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Fission-Product-Sorption Parameters For Hanford 200 Area Sediment Types

Prepared for the United States
Department of Energy
Under Contract DE-AC06-77RL01030

Rockwell International

Rockwell Hanford Operations
Energy Systems Group
Richland, WA 99352

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FISSION-PRODUCT-SORPTION PARAMETERS FOR
HANFORD 200 AREA SEDIMENT TYPES

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ABSTRACT

Studies were conducted to measure the Hanford Site 200 Separation Areas sorption properties for trace strontium (^{85}Sr), cesium (^{137}Cs), and cobalt (^{60}Co). Scintillation logs of ground disposal facilities and particle size plus calcium carbonate sediment data were used to independently delineate sediment types. Good agreement was found between the sediment types from the two methods. Twenty-one sediment types were delineated from five wells.

A preliminary study was conducted to select an improved predictive method for relating the distribution coefficient (K_d) value to the equilibrium solution concentration of sodium (Na^+), calcium (Ca^{+2}), and potassium (K^+). An empirical, statistical method developed by Box-Behnken was selected and found to be: 1) the most economical; 2) equally precise; and 3) equally unbiased of the three methods investigated. This method combines a three-level, factorial design with internal replication to develop empirical predictive K_d value equations.

Sixty-three empirical K_d value equations were developed for trace strontium, cesium, and cobalt sorption on 21 sediment types from the 200 Separation Areas. The coefficients in these equations for all three trace ions were internally of the same general form. However, there were marked differences between comparable coefficients for the different trace ions. Average coefficient values were computed for each trace ion and compared. Strontium sorption was: 1) controlled to a large extent by Ca^{+2} ; 2) controlled to lesser extent by Na^+ ; and 3) independent of K^+ . In contrast, cesium sorption was: 1) controlled to a large extent by K^+ ; 2) controlled to a lesser extent by Na^+ ; and independent of Ca^{+2} . Cobalt sorption was controlled only by Ca^{+2} . Ion exchange parameters were determined for the 21 sediment types including cation exchange capacities, selectivity coefficients for calcium-magnesium, sodium-calcium, and sodium-potassium exchanges, and solid phase activity correction coefficients. These data are required for the transport modeling of ^{90}Sr , ^{137}Cs , and ^{60}Co in varied sodium, calcium, and potassium solutions.

A sensitivity analysis of retardation factor values for two selected sediment chemical systems were evaluated to determine if additional 200 Separation Areas sediment measurements are required. Retardation factors were compared for paired sediment types which occupy similar stratigraphic locations in the sampled wells. These values were generally within a factor of two which is within the range expected considering both experimental and sampling errors. Thus, no additional sorption property measurements are required for the areas enclosed by these wells.

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INTRODUCTION

Since 1944, the Hanford Site has been the location for nuclear reactor operations, chemical separation of nuclear materials, and the storage of radioactive wastes. These activities resulted in the storage and disposal of fission product and transuranic (TRU) radioactive wastes in the near-surface sediments above the water table (vadose zone). Sorption studies have been conducted since early site operation to guide operations concerning the disposal of large-volume, low-level wastes. Sorption measurements have changed with time from generic to waste-specific/site-specific and, finally, to waste property areal/site-specific, based on a transport model (Routson and Serne, 1973, Routson et al., 1980).

This multicomponent mass transport (MMT) computer model was developed to assess potential migration of the fission products from contaminated soils and sediments of the Hanford Site (Ahlstrom et al., 1977). The long-term objective of this research is to obtain sufficient sorption data to meet the assessment needs of the MMT model. These data will be site-specific for the vadose zone of the Hanford Site Separation Areas, where a large portion of the fission product wastes reside. This work was conducted under the Contaminated Soils and Sediments Program.

A laboratory-verified submodel, PERCOL, was developed to predict the transport of radionuclides through the unsaturated and saturated sediments of the Hanford Site (Routson and Serne, 1973) and contains the chemical reactions and sorption portion of the MMT model. One of the sorption parameters in the PERCOL model is the distribution coefficient (K_d) value.

The equilibrium Kd is

$$K_d = \frac{A_s/W}{A_l/V} \quad (1)$$

where:

A_s = equilibrium radioactivity sorbed on the solid phase

W = weight of solid phase

A_l = equilibrium radioactivity of the solution

V = volume of solution.

The Kd is a variable system parameter whose numerical value is a function of soil type and the equilibrium concentration of all macroions. (Routson and Serne, 1973).

Macroions are solutes which exist in solution in concentrations high enough to make an appreciable contribution to a system's ionic strength and chemical reactions. Macroions in natural soil systems are generally sodium (Na^+), potassium (K^+), calcium (Ca^{+2}), and magnesium (Mg^{+2}). In contrast, trace ions (fission products in soil systems) exist in solution in such low concentrations ($\leq 10^{-6}\text{M}$) that they make a negligible contribution to the system's ionic strength and chemical reactions other than reactions affecting the trace ion itself, such as sorption. The Kd value for a trace ion is constant in a given soil type-macroion system.

Radionuclide concentrations in solution range up to a maximum concentration of approximately 10^{-6}M at Hanford in high-level waste tank leak systems (Routson et al., 1979) and are generally several orders of magnitude lower. In contrast, macroions in Hanford soil systems range from a low of approximately 10^{-3}M in ground water systems to over 3M Na^+ in tank leak systems. Thus, macroions are at least three and generally six orders of magnitude more concentrated than are their counterpart trace ions.

Recent non-Hanford studies have evaluated at what solution concentrations strontium (Sr) and cesium (Cs) solutes can no longer be treated as trace solutes in various soil and mineral systems. Seitz et al., (1980) found that Sr acted as a trace ion in a ground limestone system up to concentrations of at least 10^{-6} M. In contrast, they found that Cs^+ no longer behaved as a trace ion at concentrations as low as 10^{-8} M. However, a ground limestone system is not a soil system. Gillham et al., (1980) found that Cs behaved as a trace ion up to a concentration of approximately 10^{-5} M in several low-exchange sandy soils similar to those at Hanford, which is approximately the concentration of Cs in some high-level waste tank systems. Thus, apparently:

- Sr in all Hanford wastes can be treated as a trace component
- Cs in all Hanford wastes except high-level wastes can be treated as a trace component
- Cs in Hanford high-level waste tank systems probably behave as a trace component.

Macroion reactions include ion-exchange, precipitation/dissolution, and ion-pairing reactions.

Two separate but interrelated studies are reported:

1. a sorption parameter measurement study to characterize the fission product sorption behavior of the Hanford Site 200 Separation Areas vadose zone sediments
2. an evaluation of three alternative measurement methods to select the most reasonable for use in the sorption parameter measurement study.

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MATERIALS AND METHODS

PRELIMINARY STUDY

To select a measurement method for use in the sorption parameter measurement study, an alternative measurement method evaluation was performed. The objective of this preliminary research was to evaluate three alternative methods of measuring the relationships between K_d values for Sr, Cs, and cobalt (Co) as a function of the equilibrium concentrations of macroions Na^+ , K^+ , and Ca^{+2} . Three K_d predictive methods were investigated (Routson et al., 1981).

The general approach used for the investigation of these methods was to measure K_d values in "pure" (single-macroion) systems and to use theoretical techniques to calculate K_d values in mixed systems (natural soil-sediment systems). A theoretical method (Mercer et al., 1967) has been used for estimating mixed-system K_d values from single-macroion system data.

Method 1

A theoretical measurement method (Mercer et al., 1967) applied mass action principles to develop a method for estimating the K_d in mixed-ion systems: Mercer's equation is

$$\sum_{i=1}^n \left[\frac{(K_{d_{A^*}})^a (C_i)^b}{(K_{A^*N})} \right]^{a/b} = 1 \quad (2)$$

where:

A^* = trace ion

N = macroion

$K_{d_{A^*}}$ = the distribution coefficient of trace ion in the mixed-ion system in mL/g

a and b = the integers found by balancing a mass action ion exchange formula

n = the number of macroions being considered in the system

C_n = the equilibrium activity of macroion n in the ion exchange system

K_{A*N} = selectivity coefficient in a trace-macroion system.

For the Sr trace sorption in CaNa macroion system, Eq. 2 reduces to

$$\frac{K_{d_{SrCaNa}}}{K_{d_{SrCa}}} + \left(\frac{K_{d_{SrCaNa}}}{K_{d_{SrNa}}} \right)^{1/2} = 1 \quad (3)$$

where (Mercer, 1967):

$K_{d_{SrCaNa}}$ = the distribution coefficient for Sr in the mixed CaNa macroion system

$K_{d_{SrCa}}$ = the distribution coefficient for Sr in the single-macroion Ca system at the equilibrium concentration of Ca being considered

$K_{d_{SrNa}}$ = the distribution coefficient for Sr in the single-macroion Na system at the equilibrium concentration of Na being considered.

Method 2

A second theoretical method (resistance) was considered in the study. It appeared that the K_d in mixed systems was somewhat analogous to parallel resistance in an electrical circuit. By inference, the resistance method was tested

$$\frac{1}{K_{d_{SrCaNa}}} = \frac{1}{K_{d_{SrNa}}} + \frac{1}{K_{d_{SrCa}}} \quad (4)$$

Method 3

The statistical method investigated is a three-level factorial experimental design with internal replication developed by Box and Behnken (1960). The internal replication results in a significant

experimental decrease in replication over that of the two-range, four-replicates-per-data point, full two-level factorial design used in developing the PERCOL model. The concentration combinations of Na^+ , K^+ , and Ca^{+2} were determined using the statistical method which uses individual t-tests to test the estimated coefficients in the equation:

$$F(x) = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad (5)$$

where:

$F(x)$ = natural logarithm ($\ln$) K_d

X_1 = a function of the equilibrium concentration of Na

X_2 = a function of the equilibrium concentration of Ca

X_3 = a function of the equilibrium concentration of K

$\beta_0 - \beta_{23}$ = the statistically determined coefficients.

Not all β values are found to be statistically significant and are not included in the equation for a given sediment type and radionuclide.

