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REPORT ON STRONTIUM MOBILIZATION USING POTENTIAL CHEMICAL LIXIVIANTS AT THE HANFORD 100-N SITE

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1. INTRODUCTION

Nonradioactive samples of the Ringold "E" formation from a location near the Hanford 100-N area were treated with a variety of chemicals to determine the conditions under which the exchangeable strontium (Sr) in the sediments could be mobilized. First, quick batch (bottle roll) tests were conducted on sand fraction (minus ¾ inch) material to survey numerous, potentially effective chemistries. Then, three of the most promising chemistries were selected for long-term column testing using a more representative size fraction (minus 2 inch) of the Ringold "E" material. The most favorable chemistries reduced the apparent Kd of Sr in the samples from approximately 16 liters per kilogram (L/kg) to less than 1 L/kg.

Solutions of 0.5 molar weight (M) potassium chloride (KCl) plus 0.05M potassium bicarbonate ($KHCO_3$) were tested in one column, 0.2M potassium citrate in another column, and an organic clay stabilizer in a third column. Before introducing the chemical lixiviants into the columns, artificial ground water (AGW) was flushed through the columns to determine the steady-state concentration of Sr in the column effluents. This concentration was established to be between 0.1 and 0.2 mg Sr/L. The lixiviant solutions were introduced and flushed for several (approximately seven) pore volumes, removing large amounts of Sr from each column. The chemical flushes were followed by an artificial ground water wash of the columns, and the new steady state concentration of Sr in the effluent was measured. In both columns using potassium, the new steady-state Sr level in the effluent had dropped to less than 0.01 milligram (mg) Sr/L. In the column treated with clay stabilizer, less Sr was removed and the final effluent contained higher concentrations of Sr.

These tests demonstrate that it is feasible to remove most of the exchangeable Sr from the adsorption sites on the sediments in very few pore volumes. These test also demonstrate that the residual concentration of Sr in the waters waters contacting the sediments is greatly reduced after treatment.

2. SAMPLE DESCRIPTIONS

To avoid working with radioactive (hot) samples and thus enable the conducting of these tests in a noncontrolled laboratory, it was originally proposed to test the chemical flushing agents on nonradioactive samples of Ringold "E" collected from the 100-N area. However, it was not possible to acquire samples from the 100-N area in the period allotted for the project. With the assistance of Hanford geologists, MSE was able to collect representative Ringold "E" samples from an outcrop on the east bank of the Columbia River in the vicinity of the 100-N site. The samples collected appeared to be representative of the outcrop—a coarse, poorly cemented gravel with smaller amounts of fine materials. It was also noted that many of the larger cobbles had a coating of fine-grained material. These sediments were exposed to the atmosphere and were unsaturated so some weathering is likely. It was expected, however, that the cation exchange characteristics of the material would be similar to those of the aquifer material at the contaminated 100-N area. Thus, the cation exchange capacity (CEC), exchangeable cation concentrations, Kd values for particular chemistries, and in particular, the available Sr of the sediments collected, are thought to be similar to those of the aquifer materials. Furthermore, it was postulated that the chemical behavior of the nonradioactive exchangeable Sr in these sediments was analogous to that of the radioactive exchangeable Sr in the contaminated aquifer.

2.1 SEDIMENT SAMPLES FOR BOTTLE ROLL TESTS

In October 1998, approximately 95 kg of raw sediment was collected and a sieve analysis was conducted to determine particle size distribution. The sieve tests demonstrated the distribution of size fractions to be as follows:

SIEVE SIZE	% FINER
4 in	100
3 in	93
2 in	87
1.5 in	68
1 in	46
0.75 in	33
0.50 in	23
0.375 in	21

Two batches of material were sieved through a ¾-inch screen to provide material for the bottle roll tests. The plus ¾-inch material from the screening was discarded. The first batch yielded about 9 kg of minus ¾ inch material. These fines were split by repeated quartering and splitting to obtain 42 samples of nominally 200 grams (g) size. The average weight of the samples was 222 g with a standard deviation of 27 g and a range of 179 to 290 g. Forty of the samples were used in bottle roll tests to determine Kd for various chemical conditions, one sample was reserved for an acid consumption test (although the test was not completed), and the second sample was submitted to the MSE-HKM laboratory for determination of CEC. The individual sample weights are shown in Table 2-1 along with other data relevant to the bottle roll tests.

The second batch yielded approximately 4.5 kg of minus ¾ inch material, i.e., 21 splits of nominal weight 200 g each, ranging from 142 g to 277 g. Twenty samples were used in bottle roll tests of various chemistries, and one sample was sent to the MSE-HKM laboratory for assay of CEC.

Table 2-1. Bottle roll test preparations.

		INITIAL VALUES													
SAMPLE #	SED WT (g)	AGW	pH	Al(Cl)3 6H2O	CIT ACID	BaCl2.2H2O	EDTA	NH4Cl	KCIT	KCl	KHCO3	NH4HCO3	CLASTA	CLAFIX	ADDED Sr mg/L
BR01GW00	290	200 mL	6.97												0
BR02GW00	229	200 mL	6.97												0
BR03GW10	273	200 mL	6.97												10
BR04GW10	249	200 mL	6.97												10
BR05CA00	179	200 mL	2.41		3.84 g										0
BR06CA00	223	200 mL	2.41		3.84 g										0
BR07CA10	247	200 mL	2.41		3.84 g										10
BR08CA10	239	200 mL	2.41		3.84 g										10
BR09BA00	220	200 mL	3.24			0.534 g									0
BR10BA00	251	200 mL	3.24			0.534 g									0
BR11BA10	248	200 mL	3.24			0.534 g									10
BR12BA10	274	200 mL	3.24			0.534 g									10
BR13ED00	265	200 mL	5.01			0.712 g	5.84 g								0
BR14ED00	233	200 mL	5.01			0.712 g	5.84 g								0
BR15ED10	215	200 mL	5.01			0.712 g	5.84 g								10
BR16ED10	210	200 mL	5.01			0.712 g	5.84 g								10
BR17AL00	230	200 mL	1.36	9.6 g	3.84 g										0
BR18AL00	208	200 mL	1.36	9.6 g	3.84 g										0
BR19AL10	199	200 mL	1.36	9.6 g	3.84 g										10
BR20AL10	210	200 mL	1.36	9.6 g	3.84 g										10
BR21NH00	209	200 mL	6.58					1.06 g							0
BR22NH00	220	200 mL	6.58					1.06 g							0
BR23NH10	195	200 mL	6.58					1.06 g							10
BR24NH10	188	200 mL	6.58					1.06 g							10
BR29CF00	187	200 mL	7.58											0.2 g	0
BR30CF00	188	200 mL	7.58											0.2 g	0
BR31CF10	234	200 mL	7.58											0.2 g	10
BR32CF10	216	200 mL	7.58											0.2 g	10
BR33CS00	199	200 mL	7.59										0.2 g		0
BR34CS00	179	200 mL	7.59										0.2 g		0
BR35CS10	190	200 mL	7.59										0.2 g		10
BR36CS10	223	200 mL	7.59										0.2 g		10
BR25CF00	211	200 mL												2.0 g	0
BR26CF10	226	200 mL												2.0 g	10
BR27CS00	223	200 mL											2.0 g		0
BR28CS10	249	200 mL											2.0 g		10
BR37CA00	201	200 mL	3.06		3.84 g										0
BR38CA10	214	200 mL	3.06		3.84 g										10
BR39AL00	201	200 mL	3.08	9.6	3.84 g										0
BR40AL10	195	200 mL	3.08	9.6	3.84 g										10
BR50CF00	199	200 mL												4.0 g	0
BR51CF101	219	200 mL												4.0 g	10
BR52CF102	204	200 mL												4.0 g	10

