All experiments were run in triplicate, and the concentration values and sorption ratios given in the tables in Chap. 3 of this report are the mean ±1 standard deviation of the replicate values. The amount of radioactive tracer used in the tests limited the measurement of sorption ratios to values of ~3000 L/kg or less. A few higher R_s values are recorded in some tables in Chap. 3; however, the precision is poor since, at this high an R_s value, the count rate of the solution was approaching the background count rate.

In two series of tests with europium and uranium, the pH of the soil/groundwater system was deliberately adjusted to more acidic values to study the effect of pH on sorption. For these tests, a mixture of ~125 g of soil and ~650 mL of groundwater was adjusted with HCl to the desired pH. The pH was periodically readjusted to the desired value by the addition of more HCl until the pH was stable. The pH-adjusted soil and groundwater were then separated by decantation and filtration and used in sorption tests, as described above.

In one series of tests, organic compounds were added to the groundwater to explore the effect of potential complexing reagents on the sorption of europium. The reagents used were naphthalene (typical of scintillation fluids), EDTA (disodium ethylenediaminetetraacetate, typical of complexing reagents), TBP (tributyl phosphate, used in many solvent extraction steps), and toluene and chloroform (typical waste site organic contaminants).

3. RESULTS

3.1 RADIONUCLIDE SORPTION ISOTHERMS

Sorption isotherms were run to measure the element sorption ratios as a function of concentration. In addition, parallel isotherms were run in the presence of all the elements at the highest concentration tested to investigate competition for sorption sites. Prior to running

Table 3.1. Cesium isotherms

Initial groundwater Cs (mol/L)	After 24-h contact			
	pH	Soil Cs (mol/kg)	Groundwater Cs (mol/L)	R_s (L/kg)
Cesium only[a]				
10^{-3}	7.3	(4.99 ± 0.00)E-03	(2.0 ± 0.9)E-06	3347 ± 2054
10^{-5}	7.3	~5 E-05	At detection limit[b]	>3000
10^{-7}	7.3	~5 E-07	At detection limit	>3000
10^{-9}	7.4	~5 E-09	At detection limit	>3000
10^{-10}	7.4	~5 E-10	At detection limit	>3000
Cesium + others[c]				
10^{-3}	7.3	(4.99 ± 0.00)E-03	(2.1 ± 0.4)E-06	2500 ± 465
10^{-5}	7.4	~5 E-05	At detection limit[b]	>3000
10^{-7}	7.4	~5 E-07	At detection limit	>3000
10^{-9}	7.4	~5 E-09	At detection limit	>3000
10^{-10}	7.4	~5 E-10	At detection limit	>3000

[a]The initial groundwater contained only cesium at the concentrations indicated.

[b]The count rate of ^{137}Cs in solution after contact was near the background count rate; this gave a calculated R_s value of >3000 L/kg. The actual R_s values may have been higher.

[c]The initial groundwater contained cesium at the concentrations indicated plus 1×10^{-3} mol/L each of cobalt, strontium, and uranium and 1×10^{-5} mol/L of europium.

Table 3.2. Cobalt sorption rate

Contact time (h)	After contact[a]			
	pH	Soil Co (mol/kg)	Groundwater Co (mol/L)	R_s (L/kg)
24	7	(4.95 ± 0.00)E-03	(0.96 ± 0.15)E-05	527 ± 77
48	7.1	(4.96 ± 0.00)E-03	(0.69 ± 0.09)E-05	738 ± 108
72	7.0	(4.96 ± 0.00)E-03	(0.76 ± 0.05)E-05	659 ± 43

[a]Initial concentration: 10^{-3} mol/L cobalt.

Table 3.4. Europium isotherms

Initial groundwater Eu (mol/L)	After 24-h contact			
	pH	Soil Eu (mol/kg)	Groundwater Eu (mol/L)	R_s (L/kg)
Europium only[a]				
10^{-5}	7.4	~5E-05	At detection limit[b]	>3000
10^{-7}	7.3	(4.99 ± 0.00)E-07	(1.7 ± 0.2)E-10	2919 ± 340
10^{-9}	7.4	(4.99 ± 0.00)E-09	(1.8 ± 0.5)E-12	3200 ± 1274
10^{-10}	7.4	(4.99 ± 0.00)E-10	(1.8 ± 0.7)E-13	3239 ± 1102
Europium + others[c]				
10^{-5}	7.3	(4.99 ± 0.00)E-05	(1.0 ± 0.3)E-08	5630 ± 1995
10^{-7}	7.3	(4.99 ± 0.00)E-07	(1.4 ± 0.2)E-10	3602 ± 683
10^{-9}	7.3	(4.99 ± 0.00)E-09	(1.3 ± 0.8)E-12	4923 ± 2113
10^{-10}	7.3	(4.99 ± 0.00)E-10	(1.1 ± 0.4)E-13	5886 ± 2964

[a]The initial groundwater contained only europium at the concentrations indicated.