In addition, a procedure called "stepwise regression analysis" (Hollander and Wolf, 1973) was used. Stepwise regression analysis computes a sequence of multiple linear regression equations in a stepwise manner.

Assessment

The preliminary study was conducted to assess which of the methods evaluated was the most precise, unbiased, and economical.

The initial part of the preliminary study was designed to determine if Mercer's theoretical method was capable of predicting $K_{d_{\text{Sr}}}$ as a function of the solution concentration of Na^+ and Ca^{+2} . Two sediments considered representative of the subsoils occurring in waste disposal areas of the Hanford Site were used. (These are the same two sediments used in the column verification studies for the PERCOL model.) A third sediment type from Well E17-4 (Burbank sand and Tank Farm sandy loam) was used in a later portion of the preliminary study. Properties of the sediments used in the preliminary study are listed in Table 1.

TABLE 1. Textural Properties, Cation Exchange Capacity (CEC), and CaCO_3 Content of Sediments Used in the Preliminary Study.

Sediment	CaCO_3 , mg/g	Silt, %	Clay, %	CEC (pH 7.0), meq/100 g
Burbank Sand	0.8	10	0.5	4.9
Tank Farm Sandy Loam	26	30	4.9	4
E17-4, 35-255 ft	34	8.3	1.9	3.6

The $K_{d_{\text{Sr}}}$ was measured in a batch equilibrium system at a 1:1 (25 g to 25 ml) solution-to-soil ratio. Sorption values were measured on solutions composed of calcium nitrate [$\text{Ca}(\text{NO}_3)_2$] in concentrations of 0.002, 0.02, 0.05, 0.10, and 0.20M, and sodium nitrate (NaNO_3) in concentrations of 0.015, 0.030, 0.75, and 3.0M.

Tare weights were determined on 250-ml polyethylene, screw-cap, centrifuge bottles. Approximately 25 g of cone and quartered and well-mixed soil were weighed into the tared centrifuge bottles. Twenty-five milliliters of the Na^+ or Ca^{+2} solution (without spike) were placed in each bottle. Bottles were placed on a shaker and moderately agitated for 20 to 30 min. The bottles were then centrifuged at 20 to 30°C for approximately 30 min. at 4,000 rpm and the supernatant aspirated from the soil. Two additional prewashes of the matrix solution (without spike) were performed. After the third aspiration, the bottles were reweighed and the residual solution calculated by difference.

Twenty-five milliliters of the Na^+ or Ca^{+2} solution was spiked with ^{85}Sr to approximately 2,000 cpm/ml of ^{85}Sr and placed into 250-ml bottles. The soil was swirled to assist the initial mixing. The bottles were then agitated at moderate rates for 21 to 24 hrs. Following agitation, the bottles were centrifuged as before and the supernatants aspirated into 50-ml polyethylene bottles for counting.

Equilibrium pH values were measured for selected samples. The pH values were within 0.1 pH unit of influent solution pH. Initial and equilibrium ^{85}Sr activities were measured with a 400-channel, gamma-counting spectrometer with a 4-in. well crystal.

Laboratory Kd values were estimated by

$$K_d = \frac{(rC_o - C_e)}{C_e} \frac{A}{B} \quad (6)$$

where:

A = total milliliter solution in the last treatment, 25 ml + residual solution from prewashes

B = total grams of soil present

r = ratio of traced solution to total solution, 25/(25 ml + residual solution from prewashes)

C_o = concentration of trace constituent in initial solution, cpm/ml

C_e = concentration of trace constituent in final solution, cpm/ml.

The solution pH of selected samples was monitored with a single electrode pH meter. For characterizing the soils, the soil pH was measured in 0.01M CaCl_2 with a single electrode pH meter. Cation exchange capacity (CEC) was measured by a small column procedure (Routson et al., 1972). Calcium carbonate content was measured by a volumetric calcimeter method (Allison and Moodie, 1965).

In the second part of the preliminary study, both the theoretical and statistical methods were investigated. In addition, the study was expanded to include Sr, Cs, and Co sorption and Na, K, and Ca systems. The sediment used in the study was composited from the 35- to 255-ft level of Well E17-4 on the Hanford Site (Table 1).

Methods used were similar to those used in the first part of the preliminary study with the following exceptions: the solution-to-soil ratio used was approximately 6:1 (30 ml to 5 g) and the equilibrium

times were expanded to 4 days. In the case of the Sr sorption, Kd values were determined from the equilibrated solution and by counting the Sr sorbed in the sediment. Calculation of Kd_{Sr} from the sediment was based on

$$Kd_{Sr} = \frac{C_{se}}{C_e} \frac{A}{B} \quad (7)$$

where:

C_{se} = the quantity of ^{85}Sr in the sediment.

SORPTION PARAMETER STUDY

Subdividing the vadose zone sediments of the Hanford Site Separation Areas into several general sediment types was accomplished by examining in-well scintillation logs of Separation Areas crib-monitoring wells (Fecht et al., 1977). Sharp breaks in gamma radioactivity distributions were equated with changes in sediment sorption types which were then compared with sediment types delineated in the Separation Areas tank farms from granulometric and carbonate data (Fecht, 1977).

Table 2 lists the well and crib areas considered in the analysis. Figure 1 presents generalized cross sections based on the above analysis. Comparison of Figure 1 with Figure 2 shows a good correspondence between sediment types based on sorption and particle size. This strongly suggests that the existing stratigraphic map of the 200 East and 200 West Areas tank farms and crib areas can be used to delineate sediment sorption behavior.

Six well locations were chosen near the tank farms and major crib disposal areas (Figures 3, 4 and Table 3) for the initial characterization effort. Selected sediment types are listed in Table 3. Samples were composited for each sediment type by quartering from drilling samples.

TABLE 2. Cribs, Crib Areas and Associated Wells Used to Develop Figure 1 in This Document.

200 East Area				200 West Area			
Crib	Well	Crib	Well	Crib	Well	Crib	Well
A5	E24-10	B14 to B19(BC)	E13-1 E13-2 E13-21	S1, S2	W22-2 W22-15 W22-18 W22-1A W22-1B W22-3A W22-10	T7	W10-1 W10-67 W10-68 W10-72 W10-69
A8	E25-6A E25-4 E25-5 E25-6 E25-7 E25-8	B43 to B50(BY)	E33-1 E33-2 E33-3 E33-22 E33-4 E33-23 E33-5 E33-7	S7	W22-13A W22-14 W14-2A W22-12 W22-13 W22-14 W22-32	T19	W15-4 W15-80 W19-3
A9	E24-4					T28	W11-11 W14-2 W14-3 W14-4 W14-1
A10	E17-1 E17-2 E24-2 E25-59 E24-60						
A24	E26-5 E26-7 E26-4 E26-2			S9	W22-21 W22-26 W22-34 W22-35	T35	W11-17 W11-15 W11-18
A36A- A36B	E17-4 E17-2 E17-9 E17-5			T3	W11-7 W11-15 W11-18	U1, U2 Z7 Z9	W19-3 W15-7 W15-5 W15-6

FIGURE 1A. Sorption Cross Section of Crib Areas - 200 West Area.
(Dots Represent Sharp Breaks in Total Gamma Radioactivity
Distribution in Ground Disposal Facilities.)

FIGURE 1B. Sorption Cross Section of Crib Areas - 200 East Area.
(Dots Represent Sharp Breaks in Total Gamma Radioactivity
Distribution in Ground Disposal Facilities.)

FIGURE 2. Geologic Cross Sections of the 200 Areas.

200 EAST AREA

FIGURE 3. Disposal Areas (Showing Locations of the Sample Wells) for 200 East Area.

200 WEST AREA

FIGURE 4. Disposal Areas (Showing Locations of the Sample Wells) for 200 West Area.

TABLE 3. Selected Well Locations and Sediment Types for Characterization of 200 Areas.

Well Location	Crib	Tank Farm	Sediment Designation	Sediment Interval (ft)
<u>200 East Area</u>				
E13-8	BC		1	0 - 40
			2	45 - 60
			3	165 - 220
			4	225 - 265
			5	270 - 320
E33-22	BY	B	6	0 - 35
		BX	7	40 - 80
		BY	8	85 - 195
			9	195 - 240
E17-4	A5, A10, A36		10	0 - 30
			11	35 - 255
			12	260 - 300
Near E28-17	A8, A24	A ^a		
		AX		
		AY		
<u>200 West Area</u>				
W22-25	S	S	13	0 - 40
		SX	14	45 - 65
		SY	15	70 - 120
		U	16	125 - 145
			17	150 - 205
W10-9	T	T	18	0 - 40
		TX	19	45 - 80
		TY	20	80 - 185
		U	21	190 - 225

^aNot selected.

In the 200 East Area, all major crib areas are represented except for a channeled area near the A24 and A8 cribs where no appropriate samples are presently available. The existence of an old river channel near these cribs suggests that sorption data for Well E17-4 may not be applicable for characterizing sorption in this area. In the 200 West Area, only two wells were selected in the characterization. The sediments in 200 West Area are known to grade in a predictable manner. From

north to south, these sediments tend to become finer and dip a few degrees to the southwest. The 200 West Area wells are located near the extremes of the mapped cross section (Figure 1) and thus, may be expected to span the extremes of sorption in the area.

Sediment and mineralogical properties of the 21 selected 200 Separation Areas sediments are listed in Tables 4, 5, 6, and 7.

TABLE 4. Textural Properties, Cation Exchange Capacity (CEC), and CaCO_3 Content of Hanford Site Separation Areas Sediments.

