EXPERIMENTAL SUPPORT STUDIES
FOR THE PERCOL AND
TRANSPORT MODELS

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Battelle

Pacific Northwest Laboratories
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1972

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by

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R. J. Serne

Water and Land Resources Department

1972

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SUMMARY

A group of support studies conducted during development of a transport model for the Radionuclides in Soils Program is described in this report.

Measurement studies for sorption parameters concluded that: 1) small calcium experiments are more useful than batch experiments for measuring the K_d of trace solutes which are sorbed by ion-exchange, unless the batch system is pre-washed several times with influent prior to measuring the K_d ; 2) the decrease in K_d often reported with an increasing soil-to-solution ratio is the result of the reaction of the soil solid phase with the influent solution; 3) batch and small column K_d s will agree if the equilibrium chemical environment is equivalent; and 4) the number of regression equations required to adequately define sorption in soil column work is a determinable function for each soil.

The sorption of Eu was found to depend upon both ion exchange and the filtration of radiocolloids formed by solution hydrolysis in the soil. Either centrifugation or filtration was capable of removing radiocolloidal Eu from solution. Formation of radiocolloidal Eu is a predictable function of pH and solution concentration of Ca (Ca). It is independent of the solution concentration of Na. Multiple

regression analysis was used to develop regression equations for predicting Eu hydrolysis as a function of equilibrium pH and (Ca) over 3 pH ranges. Regression coefficients (r) for the 3 ranges were 0.96, 0.96, and 0.54, showing the high correlation of hydrolysis with pH and (Ca). Once radio-colloidal Eu was removed by centrifugation or filtration, Kd values could be determined for the balance of the Eu.

In further study a method was developed for calculating activity coefficients for solutions with ionic strengths greater than 0.5. This method allows extension of the PERCOL¹ model to high ionic strength solutions.

A method was developed to estimate the KdSr in Hanford groundwater as a function of the soil's transmissivity. Data from 5 wells were used to make a regression analysis. KdSr was found to be a linear function of the log of the permeability and the regression coefficient for the equation was found to be 0.799.

Unsorbed solute was measured through soil columns using Cl⁻ and ³H. The effective porosity was found to be 7.7 ± 2 percent smaller than the calculated porosity. These data were also used to calculate dispersion for the soil columns.

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EXPERIMENTAL SUPPORT STUDIES FOR THE PERCOL AND TRANSPORT MODELS

INTRODUCTION

The PERCOL model was developed for the Radionuclides in Soils Program to account for the significant chemical reactions which control the movement of macroions and radionuclides through multi-ion soil systems. The chemical reactions portion of the PERCOL model has been incorporated directly into the transport model to account for the soil sorption of radionuclides. Details of the PERCOL and transport models are given in BNWL-1718¹ and BNWL-1715,² respectively.

Chemical reactions considered by the PERCOL model include ion-exchange of macroions, including Na, K, Ca, and Mg, sorption of microions, dissolution-precipitation of CaCO_3 , F_2 , and CaSO_4 , complexation of Ca by solution CaSO_4 , and dissolution of soluble salts from an initially dry soil. The PERCOL model is sufficiently flexible to allow the addition of other significant chemical reactions which may in part control ion movement in soil systems.

A number of semi-independent soil-waste reaction studies were conducted in support of the PERCOL and transport models for the Radionuclides in Soils Program. These studies can be divided into three general categories: 1) verification of PERCOL model assumptions; 2) extension of the transport model to additional systems; and 3) development of methods to

acquire data for estimating dispersion and apparent porosity.
An introduction and description of each of these studies
follows.

VERIFICATION OF PERCOL MODEL ASSUMPTIONS

MEASUREMENT OF THE DISTRIBUTION COEFFICIENTS

The distribution coefficient (Kd) is the measured empirical sorption parameter used in the PERCOL model to calculate the sorption of radionuclides. It is defined as:

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

where:

A_s = the equilibrium concentration or activity sorbed on the solid phase

W = the weight of the solid phase in grams

A_l = the equilibrium concentration or activity of the solution phase

V = the volume of solution in milliliters

Thus, K_d is the ratio of the equilibrium sorbed activity per gram (g) of soil to the equilibrium solution activity per milliliter (ml) of solution and has the units of ml/g. Either batch or column studies can be used to measure the K_d on soils. Details of each of the above experimental methods are given in BNWL-1721.³

The use of the distribution coefficient (K_d) as a sorption parameter in the PERCOL model requires that this parameter be measurable in a large variety of soil-water systems. While K_d values had been measured in essentially all of the proposed systems by either batch or small column techniques, two problems were found to cast considerable doubt on the usefulness of the obtained values. First, the distribution coefficients were found by others to be dependent upon the soil to solution ratio used in the experiment; secondly, batch and small column K_d s did not generally give the same value.^{4,5} Therefore, methods were needed for either obtaining agreement between batch and small column K_d s and agreement for batch K_d s at differing soil to solution ratios, or for predicting data for one technique from the other.

Batch experiments using a Burbank sand were designed to 1) determine the cause of an observed decrease in the K_d for Sr with an increasing soil to solution ratio, 2) explain the

lower KdSr measured by a batch technique as compared to a column technique, and 3) determine which of the two techniques was better for measuring the KdSr for proposed factorial design experiments. Table 1 shows how the KdSr changes with an increasing soil to solution ratio for a 0.05 M (Na⁺), 0.05 M (K⁺), 0.002 M (Ca⁺⁺) and pH 9.2 influent solution. There is approximately a threefold increase in the KdSr with a tenfold decrease in the soil to solution ratio.

TABLE 1. BATCH STRONTIUM DISTRIBUTION COEFFICIENTS (KdSr) FOR BURBANK SAND AS A FUNCTION OF THE SOIL TO SOLUTION RATIO

<u>Soil to Solution Ratio</u> (g/g)	<u>KdSr</u> (ml/g)
.1	3.5
.2	2.5
.5	1.6
1.0	1.2

The equilibrium concentration of (Ca⁺⁺) was measured on duplicate batch samples; their KdSr values are listed in Table 2.

TABLE 2. BATCH STRONTIUM DISTRIBUTION COEFFICIENTS AND EQUILIBRIUM (Ca⁺⁺) CONCENTRATIONS FOR A BURBANK SAND AS A FUNCTION OF SOIL TO SOLUTION RATIO

<u>Soil to Solution Ratio</u> (g/g)	<u>KdSr</u> (ml/g)	<u>(Ca⁺⁺)</u> (M)
.1	3.7	4.1 x 10 ⁻³
.2	2.6	7.0 x 10 ⁻³
.5	1.6	14.0 x 10 ⁻³
1.0	1.2	23.0 x 10 ⁻³

Good KdSr agreement was obtained between the two replicates. It can be seen that there is a fivefold increase in the equilibrium (Ca^{++}) with a tenfold increase in the soil to solution ratio. Since the KdSr is highly dependent on the equilibrium (Ca^{++}) concentration, the solid phase was presumed to have reacted with the influent solution to increase the equilibrium (Ca^{++}) concentration. The observed increase in (Ca^{++}) was probably due to the exchange of (Na^+) and (K^+) for (Ca^{++}) and the dissolution of Ca-salts.

To check the above suppositions a batch experiment was conducted in which all soil to solution ratios were equilibrated with the influent macroions by serially washing with the influent solution. Each soil to solution ratio was given four washes. Results are summarized in Table 3. It can be seen that pretreatment washes reduced the (Ca^{++}) concentration to that of the influent (0.002 M Ca^{++}) for the two lowest soil to solution ratios but not for the two highest soil to solution ratios. The decrease in (Ca^{++}) due to washing resulted in a concomitant increase in the KdSr. Ion exchange and Ca-salt dissolution does appear to be the cause of the change in KdSr with changing soil to solution ratios.

TABLE 3. BATCH STRONTIUM DISTRIBUTION COEFFICIENTS (KdSr) AND EQUILIBRIUM (Ca^{++}) CONCENTRATION FOR A BURBANK SAND AFTER FOUR INFLUENT SOLUTION WASHES

<u>Soil to Solution Ratio</u> (g/g)	<u>KdSr</u> (ml/g)	<u>(Ca^{++})</u> (eq/l)
.1	7.3	2.0×10^{-3}
.2	7.8	1.9×10^{-3}
.5	4.9	2.6×10^{-3}
1.0	3.5	3.7×10^{-3}

A small column experiment using the same influent solution was conducted to compare the results with the equilibrium Kds produced by the above batch techniques. The Kd measured by the small column technique was 7.6, a good agreement with the equilibrium batch Kd.

This study indicates that

- small column experiments are more useful than batch experiments unless the soil is prewashed several times with the influent solution prior to measuring the K_d Sr;
- the decrease in the K_d Sr with an increasing soil to solution ratio is the result of the reaction of the soil solid phase with the influent solution; and
- batch and small column K_d s will agree if the equilibrium chemical environments of the two systems are equivalent.

ESTIMATION OF THE NUMBER OF LINEAR SORPTION EQUATIONS

In the PERCOL and transport models the radionuclide sorption is determined empirically as a function of the soil type, macroion equilibrium concentrations and pH of the solution. Statistical two-level factorial design experiments are conducted to obtain the K_d predictor equations. Over order of magnitude solution concentration ranges of macroions the effect of macroion concentration on the K_d cannot be expected to be linear. This is especially true for a K_d which is sensitive to the solution concentration of a macroion (such as the K_d of strontium, which is affected by the solution concentration of calcium).⁵ In such cases, when more than a single empirically derived equation is necessary to adequately predict the sorption of a trace radionuclide in a soil-water system, a method is required to determine the number of equations needed. Following is the description of a method which has been used for this purpose.