Table 2-1. Bottle roll test preparations.

		INITIAL VALUES													
SAMPLE #	SED WT (g)	AGW	pH	Al(Cl)3 6H2O	CIT ACID	BaCl2.2H2O	EDTA	NH4Cl	KCIT	KCl	KHCO3	NH4HCO3	CLASTA	CLAFIX	ADDED Sr mg/L
BR53CS00	221	200 mL											4.0 g		0
BR54CS101	196	200 mL											4.0 g		10
BR55CS102	198	200 mL											4.0 g		10
BR56AG00	198	200 mL	5.5												0
BR57AG10	189	200 mL	5.5												10
BR58KC00	166	200 mL	6.48						13 g						0
BR59KC10	191	200 mL	6.48						13 g						10
BR60AB00	200	200 mL	6.71					0.74 g				0.48 g			0
BR61AB10	175	200 mL	6.71					0.74 g				0.48 g			10
BR62AB00	208	200 mL	6.48									1.58 g			0
BR63AB10	190	200 mL	6.48									1.58 g			10
BR64AL004	202	200 mL	4	9.6 g	3.84 g										0
BR67AL104	183	200 mL	4	9.6 g	3.84 g										10
BR69AL007	204	200 mL	7.02	9.6 g	3.84 g										0
BR70AL107	201	200 mL	7.02	9.6 g	3.84 g										10
BR66PC00	218	200 mL	6.92							7.5 g	1.0 g				0
BR68PC10	186	200 mL	6.92							7.5 g	1.0 g				10
BR81KC001	203	200 mL							26 g						0
BR82KC101	241	200 mL							26 g						10
BR83KC002	273	200 mL							13 g						0
BR84KC102	258	200 mL							13 g						10
BR85KC003	191	200 mL							9.1 g						0
BR86KC103	220	200 mL							9.1 g						10
BR87KC004	172	200 mL							5.2 g						0
BR88KC104	174	200 mL							5.2 g						10
BR89KC005	201	200 mL							2.6 g						0
BR90KC105	251	200 mL							2.6 g						10
BR91AG00	197	200 mL													0
BR92AG10	248	200 mL													10
BR93KB001	168	200 mL								3.0 g	0.2 g				0
BR94KB101	195	200 mL								3.0 g	0.2 g				10
BR95KB002	207	200 mL								3.0 g	1.0 g				0
BR96KB102	204	200 mL								3.0 g	1.0 g				10
BR97KB003	257	200 mL								1.5 g	0.2 g				0
BR98KB103	167	200 mL								1.5 g	0.2 g				10
BR99KB004	246	200 mL								1.5 g	1.0 g				0
BR100KB104	243	200 mL								1.5 g	1.0 g				10
BR101KB005	187	200 mL									2.6 g				0
BR102KB105	189	200 mL									2.6 g				10
BR103KB006	246	200 mL								7.5 g	1.0 g				0
BR104KB106	200	200 mL								7.5 g	1.0 g				10

2.2 SEDIMENT SAMPLES FOR COLUMN TESTS

Approximately 55 kg of Ringold "E" sediment remained after the preparation of the bottle roll test samples. In addition, four 5-gallon steel pails of sediment were shipped directly from Hanford via overnight mail. The remaining original sample was sieved through a 2-inch screen and the Hanford samples were sieved by hand picking and discarding all cobbles greater than 2 inches in diameter. The sized gravel from the two sources was combined in a drum and rolled to mix. Aggregate weight of the minus 2-inch material was approximately 152 kg. The entire sample was dumped onto a plastic sheet and roughly quartered. The first two quarters taken were approximately 35 kg each and fit into Column 2 (citrate) and Column 3 (clay stabilizer). The third quarter was about 35 kg and was combined with a quarter of the fourth quarter plus some further splits, for a total of approximately 50 kg, to pack the three sections of Column 1 (chloride plus bicarbonate). The remaining minus 2-inch material, about 30 kg, was stored in a 5-gallon steel drum for future use.

2.3 WATER SAMPLES

It was preferable to use ground water from the aquifer outside, and in close proximity to the contaminated area at 100-N to prepare the solutions, but that water was not available. Therefore, artificial ground water (AGW) was prepared using deionized water with dissolved chemicals to yield concentrations of major ionic solutes similar to concentrations of those same chemicals in the actual ground water. Since the major anionic constituent of the solutes is bicarbonate, the AGW was prepared using calcium and magnesium carbonates; the carbonates were dissolved by bubbling carbon dioxide into the mixture. The exact method was as follows:

Eighteen-liters of deionized water plus 1.04 g $CaCO_3$, 0.27 g $3.2MgCO_3$ $Mg(OH)$ $3.2H_2O$ (basic magnesium carbonate), 0.18 g Na_2SO_4, 0.065 g K_2SO_4, 0.81 milliliter (mL) 1M HNO_3, and 0.50 mL 1M HCl. Bubble in carbon dioxide (CO_2) from dry ice until the solution is clear.