Sediment Type	Clay, %	Silt, %	Sand, %	>2 mm, %	CEC, meq/100 g	CaCO_3 , mg/g
1	1.71	3.57	94.72	13.6	5.2	5
2	1.50	2.20	96.30	2.3	3.5	15
3	2.03	3.20	94.77	1.6	2.4	13
4	2.14	2.33	95.53	26.1	3.8	7
5	1.11	3.50	95.39	0.0	3.1	6
6	4.36	17.96	77.68	29.5	5.4	10
7	2.9	7.64	89.46	7.8	3.0	19
8	1.34	6.90	91.76	6.8	3.5	19
9	3.14	8.85	88.01	41.0	2.7	4
10 ^a	--	--	--	10.0	3.6	21
11	1.92	8.34	89.74	3.5	3.6	34
12	3.86	15.73	80.41	14.2	3.8	8
13	3.49	18.87	81.12	4.2	5.0	22
14	3.19	17.99	78.02	20.0	3.7	17
15	2.13	10.05	87.82	0.5	3.9	17
16	9.53	43.70	46.77	5.7	2.0	20
17	4.08	18.80	77.12	24.6	4.1	12
18	2.27	38.96	58.77	14.6	5.7	0
19	2.95	10.32	87.48	20.5	6.8	0
20	5.92	40.5	53.58	2.1	5.4	0
21	7.14	28.46	64.40	12.0	6.9	0

^aInsufficient sample available to make this analysis.

TABLE 5. Mineralogy of Hanford Site Separation Areas Sediments (Sand).

Very Fine Sand 50-100 μ	Sediment																				
	1	2	3	4	5	6	7	8	9	10 ^a	11	12	13	14	15	16	17	18	19	20	21
Montmorillonite		t		t	t			t				t					t	t	t		
Vermiculite		t		t	t		t	t				t					t	t	t		
Chlorite																					
Kaolinite		t	t	t	t		t	t			t	t			t		t	t	t		
Intergrades																					
Mica	t	m	m	m	m		t	m			m			m	m		m	t	m		
Quartz	M	M	M	M	M	M	M	M	m		M	M	M	M	M	M	M	M	M	M	M
Feldspar	M	M	M	M	M	M	M	M	M		M	M	m	M	M	M	M	M	M	m	M
Hornblende							t														
Amphibole	t	m	m	t	t	t	t	m	t		m		t	t	m	t	m	t	m	t	
Olivine						t		t	t		t			m	m	t	t	m	t	t	
Biotite		t		t	t	t		t	t		t	t	t		t	t	t				t
Apatite		t				t		t	t			t	t								
Unidentified Peaks	2.91	3.78 2.71		4.52	3.79 2.57	3.78 3.01 2.72	3.01	2.92 2.72	3.01 2.78 2.72 2.65		2.72		2.71	3.00	3.49		3.78			3.78 3.00	3.50

NOTE: Blanks = not identified

t = trace

m = minor component

M = major component

^aInsufficient sample for measurements.

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TABLE 6. Mineralogy of Hanford Site Separation Areas Sediments (Silt).

Coarse Silt 20-50 μ	Sediment																				
	1	2	3	4	5	6	7	8	9	10 ^a	11	12	13	14	15	16	17	18	19	20	21
Montmorillonite	m	m		t			t					t			m		t		m		m
Vermiculite	M	M	M	M	m	m	M	M	m		M	M	M	M	m	M	M		M	m	m
Chlorite			m	t		t	m	t	t		t			t		t		m	t	t	t
Mica	m	m	m	m	m	m	m	m	m		m	t	m	m	M	m	t	t	m	M	m
Kaolinite		m	t				m	t			t				m		t		t		
Chlorite-Vermiculite Intergrades	m	t	m	t	t	m	t	t	t		m		t	t	t	t	t	t	m	t	t
Quartz	M	M	m	M	M	m	M	M	M		m	M	M	M	M	M	M	M	M	M	M
Feldspar	M	M	m	M	m	m	M	M	M		m	M	m	M	M	m	M	M	m	M	M
Apatite			t																		
Olivine	t			m			t		t		m	m	m	m	m	m	t	m	t		t
Amphibole	m	t	t	m	m	m	t	m	m		m	m	m	m	t	m	m	m	m	m	t
Biotite													t			t	t		t		
Unidentified Peaks		3.01 2.76	3.78	4.43		2.47	9.3		3.70				3.04 2.47	7.30 4.71		3.76 4.74		6.93 2.91 3.02 2.73			

NOTE: Blanks = Not identified

t = trace

m = minor component

M = major component

^aInsufficient sample for measurements.

TABLE 7. Mineralogy of Hanford Site Separation Areas Sediments (Clay).

Clay <2 μ	Sediment																				
	1	2	3	4	5	6	7	8	9	10 ^a	11	12	13	14	15	16	17	18	19	20	21
<u>Fine (0-0.2μ)</u>																					
Montmorillonite	t	m			M	M		M			t	M	M	M	M	M	M	M	m	M	M
Vermiculite	M	M	M	M	M	M	M	M	N		M	m	M	m	m	m	m	m	M	m	t
Chlorite	m	t		t		m	t	m			m	m	m	m	t	t	t			m	t
Mica	M	M	M	M	M	M	m	M	m		M	M	M	m		m	m	t	m	M	m
Kaolinite	m	t	t	t	t	m	t	m	t		m	m	m	m	t		m			m	t
Quartz			m				t	t	m		t					t					t
Feldspar		t	t			m	t	t			m		t	t		t		t			
Chlorite-Vermiculite Intergrades			M		m			m			m	M	m	m			m		m		m
Amphibole																					
Unidentified Peaks																					
<u>Coarse (0.2-2μ)</u>																					
Montmorillonite	M	M	M	m	M	m	M	t	m		M	m	M	M	M	m	M	t	M	M	M
Vermiculite	M	M	M	M	M	M	m	M	M		M	M	m	m	m	m	M		m	M	m
Chlorite	m	t		m	m	m	m	m	m		m	t	t	m	m	M		M	M	m	m
Mica	m	m	t	m	M	M	M	m	m		M	m	M	M	M	m	M	m	m	m	m
Kaolinite	m	m	m	m	m	M	m	t	t		m	m	m	M	M	m	M	t		m	
Chlorite-Vermiculite Intergrades	m		m	m	m	m	m		m			m	M	m	M	m					m
Quartz	t	m	m	t	m	M	t	t	t		M	m	m	m	m	M	m	M	M	M	m
Feldspar	m	t		m	t	m	m	m	t		m	t	t	m	M	m	t	M	m	M	m
Amphibole	t	t			t	t		m	t			t		t	t		t	t			t
Olivine											t		t		t						
Unidentified Peaks												2.9 4.01	2.91			3.79		2.75	2.91		

NOTE: Blanks = not identified

t = trace

m = minor component

M = major component

^aInsufficient sample for measurements.

Textural distribution was determined using the hydrometer method of Day (1965). Calcium carbonate content was determined by the volumetric calcimeter method of Allison and Moodie (1965). Cation exchange capacity was determined by the small column method of Routson et al., (1973). Semi-quantitative x-ray diffraction was determined using the method of Kittrick (1961).

Evaluation of selectivity coefficient in a macroion system (K_N) and solid phase correction coefficient (p) for Ca-Na, Ca-Mg, and K-Na exchange was accomplished by the method of Serne et al., (1973) using batch experiments. The K_N and p are derived by the following generalized equilibrium description of an ion exchange reaction on sediment

where:

$$M^c = Na^+ \text{ or } Mg^{+2}$$

$$M'^d = K^+ \text{ or } Ca^{+2}$$

X = sediment

c and d = charge M and M', respectively.

The mass balance equation for this reaction is

$$K_N = \frac{(a_{M'})^c}{(a_M)^d} \left[\frac{[MX]}{[M'X]} \right]^p \quad (9)$$

where:

a_M and $a_{M'}$ = the chemical activities of M and M', respectively;

[MX] and [M'X] are metal ion concentrations on the sediment.

Taking logarithms and rearranging Eq. 9 yields a linear expression relating the ln of the metal ion activity ratio in solution to the ln of the metal concentration in the sediment. The ratio may be plotted on an X-Y plot to yield slope = m and intercept = $\ln K_N$.

In the batch method, the ion-exchange sites on the sediment are loaded to saturation with one cation (Ca^{+2} or K^{+}) through repeated washing with 1-M solutions of that saturating cation. Exchange of the saturating ion by a different index ion (Na^{+} or Mg^{+2}) is then done by contacting the loaded sediment with solutions having varying concentrations of the index ion. The equilibrium solution is analyzed for the concentration of saturating and index ions. To arrive at the selectivity coefficient, one must also evaluate the concentrations, in moles per gram sediment, of the index and saturating ion on the sediment at equilibrium.

The equivalents of the index ion on the sediment is equal to the equivalents of the displaced saturating ion in solution. The amount of saturating ion remaining on the sediment is the difference between the CEC of the sediment and the amount of saturating ion displaced by the index ion.

Approximately 5-g sediment samples were prepared by cone and quartering from the bulk sample. The sediment samples were weighed in 50-ml, preweighed, polycarbonate centrifuge tubes. They were washed three times with 30 ml of acidified 1M saturating ion to remove carbonate. Excess saturating solution was removed by a wash of distilled water containing 1 ppm magnifloc and three additional washes with a 1:1 magnifloc-distilled water and methanol solution. Each wash was 30 ml, separated by centrifugation, and discarded. Following the final wash, each tube was dried in a vacuum oven at 75°C to a constant weight. Thirty milliliters of index ion at five concentrations ranging from 0.001 to 0.1M were added to the tubes and agitated for 24 hrs. The solution concentration of index and saturating ion was measured by inductively coupled plasma spectroscopy. Thus, there were 15 data points per exchange. For the Ca-Na, Ca-Mg, and K-Na exchange reactions, Ca-Na, Ca-Mg, and K-Na were the respective saturating-index ion pairs.

Linear regression analysis was used to evaluate K_N and p values and their 95% confidence limits based on these data.

SENSITIVITY ANALYSIS

A simplified model of radionuclide transport through soil systems was used in estimating if further fission product sorption sediment type studies were required to characterize the Hanford 200 Separation Areas (with the exception of sediment types in the Hanford A tank farm area where no appropriate samples are available as previously discussed).

Radionuclides are transported in solution predominantly as solutes. These solutes are capable of undergoing chemical and physical reactions with solid phases (sediments). Sorption is the reaction with, and retention of, a solute by a solid phase. Sorption has the effect of retarding the movement of sorbed radionuclides relative to that of the transporting liquid. A retardation factor (V_i/V_w) can be calculated from the following equation (Schroeder and Jennings, 1963)

$$\frac{V_i}{V_w} = \frac{1}{1 + \frac{K_d \rho}{\theta}} \quad (10)$$

where:

V_i = transport velocity of sorbed radionuclides, cm/yr

V_w = velocity of water, cm/yr

ρ = sediment bulk density, g/cm³

θ = sediment's pore fraction.