From preliminary factorial design experiments the sorption of strontium was found to be most sensitive to the macroion concentration of (Ca^{++}) in solution.⁵ By subdividing the Ca concentration range of this sensitive independent variable much better agreement can be obtained between the observed and predicted K_d s; uncertainties in the effects of the more sensitive variables are reduced and interaction terms may become insignificant, simplifying the empirical equations. Frequently the equations become nearly linear.

The K_d of radioactive Sr was measured in small columns on a Burbank sand subsoil to determine the number of empirical sorption equations required to satisfactorily predict the K_d Sr as a function of solution macroion concentration over a specified solution (Ca^{++}) concentration range. Statistical

two-level factorial design experiments were conducted in which KdSr measurements in small columns were used to derive equations for intermediate KdSr prediction. The Ca-concentration range of 0.002-0.05 M was divided into one, two and three subranges and an equation was derived for the KdSr over each subrange. Experimental details are listed in BNWL-1721.³

Table 4 gives the derived sorption equations and the macroion concentration range for which each equation is valid. K, Na, and pH concentration ranges were 0.0 and 0.05 M, 0.02 and 0.2 M and 7.0, respectively.

TABLE 4. EQUATIONS TO PREDICT KdSr (ml/g) AS A FUNCTION OF EQUILIBRIUM MACROION CONCENTRATIONS OVER THE TOTAL Ca CONCENTRATION RANGE OF 0.002-0.05 M FOR A BURBANK SAND SUBSOIL

Subrange Number	Ca range -M-	Regression Equation
1	0.0020-0.050	$\begin{aligned} \text{KdSr} = & 3.46 - 2.83X \text{ Ca1}^1 - 1.62XK^2 \\ & + 1.45 XKX\text{Ca1} - 1.35XNa^3 \\ & + 1.24XNaX\text{Ca1} + 1.00 XNaXK \\ & - 0.97XNaX\text{Ca1}XK \end{aligned}$
2a	0.0020-0.0035	$\begin{aligned} \text{KdSr} = & 5.29 - 1.04X\text{Ca2a}^4 - 2.59XK + 0.49 \\ & XKX\text{Ca2a} - 2.11XNa + 0.51XNaX\text{Ca2a} \\ & + 1.56XNaXK - 0.41XNaXKX\text{Ca2a} \end{aligned}$
2b	0.0035-0.050	$\begin{aligned} \text{KdSr} = & 2.64 - 2.10X\text{Ca2b}^5 - 1.22XK + 1.05 \\ & XKX\text{Ca2b} - 0.62XNa + 0.61XNaX\text{Ca2b} \\ & + 0.50 XNaXK - 0.47XNaXKX\text{Ca2b} \end{aligned}$
3a	0.0020-0.0035	KdSr = Same as 2a
3b	0.0035-0.0050	$\begin{aligned} \text{KdSr} = & 4.31 - 0.62X\text{Ca3b}^6 + 0.062X\text{Ca3b}XK \\ & - 1.70XK - 1.41XNa + 0.92XNaX \\ & - 0.062XKX\text{Ca3b}Na \end{aligned}$
3c	0.0050-0.050	$\begin{aligned} \text{KdSr} = & 2.22 - 1.63X\text{Ca3c}^7 - 1.01K + 0.84 \\ & X\text{Ca3c}XK - 0.64XNa + 0.56 \\ & XNaX\text{Ca3c} + 0.37 XNaXK - 0.34 \\ & XNaXKX\text{Ca3c} \end{aligned}$

Notes:

1. $X\text{Ca1} = (\text{CCa} - 0.026)/0.024$ and $\text{CCa} = \text{moles/l of Ca}$
2. $XNa = (\text{CNa} - 0.11)/0.09$ and $\text{CNa} = \text{moles/l of Na}$
3. $XK = 40CK - 1$ and $CK = \text{moles/l of K}$
4. $X\text{Ca2a} = (2\text{CCa} - 0.0055)/0.0015$
5. $X\text{Ca2b} = (2\text{CCa} - 0.0535)/0.0465$
6. $X\text{Ca3b} = (\text{CCa} - 0.00425)/0.00075$
7. $X\text{Ca3c} = (200\text{CCa} - 5.5)/4.5$

Table 5 lists selected sample calculations from equations 1, 2a, 2b, 3a, 3b, and 3c of the KdSr for some chosen macroion concentrations. K, Na and pH were held constant at 0.025 M, 0.1 M, and 7.0, respectively.

TABLE 5. KdSr PREDICTED FROM REGRESSION EQUATIONS FROM
SELECTED EQUILIBRIUM MACROION VALUES

Subrange Number	Ca-Macroion Concentration -M-	Kd -ml/g-
1	0.003	6.5
2a	0.003	5.2
3a	0.003	5.2
1	0.004	6.4
2b	0.004	4.7
3b	0.004	4.8
1	0.01	3.9
2c	0.01	3.8
3c	0.01	3.7

It can be seen that a subdivision of two or three regression equations essentially predicts the same KdSrs, suggesting that the single equation may predict a high KdSr at a low Ca-concentration (however, agreement is within experimental error at a high solution Ca-concentration). In addition, it appears that two regression equations are sufficient to predict the KdSr since no advantage is obtained by dividing the Ca range into three parts.

To further check the adequacy of subdividing by two instead of three, both sets of equations were used as input to the computer sorption model PERCOL to predict the movement of ⁸⁵Sr through a soil column. Both sets of equations gave essentially the same results. Furthermore, in a related experiment both predicted ⁸⁵Sr movements through the column agreed within 2 percent up to a normalized ⁸⁵Sr movement of 0.85 (C/Co).

STUDIES TO EXTEND THE TRANSPORT MODEL

SORPTION OF RARE EARTH RADIONUCLIDES

Rare earth and actinide radionuclides are sorbed by both ion exchange and precipitation reactions.⁶ Use of a K_d to characterize a sorption reaction assumes that ion exchange is the primary sorption controlling the removal of a radionuclide from solution.⁶ Thus, extension of the transport model to rare earth and actinide radionuclides which may be sorbed primarily by reactions other than ion exchange requires laboratory techniques for measuring sorption in these systems as a function of solution parameters. The following group of studies was conducted to obtain this capability. Because of its commercial availability and emission of a readily counted gamma radiation, Europium (Eu) was selected for this group of experiments. Since the ground disposal of large volumes of acid wastes have resulted in the lowering of the soil pH of some portions of the Hanford Reservation, the sorption of lanthanide and actinide radionuclides (such as Eu) that were present in these wastes must be measured in acid soil systems which were initially neutral or slightly alkaline. Details of these experiments are given in BNWL-1721.³

In a preliminary small column experiment the sorption of Eu was found to be nearly 100 percent, even after 200 column volumes of pH 6.0 solution had been passed through the soil. Thus, batch systems were investigated for the initial sorption of Eu.

Adjustment of soil pH in batch systems to lower than natural values requires large amounts of acid and the pH tends to initially drift upward as acid in the system reacts with the soil. Sorption of Eu is measurable, however, if the solid phase is separated from the liquid phase by centrifugation, thereby greatly reducing the reaction. The sorption of Eu in suspension was found to be reproducible and thus rapid in relation to the rate at which the soil pH was changing.

Batch experiments were conducted to determine the sorption of Eu on a tank farm sandy loam soil which had been pre-treated with acid to obtain low pH values. Sorption was determined as a function of macroion concentration, pH, and Eu spike concentration. Fractional sorption (C/C_0) was found to be constant over a difference in Eu spike concentration of nearly an order of magnitude (Table 6). Sorption was found to be independent of (Na^+) concentration, slightly dependent on (Ca^{++}) concentration, and highly dependent upon

TABLE 6. EUROPIUM SORPTION AS A FUNCTION
OF pH, (Ca), (Na), AND Co

Sample Number	C/C_o	pH	Ca (M)	Na (M)	C_o (cpm/ml)
1	.2783	1.855	.0075	.0075	20500
2	.2708	2.00	.0075	.0075	20500
3	.2796	2.1	.0075	.0075	3000
4	.2916	2.1	.0075	.0075	3000
5	.2962	2.145	.0075	.0075	3000
6	.2991	2.175	.0075	.0075	3000
7	.2099	2.33	.0075	.075	3000
8	.1964	2.58	.0075	.0075	20500
9	.1726	2.585	.0075	.075	3000
10	.1391	2.605	.0075	.075	20000
11	.1648	2.725	.0075	.075	3000
12	.1480	2.80	.0075	.075	20000
13	.259	3.040	.075	.0075	16000
14	.1520	3.14	.0075	.0075	20500
15	.1325	3.165	.0075	.0075	3000
16	.1478	3.165	.0075	.0075	3000
17	.297	3.185	.075	.075	4000
18	.1157	3.34	.0075	.075	3000
19	.262	3.40	.075	.075	17000
20	.196	3.5	.075	.0075	16000
21	.179	3.655	.075	.075	4000
22	.216	3.67	.075	.075	4000
23	.1055	3.685	.0075	.075	3000
24	.174	3.715	.075	.0075	4000
25	.181	3.775	.075	.0075	4000
26	.166	3.80	.075	.0075	4000
27	.0933	3.805	.0075	.0075	3000
28	.161	3.83	.075	.075	4000
29	.0664	3.86	.0075	.0075	20500
30	.196	3.905	.075	.075	17000
31	.0459	3.95	.0075	.075	3000
32	.0366	4.080	.0075	.075	20000
33	.0497	4.1	.0075	.075	3000
34	.121	4.15	.075	.0075	4000
35	.0447	4.23	.0075	.0075	20500
36	.0354	4.28	.0075	.0075	3000
37	.0461	4.28	.0075	.0075	3000
38	.096	4.29	.075	.075	4000
39	.0751	4.365	.075	.0075	16000
40	.0918	4.42	.075	.075	4000
41	.087	4.425	.075	.075	4000
42	.0481	4.43	.0075	.075	3000
43	.0331	4.43	.0075	.075	20000
44	.080	4.485	.075	.075	17000
45	.0258	4.620	.0075	.0075	3000