Table 2-2 shows the assays of the various batches of the AGW as well as the final concentrations. In the bottle roll tests, Sr salts were added to the AGW to yield a Sr concentration similar to that of the aquifer; however, in the column tests, Sr was deliberately omitted to determine how low the concentration would go with no Sr influent. Strontium impurity in the reagent grade calcium carbonate yielded a final Sr concentration in the column test AGW of 0.015 mg Sr/L.

Table 2-2. Artificial ground water preparation (mg/L).

SAMPLE	Ca	Mg	Na	K	Sr	Cl	NO3	HCO3	SO4
Groundwater	23	4	3.3	1.6	0.13	1	2.8	86	8.6
Bottle Roll 1	14.4	3.86	3.35	1.76					
Bottle Roll 2	22.2	3.57	3.88	4.48	0.14				
Column Inf 1	22	3.62	3.16	1.53	0.015				
Column Inf 2	20.9	3.13	3.09	3.3	0.015				
Column Inf 3	23	3.62			0.015				
Column Inf 4	19.2	2.78			0.015				
Lix Base 1	22.3	3.67	26	85	0.38				
Lix Base 2	22.4	3.45			0.03				

In preparing the AGW (lixiviant base) for the column test chemical flushing solution, a different set of chemicals was used to make the preparation faster and easier. This was acceptable because the chemicals added to mobilize the Sr (the lixiviant chemicals) would dominate in the lixiviant solutions. Unfortunately, the calcium chloride reagent used for this preparation was of inferior grade and contained Sr contamination that resulted in a relatively high Sr concentration (0.38-mg Sr/L) in the influent for that first lixiviant batch. When the second batch of lixiviant was prepared, a purer grade of calcium salt was used, and the Sr concentration decreased to 0.030 mg/L.

The methods used follows:

Batch 1
Eighteen liters of deionized water plus 1.15 g $CaCl_2$, 0.60 g $MgCl_2 6H_2O$, 0.18 g Na_2SO_4, 0.065 g K_2SO_4, 0.81 mL 1M HNO_3, and 4.0 g $KHCO_3$. Stir to dissolve.

Batch 2
Eighteen liters of deionized water plus 1.04 g $CaCO_3$, 0.27 g basic magnesium carbonate, 0.18 g Na_2SO_4, 0.065 g K_2SO_4, 0.81 mL 1M HNO_3, and HCl to clarify.

One batch of lixiviant base influent for Column 1 was improperly prepared. The weight of chemicals calculated for preparing 52 L of AGW was inadvertently used to prepare 16 L of AGW. This error resulted in a temporary high concentration of each of the constituents (including Sr) in the effluent.

3. BOTTLE ROLL TESTS

The bottle roll test format was used to perform the preliminary survey of chemical systems to determine which systems were most effective at mobilizing the Sr from the cation exchange sites. The main criterion used was the value of Kd, the distribution coefficient of Sr between the solution and the sediment. Kd is defined as:

$$Kd = C_s/C_a$$

where C_s is the concentration of Sr on the soil and C_a is the Sr concentration in the aqueous phase (Ref. 1). Serne and LeGore also use this definition of Kd in discussing adsorption-desorption characteristics of the Hanford soil (Ref. 2). The lower the value of Kd, the more effective the chemical at mobilizing Sr from the soil into the aqueous phase. A secondary criterion was the ratio of calcium to Sr in the solution; a low value of this ratio was deemed better because it indicated that a smaller amount of unwanted cations was being mobilized.

In addition to the value of Kd, the value of the amount of exchangeable Sr on the sediment (C_{so}) was calculable from the bottle roll tests. In some tests, it was evident that unexchangable cations were released by the chemicals; this was not viewed as a favorable situation since MSE wanted to confine the chemical action to exchange processes only.

For these tests, Kd might be considered an empirical indicator of the relative efficiency of different lixiviant chemicals to mobilize Sr from the soil into the aqueous phase. While these empirical values may be of limited application as constants in mathematical modeling, they readily serve the purpose intended here of selecting the most effective chemicals on which to conduct more extensive column tests. The more efficient lixiviants will show lower values of Kd.

3.1 TEST PROCEDURE

A sample split of minus ¾-inch sediment weighing nominally 200 g was weighed to the nearest gram into a 500 mL polyethylene leak proof, wide-mouthed bottle. Two-hundred milliliters of selected chemical solution measured with a graduated cylinder were added to the bottle. The bottles were placed on a roller at room temperature to keep the sediment well agitated with the solution and let roll overnight. After 12 to 16 hours, the bottles were removed and the slurry left to stand so that the sediment could settle. Approximately 30 mL of the supernatant solution was extracted from the bottle with a pipet and filtered with vacuum filtration through a 0.45 micron cellulose acetate filter disc. The filtered solutions were sent off to the MSE-HKM laboratory for assay of Sr, Ca, Mg, and other relevant metals by inductively coupled plasma (ICP).

For each chemistry, two samples were run simultaneously—one with a small amount of Sr in the added solution (the 0.13 mg/L of the AGW used as the base solution) and one with another 10 mg/L added Sr (total about 10.1 mg Sr/L).

3.2 Kd CALCULATIONS

Two sources of Sr are in each slurry sample if we confine ourselves to exchangeable cations. The first source is the Sr added in solution and the second is that originally present on the adsorption sites of the sediment sample used in the test. The amount added in solution (C_{ao}) is known, but the amount on the sediment (C_{so}) is not known. If it is assumed that the amount originally on the sediment (C_{so}) is the same from sample to sample, we can calculate that amount along with the value of Kd from the tests.