Hanford Site sediments have average bulk densities and average pore fractions of 1.6 and 0.4, respectively (Routson and Fecht, 1979). Thus Eq. 10 reduces to

$$\frac{V_i}{V_w} = \frac{1}{1 + 4K_d} \quad (11)$$

As an example of how the retardation formula can be used to estimate radionuclide transport, Hajek (1965) found that the K_d values for ⁹⁰Sr and ¹³⁷Cs with Burbank loamy sand subsoil in Hanford ground water were 420 and 43 ml/g, respectively. Substituting these values in

Eq. 11 results in a V_i/V_w of approximately 0.001 and 0.01, respectively. This is equivalent to water moving 1,000 times faster than ^{137}Cs and 100 times faster than ^{90}Sr . If the flow rate of water were 1 cm/day, the transport rates would be 0.001 cm/day for ^{137}Cs and 0.01 cm/day for ^{90}Sr . To put it another way, it would take nearly 3 years for ^{137}Cs and 1/3 year for ^{90}Sr to be transported the distance that water would move in a single day.

RESULTS AND DISCUSSION

PRELIMINARY STUDY

The $K_{d_{Sr}}$ values measured in the study of single-macroion Na and Ca systems for the tank farm and Burbank subsoils, respectively, are presented in Table 8. The $K_{d_{Sr}}$ values decrease with increasing Na^+ and Ca^{+2} .

TABLE 8. $K_{d_{Sr}}$ Values Measured in Single-Macroion Systems.

System	$K_{d_{Sr}}$ of Subsoils, ml/g^a	
	Burbank	Tank Farm
Na, M/l		
3.0	0.49	0.93
1.5	0.6	1.4
0.15	5.6	
0.1		6.7
0.015	39.0	
0.01		55
0.0015	170	
0.001		146
Ca, M/l		
0.2	0.66	0.43
0.1	1.2	1.2
0.05	1.9	2.2
0.01	7.7	5.8
0.005	12	13
0.002	13	26

^aAverage of duplicates.

Plots of the $\ln K_{d_{Sr}}$ (y) as a function of the $\ln Na^+$ and $\ln Ca^{+2}$ are shown in Figures 5 and 6 for the tank farm subsoil and in Figures 7 and 8 for the Burbank subsoil. Linear regression analysis of the data for the tank farm and Burbank subsoils in the Na and Ca systems, respectively, give:

$$y = -0.65x + 0.61$$

$$y = -0.77x - 1.58$$

$$y = -0.77x + 0.28$$

$$y = 0.70x - 1.45$$

where:

$$y = \ln K_{d_{Sr}}$$

$$x = \ln Na^+ \text{ or } \ln Ca^{+2}.$$

Squared regression coefficient (r^2) values and the standard error of the estimates (S_{yx}) for the above are 0.982, 0.984, 0.998, 0.984, and 0.086, 0.62, 0.019, and 0.27, respectively. In all cases, the r^2 values are large showing that most of the variation in the $K_{d_{Sr}}$ can be explained by the variation in Na and Ca for these two soils. In addition, these r^2 values strongly suggest that Kd values at intermediate Na and Ca can be predicted from the above regression equations.

Table 9 lists the $K_{d_{Sr}}$ values measured and those predicted by the Mercer and resistance theoretical methods for several mixed Na-Ca systems for the tank farm and Burbank subsoils, respectively. No one method gives the best estimate of the measured Kd values. It is possible to use a combination of the methods to estimate the $K_{d_{Sr}}$ value for the PERCOL model. The last column of Table 9 lists the selected estimated $K_{d_{Sr}}$ values using:

- the resistance theoretical method for $K_{d_{Sr}}$ values 1 to 8
- the Mercer theoretical method for $K_{d_{Sr}}$ values >8 .

Use of the above technique to measure the sorption parameter for the PERCOL model would result in a 53% savings in time and research effort. Since this sorption parameter is the most expensive to measure in the PERCOL model, a significant cost savings would be effected.

FIGURE 5. $\ln Kd_{Sr}$ as a Function of the Equilibrium $\ln Na^+$ for Tank Farm Subsoil.

RCP8102-20

FIGURE 6. $\ln Kd_{Sr}$ as a Function of the Equilibrium $\ln Ca^{+2}$ for Tank Farm Subsoil.

RCP8102-21

FIGURE 7. $\ln Kd_{Sr}$ as a Function of the Equilibrium $\ln Na^+$ for Burbank Subsoil.

RCP8102-22

FIGURE 8. $\ln Kd_{Sr}$ as a Function of the Equilibrium $\ln Ca^{+2}$ for Burbank Subsoil.

RCP8102-23

TABLE 9. $K_{d_{SrCaNa}}$ Values in Mixed Ca-Na Systems.

System, <u>M</u>		$K_{d_{SrCaNa}}$ of Subsoils, ml/g			
Na	Ca	Measured	Mercer	Resistance	Selected
Burbank					
0.15	0.02	1.4	1.9	2.5	1.9
0.15	0.004	4.4	3.6	4.4	3.6
0.075	0.02	2.9	3.1	2.9	3.1
0.075	0.004	5.1	4.6	5.9	4.6
0.015	0.02	2.9	2.8	3.6	2.8
0.015	0.004	14.0	7.2	9.5	9.5
Tank Farm					
0.15	0.02	1.4	1.7	2.2	1.7
0.15	0.002	4.4	3.6	4.3	4.3
0.015	0.02	1.8	2.5	3.2	2.5
0.015	0.002	14.0	8.7	12.0	12.0
0.003	0.02	1.8	2.1	2.8	2.1
0.003	0.002	17.0	12.0	15.0	15.0
0.0015	0.02	1.9	3.1	3.5	3.1
0.0015	0.002	23.0	23.0	29.0	29.0

Methods Comparison

For comparing theoretical method predicted K_d values in single-macroion Na, K, and Ca systems, the $K_{d_{Sr}}$, $K_{d_{Cs}}$, and $K_{d_{Co}}$ values were measured in several systems which are listed in Table 10 for the Well E17-4 sediment. With the exceptions of Co sorption in the Na and K systems, the K_d values generally decrease as the solution concentration of Na, K, and Ca increase. In the case of Co in the Na and K systems, both the large K_d values and abrupt change in slope of $\ln K_d$ value - $\ln Ca$ suggest that Co in these systems is not sorbed exclusively by an ion exchange reaction. Cobalt may form a radiocolloid in these systems (McCarthy, 1979). Figures 9, 10, and 11 are plots of the $\ln K_{d_{Sr}}$, $\ln K_{d_{Cs}}$, and $\ln K_{d_{Co}}$ versus $\ln Na$, $\ln K$, and $\ln Ca$ for the 35- to 255-foot level of sediment from Well E17-4, respectively.

TABLE 10. K_{dSr} , K_{dCs} and K_{dCo} Values Measured in Single-Macroion Na, K and Ca Systems of the 35- to 255-Foot Level of Well E17-4 Sediment.

Composition	K_d , ml/g ^a		
	⁸⁵ Sr	¹³⁷ Cs	⁶⁰ Co
<u>NaNO₃ Solution, M</u>			
0.0010	49	1,600	2,100
0.0015	42	1,500	
0.010	50	1,400	1,400
0.015	42	1,200	1,100
0.10	16	570	1,300
0.15	12	350	2,200
0.5	1.7	65	4,800
3.0	0.6	26	4,700
<u>Ca(NO₃)₂ Solution, M</u>			
0.0020	19	2,200	3,900
0.0050	10	2,400	2,500
0.010	4.5	2,100	2,000
0.050	1.6	1,400	640
0.10	0.5	1,100	370
0.20	0.3	790	200
<u>KNO₃ Solution, M</u>			
0.0020	36	280	550
0.0050	30	160	660
0.010	23	92	770
0.050	7.9	23	3,400
0.10	5.0	12	3,400
0.20	3.7	5.8	3,400

^aAverage of duplicates.

RCP8102-24

FIGURE 9. $\ln Kd$ as a Function of Equilibrium $\ln Na^+$ for the 35- to 255-Foot Level Of Well E17-4 Sediment.

RCP8102-25

FIGURE 10. $\ln Kd$ as a Function of Equilibrium $\ln K^+$ for the 35- to 255-Foot level of Well E17-4 Sediment.

RCP8102-26

FIGURE 11. $\ln K_d$ as a Function of Equilibrium $\ln Ca^{+2}$ for the 35- to 255-Foot Level of Well E17-4 Sediment.

Regression analysis of data for Well E17-4 for Sr, Cs, and Co in the Na, K, and Ca systems gave:

$$\begin{aligned} \ln K_{d_{SrNa}} &= 0.85 - 1.1 \ln Na - 0.081 \ln Na^2 \\ \ln K_{d_{SrK}} &= 0.48 - 0.53 \ln K \\ \ln K_{d_{SrCa}} &= -2.6 - 0.92 \ln Ca \\ \ln K_{d_{CsNa}} &= 4.5 - 0.96 \ln Na - 0.078 \ln Na^2 \\ \ln K_{d_{CsK}} &= 0.50 - 0.85 \ln K \\ \ln K_{d_{CsCa}} &= (\text{no apparent relationship}) \\ \ln K_{d_{CoNa}} &= (\text{no apparent relationship}) \\ \ln K_{d_{CoK}} &= (\text{no apparent relationship}) \\ \ln K_{d_{CoCa}} &= 4.5 - 0.63 \ln Ca. \end{aligned}$$

The r^2 and Syx values for the preceding are:

$$r^2 = 0.996, \text{ Syx} = 0.13$$

$$r^2 = 0.978, \text{ Syx} = 0.16$$

$$r^2 = 0.986, \text{ Syx} = 0.022$$

$$r^2 = 0.986, \text{ Syx} = 0.10$$

$$r^2 = 0.996, \text{ Syx} = 0.12$$

(no apparent relationship)

(no apparent relationship)

(no apparent relationship)

$$r^2 = 0.986, \text{ Syx} = 0.22.$$

In all the cases in which there was a correlation, the r^2 values are large, suggesting that most of the variation in the Kd values in these respective systems can be explained by the variations in Na, K, and Ca. In addition, these large r^2 values strongly suggest that Kd values at intermediate Na, K, and Ca concentrations can be predicted from the regression equations. In the three systems having no apparent relationship, the average Kd values, plus or minus the standard deviation(s), were $1,520 \pm 444$, $2,140 \pm 20$, and $2,040 \pm 673$. The large Kd values and relatively small standard deviations for the three uncorrelated systems were probably due to the relatively small effect of these cations over the concentration ranges chosen relative to the innate variability of the Kd measurements.