TABLE 6 (continued)

Sample Number	C/ Co	pH	Ca (M)	Na (M)	C _o (cpm/ml)
46	.0238	4.70	.0075	.0075	3000
47	.0516	4.70	.075	.075	4000
48	.0157	4.74	.0075	.0075	20500
49	.041	4.785	.075	.0075	4000
50	.0237	4.80	.0075	.075	3000
51	.041	4.810	.075	.0075	16000
52	.039	4.84	.075	.0075	4000
53	.050	4.855	.075	.075	17000
54	.041	4.855	.075	.0075	4000
55	.0113	4.90	.0075	.075	20000
56	.0066	4.925	.0075	.075	3000
57	.0389	4.99	.075	.0075	4000
58	.0092	5.06	.0075	.0075	20500
59	.0141	5.07	.0075	.075	3000
60	.021	5.08	.075	.0075	4000
61	.0237	5.08	.075	.0075	16000
62	.019	5.175	.075	.0075	4000
63	.0131	5.20	.0075	.075	3000
64	.0088	5.20	.0075	.075	20000
65	.019	5.24	.075	.075	4000
66	.0032	5.32	.0075	.075	3000
67	.015	5.33	.075	.075	17000
68	.015	5.33	.075	.075	4000
69	.012	5.355	.075	.0075	16000
70	.01226	5.45	.075	.075	4000
71	.0024	5.465	.0075	.075	3000
72	.008	5.555	.075	.075	17000
73	.0024	5.615	.0075	.075	3000
74	.0097	5.62	.075	.0075	4000
75	.0097	5.62	.075	.075	4000
76	.0011	5.70	.0075	.075	3000
77	.0023	5.70	.0075	.075	20000
78	.000	5.725	.0075	.075	3000
79	.0025	5.725	.0075	.075	20000
80	.0044	5.745	.075	.0075	4000
81	.0011	5.78	.0075	.0075	20500
82	.000	5.78	.0075	.0075	3000
83	.000	5.78	.0075	.0075	3000
84	.0008	5.82	.0075	.0075	20500
85	.0002	5.90	.0075	.0075	3000
86	.0020	5.90	.0075	.0075	3000
87	.006	6.02	.075	.075	4000
88	.0017	6.04	.075	.0075	16000
89	.004	6.082	.075	.0075	4000
90	.0021	6.10	.075	.075	4000

TABLE 6 (continued)

Sample Number	C/C_o	pH	Ca (M)	Na (M)	C_o (cpm/ml)
91	.0009	6.10	.075	.075	17000
92	.0015	6.145	.075	.0075	16000
93	.0024	6.155	.075	.0075	4000
94	.000	6.18	.0075	.075	3000
95	.0031	6.23	.075	.075	4000
96	.0015	6.240	.075	.075	17000
97	.0019	6.275	.075	.0075	4000
98	.00086	6.30	.0075	.075	20000
99	.0005	6.34	.0075	.075	20000
100	.0006	6.34	.0075	.075	3000
101	.0005	6.36	.075	.075	4000
102	.0027	6.370	.075	.0075	4000
103	.0007	6.43	.0075	.075	3000
104	.0015	6.43	.075	.075	4000
105	.000	6.432	.0075	.075	3000
106	.0018	6.44	.075	.0075	16000
107	.0008	6.49	.075	.0075	16000
108	.003	6.50	.075	.0075	4000
109	.0007	6.51	.075	.075	17000
110	.0019	6.51	.075	.075	4000
111	.0006	6.555	.075	.075	17000
112	.005	6.57	.075	.075	4000
113	.002	6.540	.075	.0075	4000
114	.00032	6.60	.075	.0075	4000
115	.0025	6.62	.075	.075	4000
116	.0011	6.680	.075	.0075	4000

the pH of the system at values below 6.5. Above a pH of 6.5 sorption was found to be essentially 100 percent for all solutions (Table 6).

Multiple regression analysis was conducted with the data to quantitatively describe the initial sorption of Eu as a function of (Ca^{++}) concentration and pH.³ Regression equations were found to best fit the data when subdivided into pH ranges of <4.7, 4.7-6.0, and 6.0-6.5. The regression equations and the multiple correlation coefficients for these respective ranges are:

$$\text{pH} \leq 4.7$$

$$C/Co = 0.430 - 0.0934 \text{ pH} + 3.99 C_{Ca} - 0.697 \text{ pH } C_{Ca} \quad (2)$$

$$r = 0.96$$

$$4.7 \leq \text{pH} \leq 6.0$$

$$C/Co = 0.0669 - 0.0114 \text{ pH} + 2.43 C_{Ca} - 0.426 \text{ pH } C_{Ca} \quad (3)$$

$$r = 0.96$$

$$6.0 \leq \text{pH}$$

$$C/Co = 0.0071 + 0.00116 \text{ pH} + 0.2997 C_{Ca} - 0.0434 \text{ pH } C_{Ca} \quad (4)$$

$$r = 0.54$$

where

C/Co = equilibrium solution activity of Eu divided by the influent solution activity and

C_{Ca} = equilibrium solution concentration of Ca in moles/l.

From the correlation coefficients from Equations 2 and 3 it can be seen that Eu sorption is highly correlated with the solution and equilibrium concentration of Ca^{++} . The lower correlation coefficient of Equation 4 is probably due in part to the counting statistics at pH values above 6.0, where only small Eu activities remain in solution. Equations 2 and 3 represent sorption of Eu due to both ion exchange and filtration of radiocolloidal Eu and thus are valid only for the initial contact with this soil. Since small column studies have shown that essentially all of the radiocolloidal Eu will be filtered by the soil and that Equations 3 and 4 will predict this, it is necessary experimentally to separate the colloidal Eu from the soluble Eu to determine Eu sorption in noncolloidal systems. Further experiments were required to measure soluble Eu sorption in other segments of the soil.

To measure the removal of the soluble Eu in the absence of a soil it is first necessary to find a means of separating radiocolloidal Eu from soluble Eu. To accomplish this, a batch experiment was designed to determine the effect of pH on the susceptibility of radiocolloidal Eu to centrifugation from solution. Results are shown in Figure 1, where solution is 0.07 M Ca^{++} and Eu activity is 2200 cpm/ml. It can be seen that at pH values of 4.0-4.5 no Eu can be removed. At pH values greater than 4.5 significant amounts of Eu can be

FIGURE 1. Fraction Centrifuged as a Function of Time and pH

removed and the process is both time and pH dependent. The higher the pH and the greater the time, the more Eu will be removed by centrifugation. The time dependence is probably due to a lack of surfaces for nucleation. At pH values above 7.0 essentially 100 percent sorption can be expected. To determine whether filtration would result in an equivalent removal, some of the above solutions were resuspended and filtered through 0.45μ filters, which are commonly used in sediment work to separate "soluble" from insoluble components. This technique also removed radiocolloidal Eu.

In another small column experiment, a solution with an Eu activity less than the equilibrium C/Co predicted by Equations 2, 3, and 4 (140 cpm/ml) was centrifuged and sorption measured as a function of pH to determine the sorption noncolloidal Eu. The solution was 0.07 M Na^+ and 0.007 M Ca^{++} . Results are shown in Figure 2. It can be seen that at pH values of less than 6.0 nearly 100 percent of the Eu remains in solution. Thus, distribution coefficients can be accurately determined with this solution below pH 6.0. The above solution was percolated through small columns of a tank farm sandy loam soil at pH values of 4.0, 4.5, and 5.1. The solutions were

FIGURE 2. Fraction of 140 cpm/ml Eu Remaining in Solution After Centrifugation (13,000 RPM for 15 minutes)

found to attain the activity of the influent solution after 250 ml of solution had passed through them, demonstrating that equilibrium was attained. K_d Eu values were 55, 106, and 521 at pH values of 4, 4.5, and 5.1, respectively. Thus, Eu sorption in the first increment of soil can be predicted using Equations 2, 3, and 4. Sorption of Eu in all subsequent segments of soil will be by exchange processes and can be predicted from K_d Eu, which can be measured with either filtered or centrifuged solutions.