As mentioned previously, the value of Kd is defined as the ratio of the equilibrium Sr concentration on the solid (C_s) to the equilibrium Sr concentration in the aqueous phase (C_a):

$$Kd = C_s/C_a$$

Only C_a, the Sr concentration in the aqueous phase, was measured so C_s must be expressed in terms of C_a and C_{so}. Given W as the weight of sediment sample in kg, V as the volume of solution in liters, M_t as the total mass of Sr in the slurry, M_s as the equilibrium mass of Sr on the solid, and M_a as the equilibrium mass of Sr in solution, the expression for Kd can be rewritten in a more functional form:

$$C_s = M_s/W = (M_t - M_a)/W = (WC_{so} + VC_{ao} - VC_a)/W, \text{ therefore}$$

$$Kd = (WC_{so} + VC_{ao} - VC_a)/WC_a = C_{so}/C_a + (V/W)C_{ao}/C_a - (V/W).$$

Any two samples of the same chemistry and same composition of solid but differing values of C_{ao} and C_a will provide two equations in two unknowns—Kd and C_{so}. These equations may be solved simultaneously to determine values of Kd and C_{so} as follows:

1) $$Kd = C_{so}/C_{a1} + (V/W_1)C_{ao1}/C_{a1} - V/W_1$$

2) $$Kd = C_{so}/C_{a2} + (V/W_2)C_{ao2}/C_{a2} - V/W_2$$

Equating these two expressions and solving for C_{so} yields:

3) $$C_{so} = \{[(C_{ao2}/C_{a2})-1]V/W_2 - [(C_{ao1}/C_{a1})-1]V/W_1\}/(1/C_{a1} - 1/C_{a2}), \text{ and}$$

Kd is calculated by substituting the value of C_{so} from 3) back into 1) or 2).

3.3 SELECTION OF CHEMICALS TO TEST

In selecting chemicals to screen, the chemicals sought were those that would have a cation for effective displacement of Sr from cation exchange sites and/or a complexant for rendering the Sr stable in solution.

For effective cations, bi- and trivalent ions such as barium and aluminum were considered because they are generally more effective than monovalent ions in competing for exchange sites. Using a weak acid with a relatively low pK was also considered to determine whether the Sr could be displaced from a weak-acid type exchanger without simultaneously attacking mineral phases subject to attack by stronger acids. Ammonium and potassium were also tested since they are monovalent cations that tend to be effective competitors for cation exchange sites. For the barium test without ethylenediaminetetraacetic

acid (EDTA), the barium sulfate was left to precipitate in the test bottle, and thus, a small amount of added barium was lost.

EDTA and citrate were evaluated as complexers. The EDTA was paired with barium to prevent barium sulfate from precipitating. The citrate was thought to be a good choice for use with aluminum because its acidic properties allowed easy pH adjustment to maintain the aluminum in solution. Citric acid was also the choice for a weak acid to acidify the solution and attempt to displace Sr by the weak-acid-type exchange reaction because the pK values for acid dissociation of citric acid permitted low pH values with buffered solutions and citric acid is relatively benign environmentally.

It was also desirable to suppress the release or mobilization of calcium; therefore, a test was run with potassium bicarbonate in an attempt to precipitate calcium carbonate released from the exchanger without simultaneously precipitating Sr carbonate.

Two clay stabilizers were tested. Rather than mobilizing Sr, these were thought to be effective at blocking the exchange sites to prevent exchange from taking place. Thus, it was believed that these might permanently immobilize the Sr on the solid substrate. The clay stabilizers used were ClayFix II, an alkylated quaternary chloride and ClaSta XP, a quaternary polyamine. These clay stabilizers were used as 2% aqueous solutions. In these tests, the sediment sample was first treated with the clay stabilizer overnight and 10 mg/L Sr was then added.

As a baseline, Kd for AGW was determined at two Sr levels with no other added chemicals.

3.4 RESULTS OF BOTTLE ROLL TESTS

The assays of the filtrates from the bottle roll tests are cataloged in Appendix A. Table 3-1 shows the Sr and Ca values, the lixiviant chemical concentrations, and the calculated values of Kd, C_{so} as well as the Ca/Sr ratio.

From the calculations, it is readily seen that each of the chemical systems greatly reduces the Kd for Sr exchange. For the AGW itself, Kd is on the order of 16 L/kg, but for the chemical systems tested, Kd varies from < 0.1 to about 4. The most effective systems are the aluminum/citrate, potassium citrate, potassium chloride/bicarbonate, and clay stabilizers. The value of C_{so}, the amount of Sr originally on the sediment, is consistently near the value of 9 mg/kg. The potassium chloride/potassium bicarbonate system showed a lowered value of Kd but a value of C_{so} consistent with the other systems indicating that Sr was not precipitated with the calcium. The lowered ratio of Ca/Sr indicated that calcium released from the exchange sites by the potassium was indeed precipitated partially as the carbonate. Aluminum citrate at neutral pH and potassium citrate yielded comparable results, showing very low Kd values, maintaining the high Ca/Sr ratio, and generating a bit of iron. Lower pH values for the aluminum system and citric acid generated higher ratios of Ca/Sr and more iron, as well as higher values of C_{so}, indicating the dissolution of mineral phases in addition to the exchange process. Ammonium worked satisfactorily but not as well as potassium or aluminum. The barium and barium/EDTA systems were of intermediate effectiveness.

Table 3-1. Calculation of Kd, initial adsorbed strontium (Cso), and Ca/Sr ratio for bottle roll tests. Sr1 and Sr2 are measured Sr in mg/L; W1 and W2 are sample weights in grams; Ca is average calcium in mg/L; Ca/Sr is ratio of solution Ca to solution Sr on a weight basis.