Equations developed by the statistical method for sediments from Well E17-4 from the data in Table 11 are:

$$\begin{aligned} \ln Kd_{Sr} = & 1.0 - 0.93X_1 - 23X_2 + 0.12X_1^2 + 31X_2^2 \\ & - 18X_3^2 + 14X_1X_2X_3 \end{aligned} \quad (12)$$

$$\ln Kd_{Cs} = 5.6 - 1.3X_1 - 37X_3 + 0.14X_1^2 + 85X_3^2 + 3.6X_1X_3 \quad (13)$$

$$\ln Kd_{Co} = 8.1 - 34X_2 - 7.6X_3 + 100X_2^2 + 31X_3^2 \quad (14)$$

The r^2 and Syx values for the preceding are:

$$r^2 = 0.964, \text{ Syx} = 0.31$$

$$r^2 = 0.982, \text{ Syx} = 0.22$$

$$r^2 = 0.987, \text{ Syx} = 0.22.$$

In all three cases, the large r^2 values suggest that most of the variation in the Kd values for the Sr, Cs, and Co trace systems were explained by the variation in concentrations of Na, K, and Ca. In addition, these large values strongly suggest that Kd values at intermediate Na^+ , K^+ , and Ca^{+2} concentrations can be predicted by the determined equilibrium solution concentration of Na, K, and Ca. Thus, both theoretical and statistical methods have the ability to predict Kd values in mixed Na, K, and Ca systems. The next objective is to compare the theoretical and statistical methods to determine which is the better, both from a predictive and cost-effectiveness standpoint.

TABLE 11. Kd Values in Mixed Macroion Systems of Sediment from the 35- to 255-Foot Level of Well E17-4.

Systems, M			Kd Values, ml/g		
NaNO_3	$\text{Ca}(\text{NO}_3)_2$	KNO_3	^{85}Sr	^{137}Cs	^{60}Co
3.0	0.2	0.1	0.029	4.7	150
3.0	0.002	0.1	0.30	4.4	1200
0.001	0.2	0.1	0.12	13	140
0.001	0.002	0.1	2.2	13	2000
3.0	0.1	0.2	0.081	3.0	220
3.0	0.1	0.002	0.081	21	330
0.001	0.1	0.2	0.12	6.0	190
0.001	0.1	0.002	0.35	370	60
1.5	0.2	0.2	0.032	3.2	140
1.0	0.2	0.002	0.022	45	200
1.5	0.002	0.002	0.80	47	3200
1.5	0.1	0.1	0.16	6.2	240
1.5	0.1	0.1	0.13	6.0	200
1.5	0.1	0.1	0.10	6.4	180

A general objective of evaluating predictive performance of any set of methods is to answer the following questions:

1. Is one method better than the others?
2. Is one method more unbiased than the others?
3. Is one method more precise than the others?

The answers to these questions can be assessed by analyzing residuals. For any method, the residual (R) of any observation is defined as:

$$R = O - P \quad (15)$$

where:

O = the measured (or observed) value

P = the predicted value.

If a method is unbiased, the expected value of R is zero. Furthermore, if a method has better precision, the R-variance is smaller.

The ultimate goal of this statistical assessment is to determine which method predicts K_d values as a function of the equilibrium solution concentrations of Na, K, and Ca best. However, the criteria available to objectively make this assessment depend on the assumptions made about the distributional properties of the residuals. The normal frequency distribution is the one assumed in statistical applications. If normality is assumed for the distributional properties of R, tests of statistical hypotheses can be made based on this assumption. However, residual normality should be confirmed before applying any test, if possible.

In this study, the distributional properties of the data were assessed using the Kolmogorov-Smirnov test (Draper and Smith, 1966). This test is a nonparametric test applicable to continuous frequency distribution such as the normal distributions to test the "goodness of fit". It is based on the absolute differences between the observed and expected cumulative frequency distributions.

From an analysis of the "goodness of fit," it was determined that there were no discernible deviations from normality in the data in Tables 8 through 11. Thus, the properties are probably distributed normally and parametric tests based on the normal assumption were used to evaluate the methods. The initial parametric test used to determine how biased the methods were was the one-sample t-test (Zar, 1975a). A second parametric test used to assess precision was the expected squared error test (Zar, 1975b). The method yielding the lower average squared error would be judged to be superior.

The conventional F-ratio test was not used in this analysis of model performance. The F-test requires the errors produced by one model to be uncorrelated with those produced by the other: such was not the case.

The equations established by the statistical and theoretical techniques used to calculate Kd values for mixed systems were tested on independently measured Kd data. These data are summarized in Table 12 for the various concentrations of mixed systems and the observed Kd values for ^{137}Cs , ^{60}Co , and ^{85}Sr . In Table 13, the corresponding predicted Kd values are given for the Mercer, resistance, and statistical methods.

TABLE 12. Kd Values in Selected Mixed Chemical Sediments
System from the 35- to 255-Foot Level of Well E17-4.

Systems, M			Kd Values, ml/g		
NaNO ₃	Ca(NO ₃) ₂	KNO ₃	⁸⁵ Sr	¹³⁷ Cs	⁶⁰ Co
0.001	0.2	0.002	0.16	88.0	62
0.001	0.2	0.2	0.093	4.5	51
0.001	0.1	0.1	0.18	9.9	73
0.001	0.002	0.002	6.9	24	81
0.001	0.002	0.2	0.97	6.3	46
1.5	0.2	0.1	0.37	4.0	55
1.5	0.002	0.1	0.48	5.0	60
1.5	0.1	0.002	0.15	36	84
1.5	0.1	0.2	0.089	2.6	67
3.0	0.2	0.002	0.015	15	55
3.0	0.2	0.2	0.18	1.8	60
3.0	0.1	0.1	0.02	3.2	82
3.0	0.002	0.002	0.32	29	41
3.0	0.002	0.2	0.051	26	82

TABLE 13. Model Predicted Values for the 35- to 255-Foot Level of Well E17-4 in the Chemical System Described in Table 7.^a

Mercer			Resistance			Statistical		
⁸⁵ Sr	¹³⁷ Cs	⁶⁰ Co	⁸⁵ Sr	¹³⁷ Cs	⁶⁰ Co	⁸⁵ Sr	¹³⁷ Cs	⁶⁰ Co
0.26	120	95	0.31	200	200	0.09	260	200
0.21	5.7	140	0.29	6.4	200	0.04	5	150
0.34	9.8	180	0.48	11	280	0.31	16	190
5.9	160	520	11	240	530	2.6	260	3000
2.3	5.8	520	11	6.4	530	1.3	5.4	2200
0.18	5.6	150	0.19	9.6	200	0.038	5.8	130
0.97	5.6	710	0.47	9.6	530	0.70	5.8	190
0.49	28	130	0.78	47	280	0.12	54	300
0.34	3.8	210	0.74	11	280	0.088	3.3	220
0.14	17	100	0.21	25	200	0.016	22	200
0.12	2.9	150	0.21	19	200	0.043	3.8	150
0.14	4.3	220	0.28	8.1	280	0.082	4	190
0.51	16	270	0.63	25	530	0.45	22	3000
0.36	2.9	520	0.63	19	530	0.22	3.8	2200

^aMeasured values are listed in Table 7 for comparison.Bias Testing

In Table 14, the residuals of the transformed data are given for the three models. The R can be considered to be

$$R = \theta + e_i \quad (16)$$

where:

θ = bias

e_i = random variable with mean zero.

TABLE 14. Residuals for Various Systems.

Mercer			Resistance			Statistical		
^{85}Sr	^{137}Cs	^{60}Co	^{85}Sr	^{137}Cs	^{60}Co	^{85}Sr	^{137}Cs	^{60}Co
0.48	4.9	0.42	0.66	5.4	1.2	0.55	5.7	1.2
0.81	0.24	0.98	1.14	0.35	1.4	0.73	0.18	1.2
0.64	0.0081	0.91	0.98	0.11	1.3	0.54	0.51	0.96
0.16	0.42	0.44	0.47	0.016	0.42	0.99	0.059	1.3
0.86	0.079	0.13	2.4	0.019	0.15	0.27	0.16	1.6
0.72	0.32	1.01	0.67	0.86	1.3	2.3	0.37	0.88
0.70	0.11	0.17	0.021	0.65	0.12	0.38	0.16	1.2
1.2	0.26	0.43	1.6	0.26	1.2	0.23	0.40	1.2
1.3	0.38	1.1	2.1	1.4	1.4	0.010	0.23	1.2
2.2	0.12	0.59	2.6	0.50	1.3	0.086	0.36	1.3
0.40	0.45	0.91	0.15	2.3	1.2	1.4	0.73	0.94
1.9	0.30	0.99	2.6	0.93	1.2	1.4	0.22	0.84
0.45	0.61	0.42	0.66	0.16	0.26	0.34	0.31	2.0
2.0	2.2	1.8	2.5	0.32	1.9	1.5	1.9	0.81

If the average θ is not equal to zero, as judged by the one-sample t-test, then the method is biased and the larger the absolute value of θ , the greater the bias. Table 15 lists the estimated θ values for the three methods. The only unbiased method for the ^{85}Sr system is the statistical. Comparing Table 12 with Table 13 shows that both the Mercer and resistance methods overpredict K_d_{Sr} as a function solution concentration Na, K, and Ca. In the case of predicting K_d_{Cs} , both the statistical and Mercer methods are less biased than the resistance, with the Mercer being slightly better than the statistical method. In the case of the ^{60}Co system, none of the methods are unbiased. In summary, the statistical and Mercer methods are approximately of equal utility in predicting K_d values when all systems are considered.