HIGH IONIC STRENGTH ACTIVITY COEFFICIENTS

The original PERCOL computer model used an extension of the Debye-Huckel theory to calculate the activity coefficients needed to convert the concentration data to activity data. Activity data are needed to solve the chemical equilibrium relationships that occur as wastes percolate through the soil. The theory and equations utilized in PERCOL are described in BNWL-1718.¹ The original model, which utilizes Davies' extension of the Debye-Huckel equation, could calculate activity coefficients of solutions up to a maximum ionic

strength of 0.5 m. Above this concentration the true activity coefficients would not follow the empirical equation. Since Hanford wastes often reach ionic strengths of 3.0 to 11.0 m refinements to the model were warranted.

The literature on activity coefficients was reviewed and an empirical approach based on Guggenheim's adaptation of Bronsted's specific ion interaction theory was adopted.⁷ This approach was chosen because it matched observed data for salt solutions to ionic strengths above 5 m and could be readily extended to mixed salt solutions. Two principals inherent in this approach are:

1. Specific short-range interactions exist between ions of unlike charge but not between ions of like charge (Bronsted's specific ion interaction theory).
2. In mixed electrolytes the long-range electrostatic interaction between ions of like or unlike sign requires that all ions be considered in calculating the charge density throughout the solution. This is accomplished by making the activity coefficient a function of the total ionic strength I.

Empirical interaction constants (B_{MX}) are calculated for single salt solutions from measured activity coefficients, molalities of the salt's ions and total ionic strength. Activity coefficients can be measured by osmotic pressure and/or vapor pressure experiments which are briefly described in Reference 7. The measured quantities are substituted into Equation 5 and values for B_{MX} can be calculated. Similar experiments on salt mixtures indicate that the effects in pure salt solutions can be added to describe mixed salt solutions.

The equation for the mean activity coefficient of a salt MX in a mixed salt solution is:

$$\log \gamma_{\pm MX} = - A_{\gamma} \frac{z_+ z_-}{I + I^{1/2}} + \frac{v_+}{v_+ + v_-} \sum_X B_{MX, m'_X} + \frac{v_-}{v_+ + v_-} \sum_X B_{M, X m'_M} \quad (5)$$

where

- A_γ = Debye-Huckel theoretical coefficient
 Z_+ = charge on cation of salt MX
 Z_- = charge on anion of salt MX
 I = total ionic strength of salt mixture
 ν_+ = number of cations present when salt MX dissociates
 ν_- = number of anions present when salt MX dissociates
 B_{MX} = adjustable constant of each salt evaluated at I
 m_X' = molality of individual ion X'

The first term in the equation is the Debye-Huckel term; the second is the sum of the interactions between the cation M and all the other anions present; and the third term is the sum of the interactions between the anion X and all the other cations present.

Tables of B_{MX} for 67 common 1-1 salts and 60 1-2 or 2-1 salts are available in the literature.⁷ The nomenclature 1-1, 1-2, etc. refers to the charges on the cation and anion, respectively, of the salt. For example, NaCl is a 1-1 salt and Na₂SO₄ is a 1-2 salt.

A check of Equation 5 on experimental data was made to determine the validity of this approach. First, pure salt solutions were checked and the empirical equations proved satisfactory (Table 7). Next, salt mixtures were studied. The experimental

TABLE 7. MEASURED AND ESTIMATED ACTIVITY COEFFICIENTS
FOR PURE SALT SOLUTIONS

γ_{KCl}	Exp. Value ⁸	Eq. 4
.1 m	.770	.770
1 m	.605	.6045
3 m	.569-.573	.570
5 m	.590	.592
γ_{NaNO_3}		
.1 m	.758-.761	.761
1 m	.548	.549
3 m	.437-.438	.4375
5 m	.386	.387

mean ionic activity coefficient of NaCl in a NaCl-Na₂SO₄ solution was compared with Equation 5. From Table 8 it can be seen that the agreement is good.

TABLE 8. MEASURED AND ESTIMATED ACTIVITY COEFFICIENTS FOR A NaCl-Na₂SO₄ SOLUTION

<u>Total I</u>	<u>% NaCl</u>	<u>$\gamma_{\text{NaCl exp}}^{(9)}$</u>	<u>$\gamma_{\text{NaCl (eq.4)}}$</u>	<u>% Difference</u>
1 m	74.70%	.634	.637	+ .4%
1 m	12.13%	.601	.588	-2.0%
3 m	75.00%	.639	.663	+3.6%
	25.06%	.556	.568	+2.2%

The experimental mean ionic activity coefficient of NaCl in a NaCl-MgCl₂ solution was compared with Equation 5, as well as the experimental mean ionic activity coefficient of Na₂SO₄ in NaCl-Na₂SO₄ solution. From Tables 9 and 10 it can be seen that the agreement is good.

TABLE 9. MEASURED AND ESTIMATED ACTIVITY COEFFICIENTS FOR A NaCl-MgCl₂ SOLUTION

<u>Total I</u>	<u>% NaCl</u>	<u>$\gamma_{\text{NaCl exp}}^{(10)}$</u>	<u>$\gamma_{\text{NaCl (eq.4)}}$</u>	<u>% Difference</u>
.5 m	35.64	.702	.683	-2.7%
1.0 m	75.21	.661	.658	-0.5%
1.0 m	33.15	.670	.648	-3.3%
3.0 m	78.53	.730	.724	-0.8%
3.0 m	33.94	.758	.741	-2.2%
5.0 m	83.17	.873	.892	+2.2%
5.0 m	25.96	.889	.951	+7.0%

TABLE 10. MEASURED AND ESTIMATED ACTIVITY COEFFICIENTS
FOR A NaCl-Na₂SO₄ SOLUTION

<u>Total I</u>	<u>% Na₂SO₄</u>	<u>γ_{Na₂SO₄ exp⁽¹¹⁾}</u>	<u>γ_{Na₂SO₄ (eq.1)}</u>	<u>% Difference</u>
1.0 m	90%	.317	.301	-5.1%
1.0 m	50%	.327	.320	-2.1%
1.0 m	9.58%	.338	.341	+0.9%

Therefore, the above checks, Tables 7 through 10, indicate that Equation 5 does in fact predict the activity coefficients of mixed salt solutions over a range of concentrations similar to those encountered in the Hanford system.

Unfortunately no activity coefficient data on mixed nitrate salts were found in the literature and thus the validity of Equation 5 on mixed nitrate salts could not be checked without initiating new experiments. Since high nitrate content waste solutions are common on the Hanford Reservation, several experimental nitrate studies were performed before adopting Equation 5 to estimate activity coefficients.

A calcium nitrate-sodium nitrate system was prepared at five different ionic strengths. At each ionic strength the percentages of sodium nitrate were varied to cover the range 0-100 percent. Specific ion electrodes were used to experimentally determine the activity coefficients of the binary salt mixtures. Huston, Butler and Synnott^{9,10,11,12} describe in detail the use of specific ion electrodes to measure the activity of ions in solution. The specific ion electrode measures the activity of the ion of interest; by comparing the activity in the solution with a reference solution in which both the activity and activity coefficients have been independently determined, and knowing the concentration of the measured ion, one can determine the activity coefficient of the ion from the measured activity. The mean activity coefficients for sodium nitrate in the mixed electrolyte were calculated using the following equation based on the works of Butler, et al. mentioned previously:

$$E-E_o = \frac{RT}{F} \ln \frac{(m_{Na^+}) (m_{NO_3^-}) (\gamma_{\pm NaNO_3})^2}{(m_{Na_o}) (m_{NO_3_o}) (\gamma_o)^2} \quad (6)$$

where the subscript (o) represents the pure sodium nitrate reference solution. The molalities of the reference solution m_{NaO} and m_{NO_3} and the molalities of the mixed solution m_{Na^+} and $m_{\text{NO}_3^-}$ are known values. γ_o is the activity coefficient of the pure sodium nitrate solution. γ_o is obtained from the literature.⁸ The experimental millivolt difference $E-E_o$ is measured with specific ion electrodes and $\gamma_{\pm\text{NaNO}_3}$ calculated.

The electromotive force E is directly related to the activity using the Nernst equation

$$E - E' = + \frac{RT}{nF} \ln a \quad (7)$$

where

E = electrode potential

E' = reference electrode potential

a = activity of the solution

The mean activity coefficients for calcium nitrate in the mixed electrolyte were calculated using Equation 8, which is similar to Equation 6:

$$E-E_o = \frac{RT}{2F} \ln \frac{(m_{\text{Ca}^{++}}) (m_{\text{NO}_3^-})^2 \left(\gamma_{\pm\text{Ca}(\text{NO}_3)_2} \right)^3}{(m_{\text{CaO}}) (m_{\text{NO}_3\text{O}})^2 (\gamma_o)^3} \quad (8)$$

Here the subscripts (o) refer to the pure calcium nitrate reference solution. Activity coefficient results for the sodium-calcium mixed salt system are presented in Table 11, where the experimental activity coefficients are compared to coefficients derived using Equation 5.