ID NUM	TYPE	WT 1 (g)	WT 2 (g)	Sr1 (mg/L)	Sr2 (mg/L)	Cso	Kd	Ca	Ca/Sr
1 & 3	AGW	290	273	0.19	0.39	6.84	35.77	37	195
2 & 4	AGW	229	249	0.2	0.4	7.91	39.26	38	190
5 & 7	CIT ACID	179	247	4.97	10.9	9.40	0.80	2060	414
6 & 8	CIT ACID	223	239	5.46	11	8.75	0.73	1900	348
9 & 11	Ba	220	248	1.8	3.6	8.28	3.76	295	164
10 & 12	Ba	251	274	1.8	3.6	7.41	3.38	298	166
13 & 15	Ba+EDTA	265	215	4.7	7.5	13.30	2.10	3000	638
14 & 16	Ba+EDTA	233	210	4.1	9.3	6.70	0.80	3355	818
17 & 19	Al+CIT AC	230	199	13.2	18.6	18.26	0.52	3600	273
18 & 20	Al+CIT AC	208	210	10.6	20.2	10.56	0.05	3375	318
21 & 23	NH4Cl	209	195	3.87	8.57	7.82	1.10	646	167
22 & 24	NH4Cl	220	188	4.12	8.44	8.77	1.25	633	154
29 & 31	CLAFIX(0.1%)	187	234	0.48	1.03	7.47	14.78	86	179
30 & 32	CLAFIX(0.1%)	188	216	0.48	1.1	7.11	14.04	86	179
33 & 35	CLASTA(0.1%)	199	190	0.44	1.03	7.66	16.71	80	182
34 & 36	CLASTA(0.1%)	179	223	0.44	0.99	7.16	15.49	80	182
25 & 26	CLAFIX(1%)	211	226	3.1	6.19	9.11	2.03	500	161
27 & 28	CLASTA(1%)	223	249	2.88	5.94	7.93	1.90	500	174
37 & 38	CIT ACID	201	214	5.11	10.1	10.03	0.99	1850	362
39 & 40	AlCIT(pH3)	201	195	8.24	16.5	9.57	0.18	2500	303
50 & 51	CLAFIX(2%)	199	219	4.65	10.1	8.42	0.83	775	167
50 & 52	CLAFIX(2%)	199	204	4.65	10.1	8.42	0.83	746	160
53 & 54	CLASTA(2%)	221	196	5.37	12.2	6.79	0.38	955	178
53 & 55	CLASTA(2%)	221	198	5.37	12.6	6.39	0.31	939	175
56 & 57	AGW	198	189	0.55	1.17	9.18	15.93	95	173
58 & 59	KCIT	166	191	7.18	17	9.42	0.13	723	101
60 & 61	NH4Cl+HCO3	200	175	3.25	6.91	9.13	1.85	323	99
62 & 63	NH4HCO3	208	190	2.07	4.31	9.22	3.55	109	53
64 & 67	AlCIT(pH4)	202	183	6.86	13.8	9.25	0.38	1780	259
69 & 70	AlCIT(pH7)	204	201	6.66	13.5	9.34	0.44	1115	167
66 & 68	KCl+HCO3	218	186	10.2	18.7	9.23	-0.001	1625	159
Potassium Citrate Optimization Tests Follow									
91 & 92	AGW	197	248	0.179	0.401	6.40	35.46	33	184
81 & 82	0.2 M	203	241	9.3	18.8	10.81	0.19	1535	165
83 & 84	0.1 M	273	258	8.55	18.7	5.75	-0.05	1495	175
85 & 86	0.07 M	191	220	7.2	17.2	8.09	0.09	1320	183
87 & 88	0.04 M	172	174	4.95	11.6	8.49	0.58	972	196
89 & 90	0.02 M	201	251	2.3	4.8	8.03	2.55	606	263
Potassium Chloride/Bicarbonate Optimization Tests Follow									
93 & 94	0.2M/0.01M	168	195	5.3	13.4	7.97	0.34	784	148
95 & 96	0.2M/0.05M	207	204	5.75	11.8	9.01	0.62	425	74
97 & 98	0.1M/0.01M	257	167	4.65	10.2	6.36	0.61	638	137
99 & 100	0.1M/0.05M	246	243	4.45	9.4	7.19	0.83	465	104
101 & 102	0.0M/0.13M	187	189	1.05	3.35	4.69	3.53	65	62
103 & 104	0.5M/0.05M	246	200	6.45	16.2	4.50	-0.10	670	104

Based on these bottle roll tests, it was determined that further testing of three systems—a clay stabilizer (CS), the potassium chloride/potassium bicarbonate (KB) and the potassium citrate (KC) was necessary. The potassium citrate was chosen rather than the aluminum citrate simply because the aluminum could present more difficulties in any ex situ recovery system and is no more effective in displacing Sr. The bicarbonate was chosen to take advantage of the lowered Ca/Sr ratio. The clay stabilizer was chosen because it might have the two-fold advantage of low Kd and deactivation of exchange sites.

For the KB and KC systems, some batch tests were conducted at lower concentrations to try to determine optimum concentrations for column influents. Those results are also shown in Table 3-1. After these tests, high concentrations of influent lixiviant chemicals were used to attempt to remove the Sr in as few pore volumes as possible.

4. COLUMN TESTS

In the bottle roll tests, the sediment is flooded with an excess of chemical reagent all at once, so in a sense the extraction of Sr is optimized. Furthermore, reactions producing precipitates are relatively unimportant, since there is no flow to retard. In column flow tests, on the other hand, the lixiviant chemicals are introduced in such a way that they become depleted at the front where the chemicals contact fresh sediment. Concentrations of extracted species, like Sr and calcium, on the other hand build up at the front. This can result in ineffective leaching and possible redeposition of Sr. Furthermore, side reactions may occur to bring about precipitation of phases that significantly reduce the permeability of the sediment. Thus, while bottle roll tests are quick and give valuable preliminary indications of favorable systems, it is necessary also to determine the behavior of the chemical system in a longer-term column format.

4.1 COLUMN DIMENSIONS AND SETUP

Based on the work of Serne (Ref. 2), it was desired that the residence time of the lixiviant solution in the column be on the order of a couple of days. The columns had to be long enough to see the effect of lixiviant depletion and displaced-ion build up. Furthermore, MSE believed it valuable to use a more representative particle size than just the fines, so the cobbles were retained up to 2 inches in diameter. It was impractical to retain cobbles larger than 2 inches because we wanted to avoid edge effects in the column. Experience has shown that the column diameter should be >3 times the diameter of the largest particles. Therefore, we used columns of 6-inch diameter. These columns require approximately 35 kg of sized sediment per meter of length. For the tests of KC and CS, we used single columns of 1-meter length. Total volume was approximately 17 liters, so it was anticipated that for saturated flow (up-column) one pore volume would occupy about 5 liters. A flow rate of nominally 2 mL/min for a residence time of 2,500 minutes = 42 hours was chosen. If every tenth pore volume for some intervals were sampled, that would mean a sample every 500 mL or every 4.2 hours. Therefore, it was planned that 50 mL samples would be taken.

For the KB test, three ½ -meter length columns in series were used. Solution was to flow up one column, pass through a sampling port (Port A), and move on to the second column. When solution left the top of the second column, it passed through another sampling port (Port B) and then flowed into the third section of column and out to the effluent. This configuration was used to enable monitoring the progress of the calcium carbonate precipitation anticipated for this chemistry. About 50 kg of sediment was used to pack this series of columns; however, weight of sediment in the individual column sections was not measured. The expected pore volume for this test was approximately 7 liters with a residence time of about 60 hours.