TABLE 15. Estimated Bias of Kd Models for the 35- to 255-Foot Level of Well E17-4.

Radionuclide	Estimate of θ		
	Statistical	Mercer	Resistance
^{85}Sr	-0.12	-0.81 ^a	-1.24 ^a
^{137}Cs	-0.46	-0.23	-0.88 ^a
^{60}Co	-1.36 ^a	-0.62 ^a	-0.95 ^a

^aStatistically significant at the 0.05 level giving an overall significance level of 0.1.

Precision Testing

From an examination of the residuals of the various methods, it was found that there was a significant correlation between methods. Therefore, as was previously mentioned, the usual variance ratio or F-test was inappropriate. Thus, the squared expected errors test was used. The squared expected errors test compares the average variance (standard deviation squared) of the models. If one variation is significantly more precise, it will have a P-value of less than 0.05 at the 0.1 level. Table 16 lists a comparison of the various methods. None are significantly more precise than any other.

TABLE 16. Paired Estimated Variances and P-Values for the 35- to 255-Foot Level of Well E17-4.

Method Under Comparison	Estimate of Variance			P-value		
	^{85}Sr	^{137}Cs	^{60}Co	^{85}Sr	^{137}Cs	^{60}Co
Statistical vs. Mercer	1.05 0.78	2.6 2.3	0.4 0.39	0.19	0.067	0.45
Statistical vs. Resistance	1.05 1.2	2.6 2.2	0.4 0.46	0.38	0.4	0.41
Mercer vs. Residence	0.77 1.2	2.3 2.2	0.39 0.95	0.052	0.44	0.3

Since no method is both significantly more unbiased or more precise, the decision on which method should be used can be made strictly on the basis of cost effectiveness. The Mercer method would result in approximately a 53% savings of research effort over that of the original PERCOL model. In contrast, the statistical method would result in a 78% savings. Thus, the statistical method is the more cost effective and was used in all further experiments.

SORPTION PARAMETER MEASUREMENTS

The objective of the sorption parameter measurements is to characterize the fission product sorption behavior of the Hanford 200 Separation Areas vadose zone sediments in sufficient detail to meet Hanford assessment needs for using the MMT transport model.

Tables 17, 18, and 19 list the β values (Eq. 5) for 21 Hanford Separation Areas sediment types for Sr, Cs, and Co, respectively. The average values of the columns are listed in the final row of each table for comparison. The average values do not differ greatly from the individual values suggesting that many of the sediment types are similar in nature; and, sorption of a given trace ion is probably controlled by a similar sorption process. The moderate to large r^2 values listed in the next to last column of each table suggest that the statistical method is adequate for assimilating the data; and, sorption at intermediate solution concentrations of macroions can be adequately predicted by these equations.

Table 20 lists the average β values for the 21 Hanford 200 Separation Areas sediment types. In general, the larger the β value, the greater the control of the K_d value by a corresponding macroion. Negative β values subtract from the K_d value and positive β values add to the K_d value. The $e^{1n \beta_0}$ value from Eq. 5 is equal to the K_d value at the average concentration of Na^+ , Ca^{+2} , and K^+ (1.5M Na^+ , 0.1M Ca^{+2} and K^+). These equations are valid only over the K_d ranges of the experiment. From Table 20, it can be seen that Sr sorption is controlled to a great extent by the solution concentration range of Ca (β_2 , β_{22} , β_{12}) and, to a lesser extent, by the solution concentration of Na (β_1 , β_{11} , β_{13}). This is true even though the concentration range of Na^+ is much greater than for Ca^{+2} (3.0 versus 0.2M). This suggests that Sr is sorbed primarily by ion exchange; since divalent Ca^{+2} competes more effectively for exchange sites with Sr than does monovalent Na^+ .

TABLE 17. Statistical Equations Predicting the K_d _{Sr}
as a Function of the Equilibrium Macroion Solution
Concentration of Sodium, Calcium, and Potassium
for 21 Hanford Separation Areas Sediment Types.

Sediment	Sr Equations ^a										Significance	
	β_0	β_1	β_2	β_3	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	r^{2b}	Syx ^c
1	-2.06	-0.652	-1.07	-	-	0.450	0.379	0.262	0.447	-	0.977	0.21
2	-2.43	-0.828	-1.00	-	-	0.975	-0.559	0.518	-	-	0.887	0.51
3	-2.98	-	-1.77	-	-	-	-	-	1.284	-	0.799	0.80
4	-2.63	-1.24	-1.90	-0.891	-0.218	0.404	-0.331	-	-0.422	-0.810	0.996	0.20
5	-4.21	-1.14	-1.68	-0.396	0.755	1.36	-	-	0.723	-	0.958	0.49
6	-1.16	-0.738	-0.941	-0.450	-	0.448	-0.584	-	-0.524	-	0.943	0.36
7	-1.77	-1.03	-1.18	-	-0.182	0.427	-0.414	-	0.504	-0.563	0.990	0.20
8	-1.73	-0.633	-1.09	-0.188	-	0.329	-	0.254	-	-	0.992	0.28
9	-1.77	-0.723	-1.26	-	-	0.384	-	-	-	-	0.919	0.38
10	-2.32	-1.24	-1.27	-	-	1.10	-0.469	-	-	-	0.901	0.58
11	-2.87	-0.857	-1.39	-0.542	-	0.892	-	-	-	-	0.890	0.56
12	-2.32	-1.26	-1.78	-0.177	-	0.328	-0.301	-	0.656	-0.252	0.990	0.27
13	-2.28	-0.812	-1.06	-0.282	-	1.12	-	0.300	-	-	0.965	0.28
14	-2.98	-1.32	-1.43	-0.654	0.365	0.964	-	-0.392	-	-0.303	0.981	0.35
15	-2.31	-1.58	-2.15	-	-1.11	-	-	-0.660	-	-	0.876	0.97
16	-0.683	-0.589	-0.853	-	-	0.362	-	-	-	-	0.956	0.20
17	-0.982	-0.415	-0.555	-0.110	-	0.484	-	0.336	-	-	0.988	0.082
18	-1.72	-0.838	-1.35	-0.267	-	0.619	-	-	-	-	0.983	0.19
19	-1.14	-0.648	-0.841	-0.200	-0.207	0.426	-	0.221	0.237	-	0.975	0.20
20	-1.26	-0.880	-1.41	-	-	-	-	-	-	-	0.868	0.53
21	-1.32	-0.668	-1.01	-0.184	-0.366	0.641	-	-0.150	0.206	0.340	0.996	0.10
Average	-2.13	-0.864	-1.29	-0.207	0.046	0.558	-0.108	0.033	0.147	-0.002	0.944	0.37

$${}^a \ln K_d_{Sr} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3; \begin{matrix} X_1 = 2/3 (Na^+) \\ X_2 = 10 (Ca^{+2}) \\ X_3 = 10 (K^+) \end{matrix}$$

^br = correlation coefficient

^cSyx = standard error of the estimate

TABLE 18. Statistical Equations Predicting the K_d^{Cs} as a Function of the Equilibrium Macroion Solution Concentration of Sodium, Calcium, and Potassium for 21 Hanford Separation Areas Sediment Types.

Sediment	Cs Equations ^a										Significance	
	β_0	β_1	β_2	β_3	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	r^{2b}	S_{yx}^c
1	1.15	-0.438	-	-1.70	1.12	0.547	0.715	-	1.12	0.293	0.994	0.17
2	2.21	-0.703	-	-1.43	0.275	-	0.945	-	0.546	-	0.975	0.27
3	2.29	-0.644	-	-1.41	0.226	-	0.981	-	0.414	-	0.979	0.24
4	2.33	-0.688	-0.150	-1.37	0.158	-	0.918	-	0.366	-	0.994	0.13
5	2.08	-0.363	-	-1.13	-	0.268	0.712	-	-	-	0.948	0.27
6	2.64	-0.645	-	-1.47	0.223	-	-1.00	-	0.470	-	0.980	0.24
7	2.16	-0.965	-0.374	-1.73	-0.175	-0.464	1.10	-0.200	0.400	-0.508	0.999	0.092
8	2.17	-0.724	-	-1.37	0.299	-	0.902	-	0.466	-	0.970	0.29
9	1.97	-0.773	-0.204	-1.41	-0.147	-	1.04	-	0.414	-	0.991	0.17
10	1.87	-0.716	-	-1.48	0.266	-	0.988	-	0.386	-	0.967	0.26
11	1.73	-0.625	-	-1.44	0.266	-	0.919	-	0.589	-	0.973	0.27
12	2.18	-0.720	-	-1.45	-	-0.209	1.12	0.301	0.394	-	0.989	0.19
13	2.78	-0.727	-	-1.50	-	-	1.03	-	0.414	-	0.984	0.20
14	2.45	-0.632	-0.129	-1.41	-	-	0.910	-	0.237	-	0.990	0.16
15	2.63	-0.711	-	-1.38	-	-	0.916	-	0.433	-	0.968	0.28
16	2.60	-0.727	-0.122	-1.38	0.254	-	0.895	-	0.424	-	0.988	0.19
17	1.63	-0.713	-0.134	-1.40	0.298	-	1.08	0.204	0.392	-	0.987	0.22
18	2.47	-0.596	-0.106	-1.53	0.160	-	1.04	-	0.347	-	0.991	0.18
19	2.65	-0.565	-	-1.30	0.256	-	0.877	-	0.433	-	0.961	0.31
20	2.85	-0.620	-	-1.40	-	-	0.962	-	0.416	-	0.970	0.26
21	2.70	-0.628	-0.118	-1.22	0.238	-	0.872	-	0.354	-	0.987	0.18
Average	2.26	-0.672	-0.064	-1.42	0.177	0.0067	0.853	0.014	0.429	-0.010	0.980	0.22

$$^{a} \ln K_d^{Cs} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3; \quad X_1 = \frac{2}{3} (Na^+) - 1$$

$$X_2 = 10 (Ca^{+2}) - 1$$

$$X_3 = 10 (K^+) - 1$$

^b_r = correlation coefficient

^c_{Syx} = standard error of the estimate

TABLE 19. Statistical Equations Predicting the K_d as a Function of the Equilibrium Macroion Solution Concentration of Sodium, Calcium, and Potassium for 21 Hanford Separation Areas Sediment Types.