It can be seen that the experimental activity coefficients generally agree with the empirically derived values; however, the calcium nitrate activity coefficients in the strong sodium solutions were found to be systematically high. Further experimentation utilizing specific ion electrodes showed that this is caused by a breakdown in the Ca electrode's specificity for calcium. At large Na/Ca ratios, sodium is sensed by the calcium electrode. Two methods of describing this interference were found in the literature. Huston and Butler¹² use observed activity coefficients determined by an independent method and observed millivolt readings to determine a parameter for correcting for the Na interference (K). The value of K is a function of the ratio Na/Ca and total ionic

TABLE 11. MEASURED AND ESTIMATED ACTIVITY COEFFICIENTS FOR MIXED SALT SOLUTIONS

Solution	Ionic Strength .01m					
	$\gamma_{\text{Ca(NO}_3)_2}(\text{EXP})$	$\gamma_{\text{Ca(NO}_3)_2}(\text{EQ 1})$	% Difference	$\gamma_{\text{NaNO}_3}(\text{EXP})$	$\gamma_{\text{NaNO}_3}(\text{EQ 1})$	% Difference
.01m $\text{Ca(NO}_3)_2$	----	-----	----	----	.900	----
.003m $\text{Ca(NO}_3)_2$	.838	.815	+2.8	.903	.901	+0.2
.009m NaNO_3						
.00083m $\text{Ca(NO}_3)_2$	.792	.815	-2.8	.927	.902	+2.8
.0075m NaNO_3						
.00167m $\text{Ca(NO}_3)_2$	.795	.815	-2.5	.894	.902	-0.9
.005m NaNO_3						
.00225m $\text{Ca(NO}_3)_2$	.787	.815	-3.4	.910	.902	+0.9
.0035m NaNO_3						
.0025m $\text{Ca(NO}_3)_2$	.800	.815	-1.8	.902	.902	+0.0
.0025m NaNO_3						
.003m $\text{Ca(NO}_3)_2$	.802	.815	-1.6	.978	.902	+8.5
.001m NaNO_3						
.0033m $\text{Ca(NO}_3)_2$	----	.818	----	----	----	----
Ionic Strength 0.5m						
.05m NaNO_3	----	----	----	----	.811	----
.00167m $\text{Ca(NO}_3)_2$						
.045m NaNO_3	.738	.668	+10.5	.799	.812	-1.6
.00415m $\text{Ca(NO}_3)_2$						
.0375m NaNO_3	.668	.668	+0.0	.809	.813	-0.5

TABLE 11 (continued)

Solution	Ionic Strength .05m			
	$\gamma_{\text{Ca(NO}_3)_2(\text{EXP})}$	$\gamma_{\text{Ca(NO}_3)_2(\text{EQ 1})}$	% Difference	$\gamma_{\text{NaNO}_3(\text{EXP})}$
.0058m $\text{Ca(NO}_3)_2$	.717	.668	+7.3	.811
.0325m NaNO_3				.813
.00835m $\text{Ca(NO}_3)_2$	Lost	.675	Lost	.799
.025m NaNO_3				.814
.01125m $\text{Ca(NO}_3)_2$	.664	.670	-0.9	.815
.0175m NaNO_3				
.0125m $\text{Ca(NO}_3)_2$	.676	.670	+0.9	.818
.0125m NaNO_3				.816
.015m $\text{Ca(NO}_3)_2$	.679	.670	+1.3	.817
.005m NaNO_3	----		----	----
.0167m $\text{Ca(NO}_3)_2$		.672	----	----
				+0.0
Ionic Strength .1m				
.1m NaNO_3	----	----	----	.760
.003m $\text{Ca(NO}_3)_2$				
.09m NaNO_3	.635	.598	+6.8	.755
.0083m $\text{Ca(NO}_3)_2$	.622	.598	+4.0	.758
.075m NaNO_3				.764
.0116m $\text{Ca(NO}_3)_2$	.618	.599	+3.2	.760
.065m NaNO_3				.764
				-0.5

TABLE 11 (continued)

Solution	Ionic Strength .1m			
	$\gamma_{\text{Ca(NO}_3)_2(\text{EXP})}$	$\gamma_{\text{Ca(NO}_3)_2(\text{EQ 1})}$	% Difference	$\gamma_{\text{NaNO}_3(\text{EXP})}$
.0165m Ca(NO ₃) ₂	.618	.599	+3.2	.767
.05m NaNO ₃				-0.5
.0225m Ca(NO ₃) ₂	.594	.601	-1.2	.769
.035m NaNO ₃				-2.7
.025m Ca(NO ₃) ₂	.605	.600	-0.8	.770
.025m NaNO ₃				+1.4
.03m Ca(NO ₃) ₂	.607	.601	+1.0	.772
.01m NaNO ₃				+2.1
.033m Ca(NO ₃) ₂	----	.604	----	----

	Ionic Strength .5m			
	$\gamma_{\text{Ca(NO}_3)_2(\text{EXP})}$	$\gamma_{\text{Ca(NO}_3)_2(\text{EQ 1})}$	% Difference	$\gamma_{\text{NaNO}_3(\text{EXP})}$
.5m NaNO ₃	----	----	----	.618
.0167m Ca(NO ₃) ₂	.496	.429	+15.6	.621
.45m NaNO ₃				+0.8
.0415m Ca(NO ₃) ₂	.470	.431	+9.0	.626
.375m NaNO ₃				+1.3
.058m Ca(NO ₃) ₂	.460	.433	+6.2	.630
.325m NaNO ₃				+1.0
.0835m Ca(NO ₃) ₂	.447	.436	+2.5	.635
.25m NaNO ₃				+3.6

TABLE 11 (continued)

<u>Solution</u>	<u>$\gamma_{\text{Ca}(\text{NO}_3)_2(\text{EXP})}$</u>	<u>$\gamma_{\text{Ca}(\text{NO}_3)_2(\text{EQ } 1)}$</u>	<u>% Difference</u>	<u>$\gamma_{\text{NaNO}_3(\text{EXP})}$</u>	<u>$\gamma_{\text{NaNO}_3(\text{EQ } 1)}$</u>	<u>% Difference</u>
.1125m $\text{Ca}(\text{NO}_3)_2$	.443	.439	+0.9	.659	.641	+2.8
.175m NaNO_3						
.125m $\text{Ca}(\text{NO}_3)_2$	.439	.439	+0.0	.673	.644	+4.5
.125m NaNO_3						
.15m $\text{Ca}(\text{NO}_3)_2$	.447	.441	+1.4	.692	.650	+6.5
.05m NaNO_3	----	.442	----	----	----	----
.167m $\text{Ca}(\text{NO}_3)_2$						
<u>Ionic Strength 1.m</u>						
1.0m NaNO_3	---	----	----	----	.548	----
.03m $\text{Ca}(\text{NO}_3)_2$	.462	.372	+24.2	.550	.554	-0.7
.9m NaNO_3						
.083m $\text{Ca}(\text{NO}_3)_2$	.419	.367	+14.2	.557	.562	-0.9
.75m NaNO_3						
.116m $\text{Ca}(\text{NO}_3)_2$	.405	.369	+9.8	.559	.567	-1.4
.65m NaNO_3						
.167m $\text{Ca}(\text{NO}_3)_2$	.398	.373	+6.7	.567	.575	-1.4
.5m NaNO_3						
.225m $\text{Ca}(\text{NO}_3)_2$	.385	.379	+1.6	.579	.584	-0.9
.35m NaNO_3						
.25m $\text{Ca}(\text{NO}_3)_2$	.387	.380	+1.8	.587	.588	-0.2
.25m NaNO_3						
.30m $\text{Ca}(\text{NO}_3)_2$	.383	.384	-0.3	.625	.596	+4.9
.10m NaNO_3						
.33m CaNO_3	----	.385	----	----	----	----

strength. The true equation for a calcium selective ion electrode in the above mixtures would be, according to Huston and Butler:¹²

$$E-E_o = \frac{RT}{2F} \ln \left[\frac{(m_{Ca}+2) (m_{NO_3}^-)^2 (\gamma_{\pm Ca(NO_3)_2})^3 + K(m_{Na}+) (m_{NO_3}^-)^2 \gamma_{\pm NaNO_3}^2}{(m_{Ca_o}) (m_{NO_3_o}^-)^2 \gamma^3} \right] \quad (9)$$

Since $\gamma_{\pm Ca(NO_3)_2}$ and $\gamma_{\pm NaNO_3}$ experimental values are not known in this case, another method is required. Alternatively, if one has complete confidence in Equation 5, values of mean activity coefficients can be calculated and K found from Equation 9.