For the columns, clear acrylic tubes were used and the lower end was capped with a glued PVC fitting. The top of each column had a glued sleeve fitting with a threaded plug to be used for opening the column to fill it or empty it of sediment. Stainless steel fittings were threaded into the bottom (influent end) of the columns and connected by compression fittings to steel tubes and latex tubing. The latex tubing was connected to peristaltic pumps delivering influent at nominally 2 mL/min. At the effluent end of each column, a pipe thread fitting was screwed into the threaded cap and connected by compression fittings to a steel tube. The steel tube was connected to rigid polyethylene tubing emptying into a large beaker. All screw fittings were put in place using polytetrafluroethylene (PTFE) plumber's tape. Fiberglass insulation matting was cut to 6-inch diameter discs and placed into the bottom of the column. Sediment was then weighed and added to the column until it reached the threads

of the threaded cap. The column was tapped with a hammer to encourage the sediment to pack tightly as it was added. Another disc of matting was added to the top of the column and the lid screwed on using PTFE tape and a wrench.

The A and B sampling ports for the KB column used two brass needle valves and a brass tee to direct the flow either to a sample beaker or on to the next part of the column. Eventually this plugged up and was replaced with a plastic tee and screw clamps on the tubing.

4.2 RUNNING THE COLUMN TESTS

The plan for running the tests was first to flow in approximately three pore volumes (PV) of AGW to establish a steady state Sr level at the effluent. The influent would then be switched to lixiviant solutions for several pore volumes, trying to keep sufficient track of the Sr level to judge when extraction was basically complete. It was not possible to get immediate feedback as to the progress of the test because samples had to be sent to the analytical laboratory by bus. After lixiviant flow was terminated, another several pore volumes of AGW was to be pumped in to wash the column and establish a new steady state Sr level. The desirable procedure is to capture the breakthrough of each new type of influent and sample every tenth pore volume for the next pore volume, then less frequently after that. When the first breakthrough of the AGW initial influent occurs, the size of a pore volume and the residence time can be measured if care has been taken to measure the amount of influent introduced to that point, assuming the packed sediment to have been dry initially.

For the KC column, the effluent concentrations of Sr, calcium (Ca), magnesium (Mg), potassium (K), and iron (Fe) were monitored. For the CS column, we monitored the effluent concentrations of Sr, Ca, and Mg. For the KB column, we monitored the effluent concentrations of Sr, Ca, Mg, K and bicarbonate. For each column, the Sr data were plotted as Sr concentration in the effluent in mg/L vs. number of pore volumes at the effluent.

All the effluent not taken for assay purposes was collected and stored and assayed separately for Sr to have a cross check on the total amount of Sr removed.

4.3 RESULTS OF COLUMN TESTS

All the analytical data for the three column tests are shown in Appendix A.

4.3.1 Potassium Citrate Column

The KC column (see Figures 4-1 and 4-2 and Table 4-1), required 5,770 mL of AGW to see the first effluent. Flow rate was 2.3 mL/min for a residence time of 41 hours (hr) 27 minutes (min). The flow rate and the residence time varied throughout the test and required occasional adjustment. It was apparent that there was a dead space of unknown volume at the top of the column, which contained no sediment packing. The size of the dead zone can be estimated based on the time it took to fill the column top vs the time it took to fill an equal length in the body of the column. The dead zone is estimated to be about 1,820 mL.

Porosity of the packed sediment computed to 0.24 using the formula:

$= (f/A)\Delta t/\Delta d$,

where ϕ is porosity, f is flow rate in mL/hr, A is cross sectional area of column in sq cm, and $\Delta t/\Delta d$ is the measured time in hours taken for the wetted portion of the column to move one centimeter when filling.

Table 4-1. Potassium citrate column

COLUMN 2 (1 PV = 5770 mL)						
SAMPLE #	**VOL EFF**	**NUM PV**	**Sr (mg/L)**	**Ca (mg/L)**	**Ca/Sr**	**WEIGHT Sr**
CO2G0	0	0.00	0.015	21.8	1453	(INFLUENT)
CO2G1	50	0.01	1.19	208	175	0.1
CO2G2	650	0.11	0.969	170	175	0.6
CO2G3	1150	0.20	0.742	131	177	0.4
CO2G4	1700	0.29	0.612	108	176	0.3
CO2G5	2750	0.48	0.428	76	178	0.4
CO2G6	3300	0.57	0.371	65.9	178	0.2
CO2G7	4350	0.75	0.31	55.2	178	0.3
CO2G8	4900	0.85	0.286	50.7	177	0.2
CO2G9	6100	1.06	0.271	47.9	177	0.3
CO2G10	7150	1.24	0.257	45.9	179	0.3
CO2G11	8200	1.42	0.245	43.8	179	0.3
CO2G12	9250	1.60	0.229	40.7	178	0.2
CO2G13	10300	1.79	0.218	39.7	182	0.2
CO2G14	11350	1.97	0.206	37.5	182	0.2
CO2G15	12400	2.15	0.196	35.7	182	0.2
CO2G16	13450	2.33	0.191	34.6	181	0.2
CO2G17	14500	2.51	0.184	33.4	182	0.2
CO2G18	15550	2.69	0.189	35.1	186	0.2
CO2G19	16600	2.88	0.717	198	276	0.8
CO2KC1	17700	3.07	24.6	4360	177	27.1
CO2KC2	18270	3.17	23.3	3860	166	13.3
CO2KC3	18850	3.27	24.4	3870	159	14.2
CO2KC4	19150	3.32	24.3	3310	136	7.3
CO2KC5	19700	3.41	23.7	2310	97	13.0
CO2KC6	20250	3.51	18.8	1990	106	10.3
CO2KC7	20800	3.60	14	1710	122	7.7
CO2KC8	21350	3.70	11.4	1500	132	6.3
CO2KC9	22400	3.88	9.5	1370	144	10.0
CO2KC10	23450	4.06	7.32	1060	145	7.7
CO2KC11	24540	4.25	6.21	913	147	6.8
CO2KC12	25590	4.44	5.25	784	149	5.5
CO2KC13	26800	4.64	4.83	722	149	5.8
CO2KC14	28900	5.01	4.2	628	150	8.8
CO2KC15	29950	5.19	3.81	556	146	4.0