[b]The count rate of ^{155}Eu in solution after contact was near the background count rate; this gave a calculated R_s value of >3000 L/kg. The actual R_s value may have been higher.

[c]The initial groundwater contained europium at the concentrations indicated plus 1×10^{-3} mol/L each of cesium, cobalt, strontium, and uranium.

3.1.4 Strontium

Initial tests (Table 3.5) showed that the strontium-spiked samples had apprently reached a steady-state condition in 24 h or less. Therefore, the sorption isotherms (Table 3.6) were run with a 24-h contact time. With groundwater containing only strontium, the sorption ratio was constant (about 78 L/kg) for samples covering a five order-of-magnitude range of initial Sr^{2+} concentrations (10^{-5} to 10^{-10} mol/L). The sorption ratio fell to 47 L/kg at the highest strontium concentration. When the other elements were added to the groundwater, the sorption ratio values were all depressed to values between 30 and 40 L/kg. This behavior suggests that one or more of the added elements was competing with Sr^{2+} for sorption sites.

3.1.5 Uranium

The sorption behavior of uranium was markedly different from that of the other elements. The preliminary tests with groundwater spiked with 10^{-3} mol/L uranium (Table 3.7) showed only low sorption ratio values of ~2 L/kg and suggested that steady-state conditions might not have been reached by the longest contact time studied (168 h), although the additional decrease in the solution uranium concentration with time was small. Because of time constraints for completion of this work, longer contact times were not explored. The sorption isotherms (Table 3.8) showed a strong dependence of the sorption ratio on the uranium concentration. At lower uranium concentrations, the sorption ratio increased to ~50 to ~60 L/kg for the uranium-only tests and to ~40 to ~50 L/kg when the additional elements were present. The results suggest that the uranium sorption sites may have been nearly saturated at the highest uranium concentrations. The results also suggest that one or more of the additional elements may be competing with uranium for sorption sites.

Table 3.7. Uranium sorption rate

Contact time (h)	After contact[a]			
	pH	Soil U (mol/kg)	Groundwater U (mol/L)	R_S (L/kg)
24	7.5	(1.36 ± 0.06)E-03	(7.28 ± 0.12)E-04	1.87 ± 0.11
48	7.4	(1.39 ± 0.04)E-03	(7.23 ± 0.07)E-04	1.92 ± 0.07
72	7.4	(1.48 ± 0.01)E-03	(7.03 ± 0.02)E-04	2.11 ± 0.02
96	7.4	(1.46 ± 0.05)E-03	(7.09 ± 0.11)E-04	2.05 ± 0.10
168	7.3	(1.54 ± 0.04)E-03	(6.93 ± 0.07)E-04	2.22 ± 0.08

[a]Initial concentration: 10^{-3} mol/L uranium.

Table 3.9. Sorption behavior of four SWSA-6 soils[a]

Element	Soil[b]		Claystone[c]		Sandstone[d]		Sandstone plus[e]	
	pH	R_s (L/kg)	pH	R_s (L/kg)	pH	R_s (L/kg)	pH	R_s (L/kg)
Cs(I)	7.3	3347 ± 2054	5.5	5035 ± 2356	5.9	1446 ± 456	5.1	151 ± 11
Co(II)	7.3	659 ± 43	6.0	229 ± 24	6.3	234 ± 28	5.8	199 ± 10
Eu(III)	7.3	>3000	5.8	>3000	6.2	>3000	5.5	>3000
Sr(II)	7.4	47.3 ± 1.1	5.7	133 ± 5	6.1	39.2 ± 1.6	5.0	49.5 ± 2.7
U(VI)	7.3	2.22 ± 0.08	6.7	6.76 ± 0.30	6.9	4.35 ± 0.31	6.7	20.1 ± 0.7

[a]Groundwater (pH 7.3) was spiked to 10^{-3} mol/L of cesium, cobalt, strontium, or uranium or 10^{-5} mol/L of europium and contacted with 2 g of the respective soil for 168 h at room temperature (~24°C). The pH was measured after contact.

[b]Soil sample from bottom of trench (soil used in all other tests).

[c]Claystone, <2 mm; from S. Y. Lee.

[d]Sandstone with manganese coatings, 2-5 mm; from S. Y. Lee.

[e]Sandstone with shale partings and clay films; from S. Y. Lee.

3.3.1 Europium

The europium sorption ratio proved to be sensitive to the test pH (Table 3.10). The sorption ratio increased from ~100 L/kg at pH ~4.3 to ~3000 L/kg at pH ~6.7 or higher. Lower R_s values were observed at the highest europium concentration used, 10^{-3} mol/L, presumably because of loading effects on the sorbent.