According to Shatkay,¹³ the calcium electrode measures a single ion activity coefficient of calcium; however, the measurement of such single ion activity coefficients is questionable. Shatkay states that the activity of Ca^{+2} is as valid as the activity of H^+ by electrode (pH). According to Shatkay's convention, the calcium electrode is only influenced by cations in solution. Equation 5 for calculating the single ion activity coefficient of Ca^{++} reduces to

$$\log \gamma_{M_i} = -A_{\gamma} z_i^2 \frac{I^{1/2}}{1 + I^{1/2}} + \sum_X B_{MX} m_X \quad (10)$$

Using Shatkay's notation, Equation 8 becomes

$$E-E_o = \frac{RT}{2F} \ln \left[\frac{(m_{Ca}^{+2})(\gamma_{Ca}^{+2})}{(m_{Ca_o})(\gamma_{Ca_o})} \right] \quad (11)$$

To validate Shatkay's approach an experiment was conducted in which the interfering salt concentration was varied while the measured salt concentration was kept constant. When the calcium specific ion electrode was being used the calcium concentration of the salt mixture was held constant and the interfering sodium ion was varied. Using this approach the effects on the specific ion electrode of other ions can be determined. The effects are quantified as an interference factor K_i . In this case the interference factor is sodium's

effect on the calcium electrode. The values of $\gamma_{Ca^{+2}}$ and $\gamma_{Na^{+}}$ were calculated from Equation 10 and used in the following equation to determine an interference factor K:

$$E-E_o = \frac{RT}{2F} \ln \frac{[(m_{Ca^{+2}})(\gamma_{Ca^{+2}}) + K_{Na}(\gamma_{Na^{+}})(m_{Na^{+}})]}{(m_{Ca_o})(\gamma_{Ca_o})} \quad (12)$$

Using the known reference solution values (pure calcium salt solutions), sample values (the mixed salt solutions), and calculated $\gamma_{Ca^{+2}}$ and $\gamma_{Na^{+}}$ a value of K_{Na} was found from the measured $E-E_o$. The value of K_{Na} was found to be independent of ionic strength and dependent on the concentration ratio $(Na^{+})/(Ca^{+2})$. Results were:

<u>Ratio</u>	<u>K_{Na}</u>
Na/Ca < 30	0
Na/Ca = 30	0.007
Na/Ca = 300	0.002
Na/Ca = 3000	0.003

The above corrections make the measured data of Table 11 reasonably compatible with Equation 5. For example, the solution 0.9 M $NaNO_3$ - 0.033 M $Ca(NO_3)_2$ has an observed, uncorrected $\gamma_{\pm Ca(NO_3)_2}$ 24.2 percent higher than predicted. Using Equation 12 combined with a form of Equation 10 for the anion activity coefficient $\gamma_{NO_3^-}$, the corrected value for $\gamma_{\pm Ca(NO_3)_2}$ is 0.377, which is only 1.3 percent high. Calcium interference on the sodium electrode was not studied in detail since results on the measured solutions without correction were satisfactory (see Table 11).

In order to check the validity of Equation 5, a second salt mixture, $NaNO_3$ - KNO_3 , was analyzed to experimentally determine the activity coefficients of potassium salts. The experimental design was similar to the calcium-sodium salt system described. Sets of solutions of varying ionic strengths with varying ratios of sodium to potassium (as shown in Table 12) were measured.

The sodium electrode functioned properly with a small potassium interference at $K/Na \geq 9$. The value of K_K does not seem to be as independent of ionic strength as is the sodium interference on the calcium electrode. Tentative values of K_K for potassium interference on the sodium electrode are:

TABLE 12. MEASURED AND ESTIMATED ACTIVITY COEFFICIENTS FOR $\text{NaNO}_3\text{-KNO}_3$

Solution	Ionic Strength .01m		% Difference	$\gamma_{\text{KNO}_3(\text{EXP})}$	$\gamma_{\text{KNO}_3(\text{EQ l})}$	% Difference
	$\gamma_{\text{NaNO}_3(\text{EXP})}$	$\gamma_{\text{NaNO}_3(\text{EQ l})}$				
.01m NaNO_3	----	.900	----	----	----	----
.001m KNO_3						
.009m NaNO_3	1.001	.901	+11.2	.940	.899	+4.6
.0025m KNO_3	.919	.900	+1.9	.887	.899	-1.3
.0075m NaNO_3						
.0035m KNO_3	.914	.901	+1.5	.886	.899	-.14
.0065m NaNO_3						
.005m KNO_3	.901	.901	+0.0	.860	.899	-4.3
.005m NaNO_3						
.0065m KNO_3	.903	.901	+0.2	.870	.900	-3.3
.0035m NaNO_3						
.0075m KNO_3	.914	.901	+1.4	.808	.900	-10.2
.0025m NaNO_3						
.009m KNO_3	.931	.901	+3.3	1.038	.900	+15.3
.001m NaNO_3	----	----	----	----	.898	----
.01m KNO_3						
Ionic Strength .05m						
.05m NaNO_3	----	.811	----	----	----	----
.005m KNO_3						
.045m NaNO_3	.828	.810	+1.5		.805	

TABLE 12 (continued)

Solution	Ionic Strength .05m			
	$\gamma_{\text{NaNO}_3(\text{EXP})}$	$\gamma_{\text{NaNO}_3(\text{EQ 1})}$	% Difference	$\gamma_{\text{KNO}_3(\text{EXP})}$
.0125m KNO ₃	.815	.810	+0.6	.805
.0375m NaNO ₃				
.0175m KNO ₃	.833	.809	+3.0	.804
.0325m NaNO ₃				
.025m KNO ₃	.852	.808	+5.4	.804
.025m NaNO ₃				
.0325m KNO ₃	.834	.807	+3.3	.804
.0175m NaNO ₃				
.0375m KNO ₃	.866	.807	+7.3	.804
.0125m NaNO ₃				
.045m KNO ₃	.959	.806	+19.0	.803
.005m NaNO ₃				
.05m KNO ₃	----	----	----	.790

Solution	Ionic Strength .1m			
	$\gamma_{\text{NaNO}_3(\text{EXP})}$	$\gamma_{\text{NaNO}_3(\text{EQ 1})}$	% Difference	$\gamma_{\text{KNO}_3(\text{EXP})}$
.1m NaNO ₃	----	.760	----	----
.01m KNO ₃				
.09m NaNO ₃	.763	.760	+0.4	.748
.025m KNO ₃	.775	.758	+2.2	.747
.075m NaNO ₃				
.035m KNO ₃	.761	.757	+0.5	.746
.065m NaNO ₃				

TABLE 12 (continued)

Solution	<u>Ionic Strength .1m</u>		<u>% Difference</u>	<u>$\gamma_{\text{KNO}_3}(\text{EXP})$</u>	<u>$\gamma_{\text{NaNO}_3}(\text{EQ 1})$</u>	<u>% Difference</u>	<u>$\gamma_{\text{KNO}_3}(\text{EQ 1})$</u>	<u>% Difference</u>
	<u>$\gamma_{\text{NaNO}_3}(\text{EXP})$</u>	<u>$\gamma_{\text{NaNO}_3}(\text{EQ 1})$</u>						
.05m KNO_3	.752	.756	-0.5				.744	
.05m NaNO_3								
.065m KNO_3	.751	.754	-0.4				.742	
.035m NaNO_3								
.075m KNO_3	.749	.752	-0.4				.741	
.025m NaNO_3								
.09m KNO_3	.778	.751	+3.6				.740	
.01m NaNO_3								
.1m KNO_3	-----	-----	-----				-----	-----
<u>Ionic Strength .5m</u>								
.5m NaNO_3	-----	.618	-----				-----	-----
.05m KNO_3	.580	.614	-5.5				.578	
.45m NaNO_3								
.125m KNO_3	.578	.608	-4.9				.572	
.375m NaNO_3								
.175m KNO_3	.583	.604	-3.5				.569	
.325m NaNO_3								
.25m KNO_3	.615	.599	+2.7				.564	
.25m NaNO_3								
.325m KNO_3	.592	.594	-0.3				.558	
.175m NaNO_3								
.375m KNO_3	.585	.590	-0.8				.555	
.125m NaNO_3								

TABLE 12 (continued)

<u>Solution</u>	<u>Ionic Strength .5m</u>			<u>Ionic Strength 1m</u>		
	<u>$\gamma_{\text{NaNO}_3}(\text{EXP})$</u>	<u>$\gamma_{\text{NaNO}_3}(\text{EQ 1})$</u>	<u>% Difference</u>	<u>$\gamma_{\text{NaNO}_3}(\text{EXP})$</u>	<u>$\gamma_{\text{NaNO}_3}(\text{EQ 1})$</u>	<u>% Difference</u>
.45m KNO ₃	.614	.585	+5.0			
.05m NaNO ₃						
.5m KNO ₃	----	----	----			
<u>Solution</u>	<u>$\gamma_{\text{NaNO}_3}(\text{EXP})$</u>	<u>$\gamma_{\text{NaNO}_3}(\text{EQ 1})$</u>	<u>% Difference</u>	<u>$\gamma_{\text{KNO}_3}(\text{EXP})$</u>	<u>$\gamma_{\text{KNO}_3}(\text{EQ 1})$</u>	<u>% Difference</u>
.90m KNO ₃	.546	.498	+9.6			
.10m NaNO ₃						
1.0m KNO ₃	----	----	----			
<u>Ionic Strength 1m</u>	<u>$\gamma_{\text{NaNO}_3}(\text{EXP})$</u>	<u>$\gamma_{\text{NaNO}_3}(\text{EQ 1})$</u>	<u>% Difference</u>	<u>$\gamma_{\text{KNO}_3}(\text{EXP})$</u>	<u>$\gamma_{\text{KNO}_3}(\text{EQ 1})$</u>	<u>% Difference</u>
1.0m NaNO ₃	----	.548	----			
.1m KNO ₃	.546	.543	+0.6			
.9m NaNO ₃						
.25m KNO ₃	.542	.534	+1.5			
.75m NaNO ₃						
.35m KNO ₃	.538	.528	+1.9			
.65m NaNO ₃						
.5m KNO ₃	.533	.520	+2.5			
.5m NaNO ₃						
.65m KNO ₃	.538	.512	+5.1			
.35m NaNO ₃						
.75m KNO ₃	.535	.506	+5.7			
.25m NaNO ₃						

Ratio

$$K/Na = 10 \quad K_K = 0.0093$$

$$K/Na = 50 \quad K_K = 0.0055$$

The potassium electrode appeared to malfunction above an ionic strength of 0.025. Consultation with the manufacturer suggested that mislabeled electrode parts might be the cause. New ionic exchange solution and membranes were obtained for the potassium electrode and new outer filling solution for the reference electrode. Experiments with the new components showed little improvement, however. The 1 M binary solutions measured within 3 mv of each other, suggesting that the electrode is totally nonselective at this ionic strength. The electrode functioned properly for pure solutions of KCl but not for pure solutions of KNO_3 . Experimental and measured activity coefficients are summarized in Table 12 and it can be seen that measured and estimated activity coefficients for $NaNO_3$ are good.