Table 4-1. Potassium citrate column

COLUMN 2 (1 PV = 5770 mL)						
SAMPLE #	**VOL EFF**	**NUM PV**	**Sr (mg/L)**	**Ca (mg/L)**	**Ca/Sr**	**WEIGHT Sr**
CO2KC16	31580	5.47	3.12	446	143	5.1
CO2KC17	35580	6.17	3.03	386	127	12.1
CO2KC18	37550	6.51	3.45	401	116	6.8
CO2KC19	39700	6.88	3.12	341	109	6.7
CO2KC20	42200	7.31	1.64	167	102	4.1
CO2KC21	44520	7.72	0.96	124	129	2.2
CO2KC22	47090	8.16	0.76	121	159	2.0
CO2KC23	50020	8.67	0.68	117	172	2.0
CO2KC24	54070	9.37	0.64	116	181	2.6
CO2KC25	55810	9.67	0.48	102	213	0.8
CO2KC26	56750	9.84	0.44	96.1	218	0.4
CO2W1	57300	9.93	0.34	79.5	234	0.2
CO2W2	58010	10.05	0.32	80.5	252	0.2
CO2W3	58550	10.15	0.3	70.8	236	0.2
CO2W4	59690	10.34	0.24	57.3	239	0.3
CO2W5	60730	10.53	0.18	42.2	234	0.2
CO2W6	61840	10.72	0.1	26	260	0.1
CO2W7	63270	10.97	0.05	10.8	216	0.1
CO2W9	67100	11.63	0.01	1.63	163	0.0
CO2W11	70650	12.24	0.005	1.02	204	0.0
CO2W13	74200	12.86	0.005	0.98	196	0.0
CO2W14	79735	13.82	0.002	0.35	175	0.0
CO2W15	83335	14.44	0.015		0	0.1
TOTAL mg Sr EXTRACTED						199.5

After AGW breakthrough, 3.0 pore volumes of AGW were pumped into the column in saturated flow (up column) configuration. The influent AGW had a Sr concentration of 0.015 mg/L, the breakthrough concentration was 1.19 mg/L, and after 3 PV the concentration had dropped to 0.19 mg/L. After the AGW influent, potassium citrate lixiviant was introduced. The 0.2 M lixiviant was prepared by dissolving 1,040 g potassium citrate monohydrate in 16 L of AGW. The first batch of AGW was prepared from $CaCl_2$ and $MgCl_2$ and contained a contamination of 0.38 mg Sr/L in the solution. The second batch of lixiviant was prepared with $CaCO_3$ and $MgCO_3$ and contained 0.03 mg Sr/L. Immediately upon breakthrough of the potassium citrate lixiviant, the effluent Sr level jumped to about 24 mg Sr/L and stayed at that high level for a half pore volume. The Sr concentration then dropped exponentially until at 9.8 PV the Sr level was 0.44 mg/L. There was a plateau of about 4 mg/L between 5 and 7 PV, and then the decrease continued. At PV 9.8, AGW wash was introduced and continued until PV 13.8. Thus, roughly 7 PV of lixiviant was used followed by 4 PV of AGW wash. At the end of the second AGW wash session, the Sr concentration in the effluent was 0.002 mg/L. This can be seen graphically in Figures 4-1 and 4-2, both of which show the plot of Sr vs. PV but at different scales.

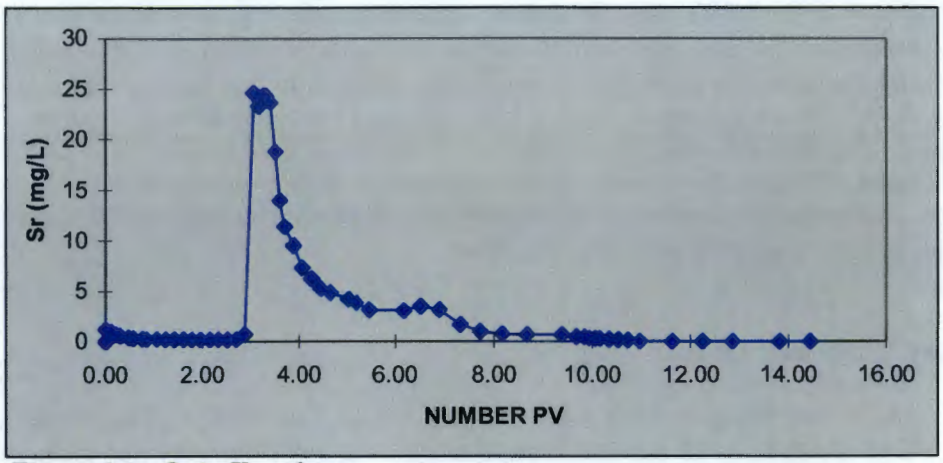

Figure 4-1. Sr in Kc column.

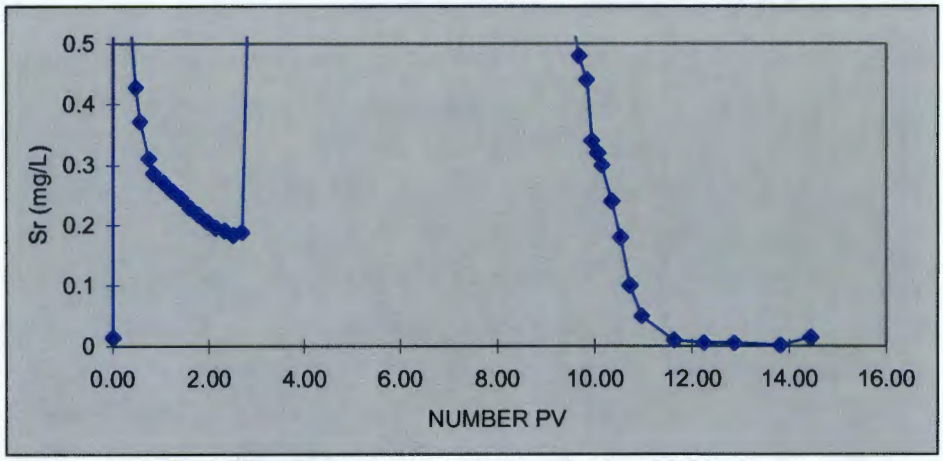

Figure 4-2. Sr in Kc column.