Table 3.10. Europium sorption isotherms as a function of pH

Initial groundwater Eu (mol/L)	After 168-h contact[a]			
	pH	Soil Eu (mol/kg)	Groundwater Eu (mol/L)	R_s (L/kg)
pH ~4.3				
10^{-3}	4.2	(4.61 ± 0.01)E-03	(7.85 ± 0.13)E-05	58.8 ± 1.1
10^{-5}	4.3	(4.74 ± 0.00)E-05	(5.16 ± 0.06)E-07	91.9 ± 1.1
10^{-7}	4.3	(4.76 ± 0.01)E-07	(4.84 ± 0.19)E-09	98.4 ± 4.0
10^{-9}	4.4	(4.75 ± 0.01)E-09	(4.98 ± 0.13)E-11	95.4 ± 2.6
10^{-10}	4.4	(4.76 ± 0.00)E-10	(4.84 ± 0.19)E-12	98.5 ± 4.3
pH ~5.6				
10^{-3}	5.3	(4.80 ± 0.01)E-03	(4.10 ± 0.15)E-05	117 ± 5
10^{-5}	5.6	(4.95 ± 0.01)E-05	(1.10 ± 0.28)E-07	487 ± 141
10^{-7}	5.7	(4.95 ± 0.01)E-07	(1.06 ± 0.07)E-09	467 ± 32
10^{-9}	5.6	(4.95 ± 0.01)E-09	(1.09 ± 0.14)E-11	461 ± 65
10^{-10}	5.7	(4.96 ± 0.01)E-10	(8.90 ± 1.91)E-13	580 ± 109
pH ~6.7				
10^{-3}	6.4	(4.96 ± 0.00)E-03	(7.7 ± 0.4)E-06	646 ± 38
10^{-5}	6.7	(4.99 ± 0.00)E-05	(1.1 ± 0.7)E-08	6326 ± 5004
10^{-7}	6.7	(4.99 ± 0.00)E-07	(1.7 ± 1.1)E-10	4115 ± 1937
10^{-9}	6.8	(4.99 ± 0.00)E-09	(1.7 ± 0.4)E-12	3054 ± 564
10^{-10}	6.8	(4.99 ± 0.00)E-10	(1.5 ± 0.3)E-13	3478 ± 765
pH ~7.4 (from Table 3.4)				
10^{-7}	7.3	(4.99 ± 0.00)E-07	(1.7 ± 0.2)E-10	2919 ± 340
10^{-9}	7.4	(4.99 ± 0.00)E-09	(1.8 ± 0.5)E-12	3200 ± 1274
10^{-10}	7.4	(4.99 ± 0.00)E-10	(1.8 ± 0.7)E-13	3239 ± 1102

3.4 EFFECT OF ORGANIC REAGENTS

Sorption tests were run with europium in the presence of a number of organic reagents typical of those that might be encountered in SWSA-6. Locations identified as solvent auger holes exist on SWSA-6 maps, but apparently no information is available as to the solvents or method of disposal used (Solomon 1986). The organics tested (at ten times the europium concentration) were naphthalene, EDTA, TBP, toluene, and chloroform. Their effect on europium was examined since europium is the largest single radioactive contaminant discharged to SWSA-6 (Beogly et al. 1985). The results (Table 3.12) were surprising. None of the organics had any measurable effect on the europium sorption ratio at this pH. This provisional finding is highly favorable to the predicted future ability of SWSA-6 to retard the release of europium since the results suggest that at least these organics may not complex with europium and decrease the high (>3000 L/kg) sorption ratio.

Table 3.12. Effect of organic reagents on europium sorption

Organic reagent (mol/L)	After contact[a]		
	Soil Eu (mol/kg)	Groundwater Eu (mol/L)	R_s (L/kg)
Naphthalene	~5E-07	At detection limit[b]	>3000
EDTA	(5.00 ± 0.00)E-07	(1.6 ± 0.7)E-10	3626 ± 1465
TBP	~5E-07	At detection limit[b]	>3000
Toluene	~5E-07	At detection limit[b]	>3000
Chloroform	~5E-07	At detection limit[b]	>3000

[a]The initial groundwater contained 10^{-7} mol/L europium. The organic reagents were then added to the groundwater at a concentration of 10^{-6} mol/L. The contact time was 168 h. The final pHs were 7.4 to 7.5.

[b]The count rate of the ^{155}Eu in solution after contact was near the background count rate; this gave a calculated R_s value of >3000 L/kg. The actual value may have been higher.

the R_S value was reduced only by one-half or less. This is a surprising result and suggests that at least some of the elements may have discrete or unique sorption sites on specific mineral phases. More evidence of competition for sorption sites had been anticipated. This finding suggests that the SWSA-6 sorption capacity for these radionuclides may not be easily compromised by the presence of other solution species.