Experimental data for potassium activity coefficients was not sufficient to validate Equation 5. But considering the agreement of this study's data for the sodium and calcium activity coefficients and the independent data presented in Tables 7 through 10, Equation 5 appears to estimate mean ionic activity coefficients of high ionic strength mixed salt systems encountered on the Hanford Reservation.

In order to utilize Equation 5 to predict the activities of the most important chemical species reacting in the soil-waste liquid regime present at Hanford, several B_{MX} specific interaction terms need to be known. As previously stated, comprehensive tables of B_{MX} constants can be found in the literature.^{7,8} Unfortunately, the specific interaction terms for a few important chemical species (for example, $CaSO_4$) are not found in the mentioned literature. The value of B_{CaSO_4} was determined from articles by Gardner and Glueckauf^{14,15} and is presented in Table 13. The values were calculated utilizing Equation 5, Gardner and Glueckauf's measured activity coefficients and the known molal concentrations of the species in the solutions. With all the known quantities, the B_{CaSO_4} can be determined by back calculation.

To experimentally verify the calculated B_{CaSO_4} values an experiment utilizing specific ion electrodes was performed.

For the experimental verification three binary mixtures of $CaSO_4$ - $NaNO_3$ at ionic strengths of 0.01 M, 0.05 M, and 0.15 M were checked using the calcium ion electrode. Mixtures

TABLE 13. EMPIRICAL INTERACTION CONSTANT (B_{CaSO_4}) FOR CaSO_4 AS A FUNCTION OF IONIC STRENGTH

<u>I</u>	<u>B_{CaSO_4}</u>
4×10^{-5}	-43.24
1.2×10^{-4}	-42.95
2.0×10^{-4}	-43.17
4.0×10^{-4}	-53.54
1.2×10^{-3}	-46.00
2.0×10^{-3}	-41.50
4.0×10^{-3}	-32.55
* 1.0×10^{-2}	-19.2
1.2×10^{-2}	-18.75
2.0×10^{-2}	-13.30
4.0×10^{-2}	- 7.52
* 5.0×10^{-2}	- 6.0
6.0×10^{-2}	- 5.17
1.29×10^{-1}	- 4.59
* 1.5×10^{-1}	- 1.3
2.07×10^{-1}	- 3.77
3.44×10^{-1}	- 3.13
6.97×10^{-1}	- 1.85
8.44×10^{-1}	- 1.58
1.01	- 1.86
2.24	- 0.84
3.09	- 0.84
4.35	- 0.79

* Experimentally determined value

of $\text{Ca}(\text{NO}_3)_2$ - NaNO_3 of the same ionic strengths and calcium concentration were used as the reference solutions. The ΔE is a measure of the difference of the $\gamma_{\text{Ca}^{+2}}$ between the nitrate and sulfate solutions. From the difference in the activity coefficient between the two solutions the value of B_{CaSO_4} was calculated. The average of B_{CaSO_4} for each ionic strength tested is also given in Table 13. At the two lower ionic strengths, the values of B_{CaSO_4} are in good agreement with the values calculated from the literature. The 0.15 M data are again affected by sodium interference on the calcium electrode.

In summary, the use of specific ion electrodes to measure activity coefficients has been somewhat complicated by interference effects. To obtain accurate activity coefficients, many solutions must be measured to determine interference constants, K_i . Greater precaution is warranted than is usually stated in the operation manuals. The tested empirical equation (Equation 5) does predict the activity coefficients of salts in mixtures to ionic strengths of 6 M or higher.

Values of the mean activity coefficients of the solute constituents can be determined from Equation 5, the tables of B_{MX} , and the concentrations of solute constituents generated in the PERCOL model. The PERCOL computer program can be set up to automatically calculate the desired activity coefficients. At present the PERCOL model includes the B_{MX} values for all sodium, potassium, magnesium and calcium salts of the anions NO_3 , SO_4 , Cl , and HCO_3 . Experimental verification has been carried out either by the work described above or by other methods for most of the salts. Additional salts can be added to the model if they are required.

ESTIMATION OF K_d IN THE HANFORD GROUNDWATER SYSTEM AS A FUNCTION OF SOIL PERMEABILITY

Due to the mixing of the relatively small volume of solution from the vadose zone with the much larger groundwater reservoir volume and to hydrodynamic dispersion and diffusion, trace radionuclides entering the groundwater are shortly in a chemical environment approaching that of the groundwater.¹⁶ As these wastes move toward the Columbia River this chemical environment tends to change relatively little since there is limited recharge in this low rainfall region. In such a system the use of a constant K_d to estimate the transport of a given trace radionuclide may be an economical and viable possibility.¹⁶ If the K_d for a given radionuclide in the groundwater can be related to a soil property which has already been determined for the Hanford Reservation, then the K_d can be estimated as

a function of position and used in a transport analysis. In the following study the possibility of correlating KdSr in a chemical system approximating the Hanford Reservation groundwater to permeability of a group of Hanford soils was assessed by Reeve's method.¹⁷

Laboratory permeabilities of KdSr were determined for five wells on the Hanford Reservation which showed a wide range of measured permeabilities as a function of depth in the saturated zone. Table 14 gives the measured transmissivities, estimated hydraulic thicknesses, and calculated depth-averaged permeabilities for these five wells. Table 15 gives the laboratory measured permeabilities and KdSr values as functions of well depth for one well; tables for four additional wells are in Appendix A.

TABLE 14. ESTIMATED TRANSMISSIVITY, HYDRAULIC THICKNESS AND PERMEABILITY OF SELECTED HANFORD WELLS

Well	Hydraulic Thickness - ft	Transmissivity ft ² /day	Permeability ft/day
38-65Q	87	4 x 10 ¹	0.46
32-70	215	1 x 10 ³	4.6
1-18	182	1 x 10 ⁴	55
31-31P	253	2.5 x 10 ⁵	990
37-43P	55	7.5 x 10 ⁴	1300

To facilitate the correlation the field permeability was assumed to be some multiple of each well's average laboratory permeability. Failure of the laboratory permeability to agree with the field permeability was probably due to structural and layering effects which were modified by sampling and repacking a soil in the laboratory. Each measured laboratory permeability was multiplied by the factor to obtain a corrected sample permeability. Linear regression analysis was used to determine the degree of correlation of KdSr with the corrected permeability. KdSr was found to be related to the corrected permeability by the equation:

$$\text{KdSr} = 3.8 \log K + 11.7 \quad (13)$$

TABLE 15. KdSr AND PERMEABILITY FOR THE SATURATED ZONE OF WELL 38-65Q

<u>Depth</u> <u>ft</u>	<u>KdSr</u> <u>ml/g</u>	<u>Permeability</u> <u>cm/min</u>
320	12.3	0.082
330	11.2	0.062
335	12.4	0.069
345	22.9	0.0030
350	23.4	0.0037
355	20.4	0.0046
365	19.6	0.0049
370	20.6	0.0027
375	24.5	0.0054
380	23.5	0.0052
385	24.7	0.0046
390	<u>38.1</u>	<u>0.014</u>
Average	19.6	0.016

where

KdSr = distribution coefficient in ml/g

K = corrected permeability in ft/day

The correlation coefficient (r) for Equation 13 was found to be 0.799, which suggests 64 percent of the variation in KdSr can be accounted for by the variability in the logarithm of the corrected permeability. The standard error of the estimate for Equation 13 was found to be ± 3.4 ml/g. Thus, KdSr can be estimated from field transmissivity data.

UNSORBED SOLUTE MOVEMENT THROUGH SOIL COLUMNS

Hydrodynamic dispersion and diffusion are the only dispersive mechanisms acting upon unsorbed solutes being transported through soil systems. Such systems can be used to estimate the effect of dispersion upon solute transport.^{18,19} In addition, the movement of unsorbed solutes through a soil can be used to estimate the effective porosity of this soil.³

If some pores in a soil are not interconnected ("dead ended") early breakthrough of solute will result. This loss of transmission porosity must be corrected for in a transport model. The effect of hydrodynamic dispersion has been shown to be flow rate dependent.¹⁹ Thus to assess the effect of dispersion and effective porosity the movement of unsorbed solute (H^3 and Cl^-) was measured through a group of five soil columns as a function of flow rate. Experimental details of the experiment are given in BNWL-1721.³ Column parameters for the five soil columns are given in Table 16 and Appendix Tables B-1, B-2, B-3, and B-4. Figures 3, 4, 5, 6, and 7 show the normalized movement of unsorbed solutes as functions of the volumes of effluent solution. From these figures it can be seen that the normalized tracer breakthrough at a C/Co of 0.5 occurs slightly earlier than would be predicted for unsorbed solutes, i.e., slightly before one pore volume has passed through the columns. This suggests that a small fraction of the soil pores do not transmit solution and that the porosity used in the sorption model should be an effective rather than a bulk porosity. Nielsen and Biggare²⁰ have shown that early breakthrough of unsorbed solute is either due to loss of transmitting porosity or to negative sorption of solute.