Sediment	Co Equations ^a										Significance	
	β_0	β_1	β_2	β_3	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	r^{2b}	S_{yx}^c
1	6.31	-	-1.06	-	-	0.705	-	-	-	-0.183	0.968	0.18
2	6.32	0.075	-1.12	-0.143	-0.168	0.618	-	0.103	0.131	-	0.922	0.11
3	6.44	-	-0.816	-	-	0.545	-	-	-	-	0.932	0.19
4	6.31	-	-0.961	-0.140	-	0.566	-	0.218	-	-	0.972	0.16
5	6.02	0.081	-1.00	-0.279	0.125	0.578	-0.076	-	0.086	0.223	0.997	0.072
6	7.08	-	-0.875	-	-	0.340	-	0.276	-	-	0.858	0.34
7	6.56	-	-1.19	-0.217	-0.171	0.738	-	-	-	0.179	0.981	0.17
8	6.55	-	-1.43	-	-	0.957	-	-	-	-	0.969	0.22
9	6.26	-	-1.42	-0.163	-	0.747	0.143	-	-	0.112	0.998	0.067
10	6.41	0.151	-1.03	-	-0.213	0.450	-	-	-	-0.264	0.977	0.16
11	6.20	-0.095	-0.970	-0.119	-0.151	0.579	-0.096	-	-	-	0.991	0.10
12	6.43	-	-0.904	-	-0.233	0.511	0.151	0.179	-	-0.203	0.980	0.14
13	7.03	-	-1.08	-	-	0.810	-	-	-	0.720	0.733	0.70
14	6.74	0.205	-0.953	-	-	0.574	-	-	-	-	0.969	0.16
15	6.71	-0.241	-0.652	-	-	0.853	-	-0.463	-	-	0.853	0.40
16	8.00	-	-0.183	-	-	0.151	-	-	0.128	-0.199	0.634	0.18
17	6.56	-	-0.735	-	-	0.269	0.151	-	-	-0.134	0.953	0.15
18	7.06	-	-1.14	-0.129	-	0.798	-	-	-0.174	-	0.972	0.19
19	7.48	-	-0.848	-	-	0.550	-0.202	0.165	-	-	0.960	0.18
20	8.16	0.364	-0.160	-	0.212	0.435	-0.346	0.487	-	-	0.887	0.25
21	6.97	-	-1.05	-	-	0.647	-	-	-	-	0.894	0.34
Average	6.74	0.026	-0.932	-0.057	-0.029	0.591	-0.013	0.046	0.0081	0.012	0.927	0.21

$${}^a \ln K_{d_{Co}} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3; \begin{matrix} X_1 = 2/3 (Na^+) \\ X_2 = 10 (Ca^{+2}) - 1 \\ X_3 = 10 (K^+) - 1 \end{matrix}$$

^b r = correlation coefficient

^c S_{yx} = standard error of the estimate

TABLE 20. Average β Values for 21 Hanford
200 Separation Areas Sediment Types.^(a,b)

Beta Parameters	Radionuclide		
	Strontium	Cesium	Cobalt
β_0	-2.13	2.26	6.74
β_1	-0.864	-0.672	-
β_2	-1.29	-	-0.932
β_3	0.207	-1.42	-
β_{11}	-	-0.177	-
β_{22}	0.558	-	0.591
β_{33}	-0.108	-0.853	-
β_{12}	-	-	-
β_{13}	0.147	0.429	-
β_{23}	-	-	-

^aSee Equation 5.^bAverage β values of <0.1 are not listed.

Potassium has little or no effect over its concentration range on Sr sorption (β_3 , β_{33} , β_{13}). In contrast, K^+ exerts a major influence on Cs sorption. This is true because Cs is sorbed primarily on selective "weathered mica-like" sites in illites, dischatedrally charged smectites, and weathered micas. The large K_d values ($e^{1n \bar{\beta}_0} = 9.6 \text{ mL/g}$) for Cs relative to Sr sorption are also due to this high selectivity.

The sorption of Co is controlled almost entirely by the solution concentration Ca^{+2} . The large K_d values ($e^{1n \bar{\beta}_0} = 850 \text{ mL/g}$) relative to Sr sorption suggest that Co sorption may be controlled in part by a precipitation-like process. Sorption of Co is probably also controlled in part by ion exchange as shown by the partial control of Ca^{+2} .

Average r^2 and Syx values for the 63 resulting sorption equations for Sr, Cs, and Co are listed in Table 21, (one sorption equation for each radionuclide on each sediment type).

TABLE 21. Average r^2 and Syx of 63 Sorption Equations for the Hanford Separation Areas.

Radionuclide	r^2	Syx
Strontium	0.944 ± 0.046^a	0.37 ± 0.22^a
Cesium	0.980 ± 0.013	0.22 ± 0.053
Cobalt	0.927 ± 0.095	0.21 ± 0.14

^aStandard deviation of 21 equations.

In all three cases, the large r^2 values and reasonable Syx values suggest that most of the variation in the Kd values for the Sr, Cs, and Co trace systems were explained by the variation in concentrations of Na^+ , K^+ , and Ca^{+2} . In addition, these large values strongly suggest that Kd values at intermediate Na, K, and Ca concentrations can be predicted by the determined equilibrium solution concentration of Na, K, and Ca.

Ion Exchange Parameters

Tables 22, 23, and 24 list the ion exchange parameters, including the CEC, selectivity coefficient (K_N), and solid phase correction coefficient (p) for the 21 Hanford Separation Areas sediment types (Routson and Serne, 1972). The generally large regression coefficients (r) listed in the last column of each table suggest that models used to fit the data are adequate for assimilating this input. The Kd value equations plus the sorption parameters are the data required to implement the MMT and PERCOL models for use in transport analyses for the vadose zone of the Hanford 200 Separation Areas. To determine if adequate data were taken, a simplified sensitivity analysis was made.

TABLE 22. Ion Exchange Parameters for K-Na Exchange for
21 Hanford Sediment Types.

Soil	CEC	Data Points Number	K-Na Exchange Reaction				
			Solid Phase Correction Coefficient (p)	Range 95% CL	Selectivity Coefficient (K _N)	Range 95% CL	Regression Coefficient (r)
1	5.2	15	1.585	1.213 -1.957	0.1686	0.1173 -0.2414	0.931
2	3.5	15	1.569	0.8053-2.332	0.08952	0.04181 -0.1917	0.791
3	2.4	12	2.718	1.565 -3.869	0.6276	0.4718 -0.8348	0.857
4	3.8	15	2.245	1.748 -2.743	0.09664	0.06606 -0.1414	0.928
5	3.1	15	3.180	2.569 -3.792	0.06424	0.04375 -0.09433	0.944
6	5.4	15	2.608	1.897 -3.319	0.08632	0.04897 -0.1522	0.910
7	3.0	14	3.377	2.423 -3.831	0.2003	0.1255 -0.3196	0.978
8	3.5	15	1.665	1.033 -2.237	0.2502	0.1670 -0.3750	0.867
9	2.7	14	1.435	1.050 -1.809	0.3688	0.2805 -0.4848	0.924
10	3.6	15	0.8392	0.4699-1.208	0.2656	0.1743 -0.4047	0.806
11	3.6	15	2.303	1.764 -2.842	0.09437	0.06264 -0.1422	0.931
12	3.8	12	0.9710	0.5439-1.398	0.3530	0.2112 -0.5900	0.848
13	5.0	15	1.534	1.185 -1.884	0.2466	0.1304 -0.3370	0.935
14	3.7	15	1.703	1.238 -2.169	0.2158	0.1530 -0.3043	0.910
15	3.9	15	1.608	1.231 -1.985	0.1121	0.07798 -0.1611	0.931
16	12.2	15	2.373	1.852 -2.893	0.03434	0.01974 -0.07860	0.929
17	4.1	15	1.941	1.554 -2.328	0.09698	0.05850 -0.1373	0.949
18	5.7	14	2.204	1.454 -2.954	0.06828	0.03139 -0.1485	0.880
19	6.8	15	2.692	1.642 -3.742	0.07139	0.02788 -0.1828	0.838
20	5.4	15	3.033	1.788 -4.278	0.01813	0.005667-0.05802	0.791
21	6.9	15	2.241	1.398 -3.084	0.1362	0.06377 -0.2699	0.847

TABLE 23. Ion Exchange Parameters for Ca-Na Exchange for
21 Hanford Sediment Types.

Soil	CEC	Data Points Number	Ca-Na Exchange Reaction				
			Solid Phase Correction Coefficient (p)	Range 95% CL	Selectivity Coefficient (K _N)	Range 95% CL	Regression Coefficient (r)
1	5.2	15	2.920	2.535-3.304	0.9261	0.5688 -1.508	0.977
2	3.5	15	3.079	2.378-3.780	0.6265	0.2756 -1.424	0.935
3	2.4	15	2.216	1.831-2.600	8.143	5.163 -12.84	0.960
4	3.8	15	2.702	2.377-3.026	2.298	1.549 -3.313	0.975
5	3.1	15	2.928	2.530-3.327	2.584	1.697 -3.934	0.971
6	5.4	14	3.766	2.697-4.835	1.072	0.3743 -3.073	0.912
7	3.0	15	3.578	2.946-4.209	1.784	1.027 -3.100	0.959
8	3.5	15	3.459	2.786-4.132	0.7817	0.3875 -1.577	0.951
9	2.7	15	2.456	1.982-2.930	4.285	2.550 -7.199	0.952
10	3.6	15	2.974	2.338-3.611	6.231	3.551 -10.93	0.942
11	3.6	15	3.604	2.969-4.240	0.7472	0.3946 -1.415	0.959
12	3.8	14	2.898	2.406-3.389	1.479	0.8768 -2.495	0.966
13	5.0	13	2.953	1.697-4.210	6.671	2.148 -20.72	0.842
14	3.7	15	2.712	2.265-3.159	1.911	1.135 -3.217	0.964
15	3.9	15	3.187	2.771-3.604	0.5907	0.3572 -0.9768	0.977
16	12.2	14	2.840	2.464-3.217	0.8120	0.4870 -1.354	0.972
17	4.1	15	3.385	2.582-4.188	4.605	2.345 -9.046	0.930
18	5.7	15	3.246	1.923-4.570	1.261	0.3145 -5.059	0.827
19	6.8	14	3.646	2.594-4.699	0.3915	0.09933-1.543	0.909
20	5.4	15	3.504	2.778-4.230	3.308	1.739 -6.294	0.931
21	6.9	15	3.051	2.507-3.596	0.4477	0.2071 -0.9678	0.958

TABLE 24. Ion Exchange Parameters for Ca-Mg Exchange for
21 Hanford Sediment Types.