4.2 SCOUTING TESTS

After completion of the sorption isotherm tests under steady-state conditions and saturated zone-relevant geochemical parameters, a few additional tests were completed to explore the effects of several parameters on the sorption behavior of selected elements. Significant observations from these tests are as follows:

1. Various soils - The geology of the SWSA-6 site is complex and poorly characterized (Boegly et al. 1985), and a variety of soil types exists at different locations and depths (Lietzke and Lee 1986). Sorption tests were run at a 10^{-3}-mol/L concentration with three different well-characterized soils for comparison with the large batch of soil used in the isotherm tests. Major differences were observed in the measured sorption ratio for the some of the elements onto the different soils. Cesium sorption ratios ranged from ~150 to ~5000 L/kg; cobalt, from ~200 to ~650 L/kg; strontium, from ~40 to ~130 L/kg; and uranium, from ~2 to ~20 L/kg. Europium sorption ratios were <3000 L/kg, near the analytical detection limit, for all soils. Most of the well-characterized soils changed the pH of the poorly buffered groundwater to pHs between 5 and 6. Apparently, these soils are mineralogically different from the soil from the bottom of a trench since they altered the test pH as well as the sorption behavior. These scouting test results suggest that modeling the mobility of radionuclides in the unsaturated zone could be complex because of the variability of soils and groundwater parameters which might exist.

2. Effect of pH - The effect of the test pH was systematically studied only for europium and uranium, the major contaminants present in SWSA-6. The R_S value for both elements was sensitive to the pH. Europium sorption decreased from >3000 L/kg at near-neutral pH to ~100 L/k g at pH ~4.3. Uranium sorption displayed a maximum R_S value of ~3000 L/kg at pH ~5.5, and the R_S value decreased at lower or higher pHs. For these elements at least, defensible mobility modeling may require knowledge of the soil/groundwater system pH along the release pathway.

Table 4.1. Provisionally recommended radionuclide sorption ratios for the SWSA-6 saturated zone (pH 7.0 to 7.5)

Element	R_s (L/kg)	Comments
Cs	3000	May be lower in leached (unsaturated) zone soils.
Co	3000	May be lower in leached (unsaturated) zone soils.
Eu	3000	May be lower at lower pHs.
Sr	30	Value accommodates site competition.
U	40	Value accommodates site competition; may be higher in leached zone; may be higher at lower pHs.

5. ACKNOWLEDGMENTS

The authors wish to acknowledge the cooperation of G. N. Case and W. J. McDowell (Chemistry Division), who made available the counting equipment used for the analyses. W. D. Arnold and G. N. Case (Chemistry Division) supplied the radioactive isotopes. S. Y. Lee and D. K. Solomon (Environmental Sciences Division) provided the soil samples used in the tests. Thanks are extended to Janice Shannon for typing the manuscript and Janice Asher for editorial services.

6. REFERENCES

Baes, C. F., Jr., and Mesmer, R. E., 1976. The Hydrolysis of Cations, Wiley-Interscience (Wiley), New York.

Boegly, W. J. et al. 1985. Characterization Plan for Solid Waste Storage Area 6, ORNL/TM-9877, Oak Ridge National Laboratory.

Langmuir, D. 1978. "Uranium Solution-Mineral Equilibria at Low Temperatures with Applications to Sedimentary Ore Deposits," Geochim. Cosmochim. Acta 42, 547-69.

ORNL/TM-10561
Dist. Category UC-512

INTERNAL DISTRIBUTION

1. J. T. Bell
2. W. J. Boegly, Jr.
3. R. B. Clapp
4. J. L. Collins
5. A. G. Croff
6. N. H. Cutshall
7. E. C. Davis
8-12. H. A. Friedman
13. R. K. Genung
14. J. R. Hightower
15. D. D. Huff
16. E. K. Johnson
17-21. A. D. Kelmers
22. J. M. Kennerly
23. R. H. Ketelle
24. D. C. Kocher
25. C. E. Lamb
26. D. W. Lee
27. S. Y. Lee
28. R. J. Luxmoore
29-32. P. T. Owen
33. E. D. Smith
34. D. K. Solomon
35. M. G. Stewart
36. S. H. Stow
37. J. R. Trabalka
38. G. T. Yeh
39. A. Zucker
40. Central Research Library
41. ORNL-Y-12 Technical Library
Document Reference Section
42-43. Laboratory Records
44. Laboratory Records - RC
45. ORNL Patent Section

EXTERNAL DISTRIBUTION

46. Office of Assistant Manager, Energy Research and Development, DOE-ORO, P.O. Box 2001, Oak Ridge, TN 37831
47-56. Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831