The movement of slightly or completely unsorbed solutes through soil systems must be measured to estimate the effects of hydrodynamic dispersion and diffusion on solute movement. In addition, if some of the pores are "dead-ended" and do not transmit solution early breakthrough will occur and a correction in the transport model must be made for this loss of transmission porosity. Thus, a group of five column experiments was conducted to obtain data for these determinations. Table 16 gives the operational parameters of one of the five column experiments; tables for the remaining experiments are in Appendix B.

Furthermore, good agreement between uncharged 3H (Figure 3) and negatively charged Cl^- (Figure 2) breakthrough data was found which suggests that non-transmitting pores, not anion expulsion, is the primary cause of the early breakthrough of these unsorbed solutes. The average porosity reduction as determined by the above data would be 7.7 percent $\pm$ 2 percent.

It can be seen from Figures 3, 4, 5, 6, and 7 that the shapes of the normalized Cl^- curves differ according to solution velocity; the greater the solution velocity the less the effect of dispersion. These curves have been used to determine dispersion coefficients and to determine how these coefficients vary as a function of solution velocity. This work is reported in another document.¹⁸

TABLE 16. COLUMN PARAMETERS FOR A TANK FARM SANDY
LOAM SOIL COLUMN

<u>Parameter</u>	<u>Magnitude</u>
Length	27.3 cm
Soil Weight	466 gms
Soil Volume	294 cm ³
Flow Rate	0.19 cm/hr
Bulk Density	1.59 gm/cm ³
Temperature	23 ± 3° C
CaCO ₃	2.6 x 10 ⁻⁴ moles/gm
pH	7.0
Influent	0.078 M CaCl ₂

FIGURE 3. Normalized Effluent Concentration (C/C_o) of Cl from a 25 cm Tank Farm Sandy Loam Soil Column as a Function of Effluent Solution Volume.

Column was Preequilibrated with a NO₃ Solution of the Same Cation Composition as the Tracer Solution. Square (□) Represents the Calculated 0.5 C/C_o Volume Point. Flow Rate was 0.19 cm/hr.

FIGURE 4. Normalized Effluent Concentration (C/C_o) of Cl from a 25 cm Tank Farm Sandy Loam Soil Column as a Function of Effluent Solution Volume (flow rate was 0.50 cm/hr)*

FIGURE 5. Normalized Effluent Concentration (C/C_o) of ^3H from a 25 cm Tank Farm Sandy Loam Soil Column as a Function of Effluent Solution Volume (flow rate was 0.46 cm/hr)*

* Column was Preequilibrated with a NO_3^- Solution of Same Cation Composition as the Tracer Solution. Square (□) Represents the Calculated 0.5 C/C_o - Volume Point.

FIGURE 6. Normalized Effluent Concentration (C/C_o) of 3 Cl from a 25 cm Tank Farm Sandy Loam Soil Column as a Function of Effluent Solution Volume (flow rate was 2.0 cm/hr)*

FIGURE 7. Normalized Effluent Concentration (C/C_o) of Cl from a 25 cm Tank Farm Sandy Loam Soil Column as a Function of Effluent Solution Volume (flow rate was 5.1 cm/hr)*

*Column was Preequilibrated with a NO_3^- Solution of the Same Cation Composition as the Tracer Solution. Square (□) Represents the Calculated 0.5 C/C_o - Volume Point.

Briefly the technique involves using an analytical solution to the one dimensional diffusion-convection equation. Measured values for the fluid velocity, column length and effluent breakthrough versus time and a trial and error procedure are then utilized to solve for D, the dispersion coefficient. Using the experimental data at several fluid velocities, the dispersion coefficient values for the different velocities were determined. The final form of the dispersion coefficient velocity relationship was found to be

$$D = aV + b \quad (14)$$

where

D = dispersion coefficient (cm^2/min)

V = fluid velocity, (cm/min)

a,b = constants which are functions of the soil type used

From the above experiments sufficient data was obtained to determine the value of the effective porosity and the velocity dependence of the dispersion coefficient. These results are used to correct the transport model to more closely represent the movement of solutes through a soil column.

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APPENDIX A

KdSr AND PERMEABILITY FOR SATURATED
ZONES OF SELECTED WELLS

TABLE A-1. KdSr AND PERMEABILITY FOR THE SATURATED ZONE
OF WELL 32-70

<u>Depth ft</u>	<u>KdSr ml/g</u>	<u>Permeability cm/min</u>
250	6.0	0.014
260	13.4	0.051
265	14.0	0.063
270	14.6	0.0058
275	12.9	0.075
280	18.6	0.075
285	19.1	0.056
290	18.9	0.039
295	19.3	0.0038
300	18.4	0.0041
305	17.1	0.0078
310	17.5	0.0067
315	16.1	0.016
320	18.5	0.0059
325	16.2	0.027
330	18.4	0.028
340	14.2	0.011
345	19.2	0.0051
350	<u>18.5</u>	<u>0.025</u>
Average	16.3	0.026

TABLE A-2. KdSr AND PERMEABILITY FOR THE SATURATED ZONE
OF WELL 1-18

<u>Depth</u> <u>ft</u>	<u>KdSr</u> <u>ml/g</u>	<u>Permeability</u> <u>cm/min</u>
140	9.6	0.14
145	8.9	0.0044
150	14.2	0.0054
155	11.9	0.0038
160	12.8	0.0040
165	9.9	0.0039
170	9.5	0.0035
175	9.3	0.0056
180	9.5	0.0051
185	12.2	0.015
190	12.0	0.011
195	7.6	0.040
200	7.8	0.034
205	15.0	0.0041
210	18.7	0.0030
215	<u>19.2</u>	<u>0.0027</u>
Average	11.7	0.015

TABLE A-3. KdSr AND PERMEABILITY FOR THE SATURATED ZONE
OF WELL 31-31P

<u>Depth</u> <u>ft</u>	<u>KdSr</u> <u>ml/g</u>	<u>Permeability</u> <u>cm/min</u>
135	12.9	0.0474
140	11.8	0.031
145	13.1	0.010
150	9.7	0.0057
155	8.1	0.0036
165	11.3	0.0031
170	11.3	0.0042
175	6.2	0.21
180	8.5	0.096
185	14.0	0.015
190	7.0	0.27
195	5.6	0.44
200	8.4	0.10
205	10.4	0.0073
210	<u>7.3</u>	<u>0.20</u>
Average	9.4	0.10

TABLE A-4. KdSr AND PERMEABILITY FOR THE SATURATED ZONE
OF WELL 37-43P

<u>Depth</u> <u>ft</u>	<u>KdSr</u> <u>ml/g</u>	<u>Permeability</u> <u>cm/min</u>
285	11.4	0.0075
305	7.7	1.7
315	9.2	0.058
320	9.0	0.042
325	9.0	0.061
335	<u>6.7</u>	<u>1.2</u>
Average	8.8	0.51

APPENDIX B

COLUMN PARAMETERS FOR A TANK FARM
SANDY LOAM SOIL COLUMN

TABLE B-1. COLUMN PARAMETERS FOR A TANK FARM SANDY LOAM SOIL COLUMN

<u>Parameter</u>	<u>Magnitude</u>
Length	24.5 cm
Soil Weight	417.2 g
Soil Volume	263 cm ³
Flow Rate	0.50 cm/hr
Bulk Density	1.58 g/cm ³
Temperature	23° ± 3° C
Influent (Ca ⁺⁺)	0.002 M
Influent (Na ⁺)	0.15 M
Influent (K ⁺)	0.01 M
Influent (Cl ⁻)	164 meq/l

TABLE B-2. COLUMN PARAMETERS FOR A TANK FARM SANDY LOAM SOIL COLUMN

<u>Parameter</u>	<u>Magnitude</u>
Length	24.9 cm
Soil Weight	428 g
Soil Volume	268 cm ³
Flow Rate	0.46 cm/hr
Bulk Density	1.60 g/cm ³
Temperature	23° ± 3° C
Influent (Ca ⁺⁺)	.002 M
Influent (Na ⁺)	0.15 M
Influent (K ⁺)	0.01 M
Influent ³ H	3.91 pci/ml

TABLE B-3. COLUMN PARAMETERS FOR A TANK FARM SANDY
LOAM SOIL COLUMN

<u>Parameter</u>	<u>Magnitude</u>
Length	27.3 cm
Soil Weight	466 gms
Soil Volume	294 cm ³
Flow Rate	2.0 cm/hr
Bulk Density	1.59 gms/cm ³
Temperature	23 $\pm$ 3° C
CaCO ₃	2.6 x 10 ⁻⁴ moles/gm
pH	7.0
Influent	0.078 <u>M</u> CaCl ₂

TABLE B-4. COLUMN PARAMETERS FOR A TANK FARM SANDY
LOAM SOIL COLUMN

<u>Parameter</u>	<u>Magnitude</u>
Length	26.6 cm
Soil Weight	454 gms
Soil Volume	286 cm ³
Flow Rate	5.1 cm/hr
Bulk Density	1.59 gms/cm ³
Temperature	23 $\pm$ 3° C
CaCO ₃	2.6 x 10 ⁻⁴ moles/gm
pH	7.0
Influent	0.074 <u>M</u> CaCl ₂

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