Soil	CEC	Data Points Number	Ca-Mg Exchange Reaction				
			Solid Phase Correction Coefficient (p)	Range 95% CL	Selectivity Coefficient (K _N)	Range 95% CL	Regression Coefficient (r)
1	5.2	14	1.060	0.9340-1.185	0.6913	0.5917-0.8078	0.983
2	3.5	15	1.020	0.7775-1.263	0.6107	0.4254-0.8767	0.929
3	2.4	9	0.6951	0.5124-0.8777	2.083	1.652 -2.627	0.959
4	3.8	12	0.8597	0.6376-1.022	0.7402	0.5733-0.9556	0.958
5	3.1	12	1.174	0.9031-1.444	0.8708	0.7177-1.056	0.950
6	5.4	15	1.188	1.073 -1.302	0.6520	0.5640-0.7538	0.987
7	3.0	11	0.5025	0.2469-0.7580	0.8217	0.5602-1.205	0.829
8	3.5	14	1.119	0.9293-1.308	0.5348	0.4319-0.6622	0.966
9	2.7	12	0.7387	0.5843-0.8930	0.9302	0.7805-1.109	0.959
10	3.6	10	0.8269	0.6972-0.9566	0.9994	0.8590-1.163	0.982
11	3.6	15	1.339	1.160 -1.518	0.5710	0.4677-0.6970	0.976
12	3.8	12	0.8750	0.7293-1.021	0.9051	0.7915-1.035	0.973
13	5.0	12	1.045	0.9181-1.172	1.235	0.114 -1.369	0.986
14	3.7	12	1.013	0.8397-1.186	0.9650	0.8385-1.111	0.972
15	3.9	13	1.292	1.156 -1.427	0.6794	0.6034-0.7645	0.988
16	12.2	13	1.035	0.9156-1.154	0.8508	0.7067-1.024	0.985
17	4.1	13	1.025	0.9549-1.095	0.6822	0.6282-0.7409	0.995
18	5.7	15	1.129	1.020 -1.238	0.6080	0.5293-0.6979	0.987
19	6.8	15	1.082	0.9810-1.184	0.7768	0.6758-0.8929	0.988
20	5.4	12	1.006	0.8781-1.138	1.089	0.9169-1.294	0.981
21	6.9	14	0.9842	0.9000-1.065	0.9331	0.8321-1.046	0.991

Sensitivity Analysis

To make a sensitivity analysis for the purpose of judging if sufficient sorption data were obtained to meet the transport needs of the MMT and PERCOL models, Eq. 8 was used, with the sorption equations in Tables 17, 18, and 19, for Sr, Cs, and Co sorption, respectively. Two macroion chemical systems were considered in the analysis:

- 0.002M in Ca^{+2} , 0.0001M in K^{+} , and 0.0001M in Na^{+} which approximates the chemical composition of Hanford Site ground waters (ERDA Staff, 1975)
- 3.0M in Na^{+} and 0.01M in Ca^{+2} which approaches the chemical composition of Hanford tank leak systems (Routson et al., 1979).

All other Hanford vadose zone systems should be intermediate in character. The V_i/V_w values are referred to as the retardation factors. This ratio is the relative transport of the respective radionuclide to that of water. If two retardation factors are equal for two sediment types, a trace ion will be transported the same distance in a given time.

Figure 12 indicates the stratigraphic relationships of the 21 Hanford 200 Separation Areas sediment types to one another. The compared sediment types occupy similar stratigraphic positions in the sampled wells. Table 25 lists the sediment types that were compared in making the sensitivity analysis. Table 26 lists the V_i/V_w values for the 21 Hanford 200 Separation Areas sediment types in the two chosen vadose zone systems. The V_i/V_w values are generally within a factor of two when such a comparison is made; although some apparent discrepancies exist. A factor of two is within expected agreement when laboratory and sampling errors are taken into consideration. Thus, no additional sorption characterization of the Hanford 200 Separation Areas, with the possible exception previously discussed, is required for these fission products.

SEDIMENTS COMPARED

FIGURE 12A. Sorption Cross Section of Crib Areas - 200 West Area.
(Dots Represent Sharp Breaks in Total Gamma Radioactivity
Distribution in Ground Disposal Facilities.)

FIGURE 12B. Sorption Cross Section of Crib Areas - 200 East Area.
(Dots Represent Sharp Breaks in Total Gamma Radioactivity
Distribution in Ground Disposal Facilities.)

TABLE 25. Sediment Types Compared in Making a Sensitivity Analysis.

200 East Area		200 West Area	
Sediment Type 1	Sediment Type 2	Sediment Type 1	Sediment Type 2
1	6	13	18
2	7	14	19
3	8	15	20
4	9	16,17	21
6	10		
7,8	11		
9	12		

TABLE 26. Sensitivity Analysis for the Hanford
200 East Separation Areas Sediment Types.

Well	Sediment Type	System	Kd Values			Vi/Vw (50%)		
			mL/g			Sr	$\times 10^{-4}$	
		<u>M</u>	Sr	Cs	Co		Cs	Co
EN13-8	1	--	3.20	1200	2500	0.078	2.1	1.0
	2	--	1.3	450	2600	0.16	5.6	0.96
	3	--	2.0	390	2400	0.11	6.4	1.0
	4	--	1.5	390	3500	0.14	6.4	0.71
	5	--	5.8	93	3900	0.041	2.7	0.64
EN17-4	10	0.002 Ca	2.1	300	1600	0.11	8.3	1.6
	11	0.0001 K	2.1	260	2200	0.11	9.6	1.1
	12	0.0001 Na	3.6	390	2200	0.065	6.4	1.1
E33-22	6	--	1.4	250	5100	0.15	10	0.49
	7	--	1.2	220	5700	0.17	11	0.44
	8	--	2.1	370	5500	0.11	6.8	0.45
	9	--	1.7	290	6600	0.13	8.6	0.38
E13-8	1	--	0.18	49	2100	0.058	51	1.2
	2	--	0.08	37	1600	0.76	68	1.6
	3	--	1.3	47	2000	0.16	53	1.2
	4	--	0.10	43	3200	0.71	58	0.78
	5	--	0.10	43	3200	0.71	58	0.78
E17-4	10	3.0 Na	0.13	33	1400	0.66	76	1.8
	11	0.01 Ca	0.30	23	1500	0.45	110	1.7
	12	--	0.07	25	1400	0.78	100	1.8
E33-22	6	--	0.70	68	2700	0.26	15	0.92
	7	--	0.05	23	4600	0.83	110	0.36
	8	--	0.31	35	5700	0.45	71	0.44
	9	--	0.35	27	5200	0.42	92	0.48

TABLE 26. Sensitivity Analysis for the Hanford 200 West Separation Areas Sediment Types (Continued).

Well	Sediment Type	System	Kd Values			Vi/Vw (50%)		
			mL/g			Sr	$\times 10^{-4}$	
		<u>M</u>	Sr	Cs	Co		Cs	Co
W22-25	13	--	3.4	530	14000	0.072	4.0	0.19
	14	--	2.7	320	3900	0.085	7.8	0.64
	15	--	0.69	430	3500	0.26	5.8	0.71
	16	--	3.0	350	3900	0.077	7.1	0.64
	17	0.002 Ca	3.7	570	8400	0.063	4.4	0.30
W10-9	18	0.0001 K	3.3	480	6600	0.070	5.2	0.38
	19	0.0001 Na	2.8	510	12000	0.082	4.9	0.21
	20	--	3.2	450	5500	0.072	5.6	0.45
	21	--	2.4	350	1900	0.094	7.1	1.3
W22-25	13	--	0.30	64	11000	0.45	39	0.23
	14	--	0.30	56	3000	0.45	45	0.83
	15	--	0.09	44	2800	0.73	57	0.89
	16	--	0.50	26	1700	0.33	96	1.5
	17	3.0 Na	0.50	26	1700	0.33	96	1.5
W10-9	18	0.01 Ca	0.56	70	7300	0.31	36	0.34
	19	--	0.32	54	4100	0.44	46	0.61
	20	--	0.42	65	9300	0.37	38	0.27
	21	--	0.60	63	4600	0.29	40	0.54

DATA USE LIMITATIONS

These data are useful for making transport analyses only for the chemical systems in which the measurements were made. These data should be used only for nitrate, chloride, and low concentration bicarbonate systems. Generally, anions have only a minor effect upon sorption, but two Hanford exceptions come to mind. One is in the case of Hanford tank leaks. Hanford tanks contain high solution concentrations of carbonate ion which is stable in the absence of appreciable Ca ion. However, when a tank leak occurs, the high concentration Na^+ exchanges with Ca^{+2} on the soil. The solubility product of CaCO_3 is exceeded and precipitation does an effective job of scavenging ^{90}Sr from solution and essentially all of ^{90}Sr is retained near the tank. The sorption equations do not cover such a system (Tables 17, 18, and 19). A second system not covered by these equations is ^{60}Co sorption in Hanford tank leak systems. Nitrite is known to form ion pairs with Co making ^{60}Co less sorbable.

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