The total amount of Sr removed from the column is obtained both by integration of the graph and by analyzing all the effluent for Sr and measuring the volume of the effluent increments, including the volumes of all the collected samples. The integrated graph yields the value 200-mg Sr, and the collected samples total up to 173-mg Sr, a discrepancy of 27 mg or about 13%.

What is not seen by the data or the graphs is that the breakthrough lixiviant effluent exited the column with a transparent amber color, i.e., free of precipitate. As the effluent stood for a few minutes, however, a white precipitate fell out. Analysis of some of the collected precipitate showed it to have the same calcium composition as calcium citrate with a very small amount of Sr present. The precipitate dissolved readily in hydrochloric acid so presented no analytical difficulties. It would be instructive to analyze the solution in equilibrium with the precipitate for calcium and for citrate to determine saturation levels of these components to adjust the citrate level of future tests to prevent this precipitation. It is not understood why the precipitate appeared in the solution only after exiting the column.

A final sample was taken from the KC column by pumping out about a half pore volume after the column sat idle for 2 weeks. The Sr concentration of this sample was 0.015 mg Sr/L. That the Sr

concentration rose on sitting is consistent with the assumption that there are mineral phases containing Sr that are still present and are slowly mobilizing Sr into the water. The rate of this mobilization is apparently quite low since the level of Sr concentration rose only to 0.015 mg/L after a quiescent period of 2 weeks. Under conditions of flow, which is more like the natural environment, the Sr level is much lower. One factor that helps keep the Sr level low is the occupation of most of the exchange sites by potassium. The tendency to displace potassium with Sr (and other ground water cations) is greatest when the exchange sites have high potassium and the ground water has low potassium; that condition prevails after flushing with potassium salts.

4.3.2 Clay Stabilizer Column

For the CS column (see Figure 4-3 and Table 4-2), 5,880 mL of AGW were pumped into the column to fill it initially, taking 42 hr 36 min at approximately 2.2 mL/min. Porosity was calculated to be 0.24 and the dead space at the head of the column was estimated at 1,700 mL. The initial effluent contained 0.92 mg Sr/L. This concentration dropped off until after 2.8 PV the Sr level was about 0.20 mg/L, and the ClaStaXP lixiviant broke though.

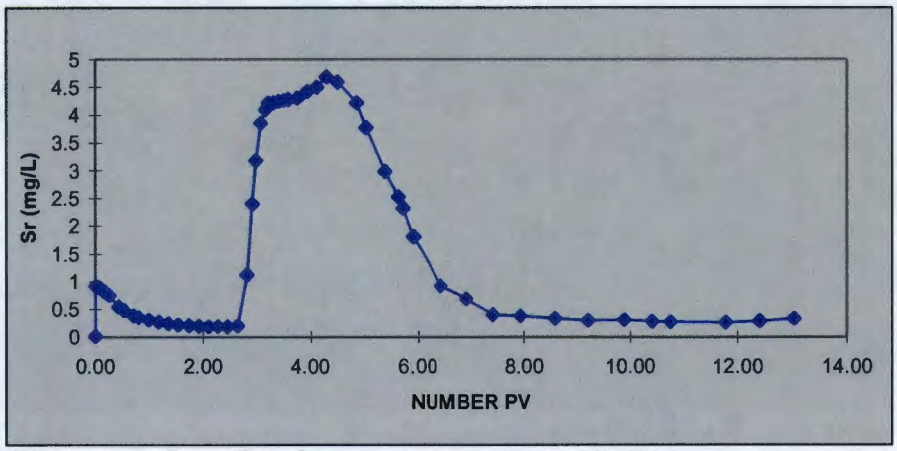

Figure 4-3. Sr in Cs column.

ClaStaXP in 2% aqueous solution was prepared by dissolving 283 mL ClaStaXP (density 1.13 g/mL) in 16 L of AGW. The AGW used in this preparation had been made with calcium chloride containing Sr contamination so that the lixiviant solution contained 0.38 mg/L Sr contamination. The lixiviant was pumped into the column for 3 PV. During this period the Sr level rose from 0.20 mg/L to 4.5 mg/L and then dropped off to 2.3 mg/L at which point AGW wash appeared in the effluent. This second AGW wash contained 0.015 mg/L Sr contamination from the calcium carbonate used in preparation.

After approximately 7 PV of AGW wash, the CS column test was terminated with a Sr level of 0.33 mg/L. The Sr concentration had actually dropped to approximately 0.30 mg/L after 6 PV of wash and then rose slightly before termination. This final concentration was higher than the Sr concentration with the initial AGW wash. This behavior is different than that of the KC column, in which the Sr concentration dropped to a very much lower value than the initial AGW wash. Compared to the 200 mg of Sr removed from the KC column, only 87 mg was removed from the CS column.

Table 4-2. Clasta XP column.

COLUMN 3 (1 PV = 5880 mL)						
SAMPLE #	**VOL EFF**	**NUM PV**	**Sr (mg/L)**	**Ca (mg/L)**	**Ca/Sr**	**WEIGHT Sr**
CO3G0	0	0.00	0.015	21.8	1453	(INFLUENT)
CO3G1	50	0.01	0.917	161	176	0.0
CO3G2	450	0.08	0.89	157	176	0.4
CO3G3	950	0.16	0.827	146	177	0.4
CO3G4	1500	0.26	0.757	134	177	0.4
CO3G5	2550	0.43	0.548	96.2	176	0.6
CO3G6	3100	0.53	0.481	85.4	178	0.3
CO3G7	4150	0.71	0.384	68.1	177	0.4
CO3G8	4700	0.80	0.353	62.8	178	0.2
CO3G9	5830	0.99	0.313	55.9	179	0.4
CO3G10	6880	1.17	0.274	49.1	179	0.3
CO3G11	7930	1.35	0.244	43.8	180	0.3
CO3G12	8980	1.53	0.224	40.2	179	0.2
CO3G13	10200	1.73	0.209	38.3	183	0.3
CO3G14	11250	1.91	0.198	36.2	183	0.2
CO3G15	12300	2.09	0.193	35.4	183	0.2
CO3G16	13350	2.27	0.19	34.9	184	0.2
CO3G17	14400	2.45	0.185	33.8	183	0.2
CO3G18	15450	2.63	0.201	36.8	183	0.2
CO3G19	16500	2.81	1.12	202	180	1.2
CO3CS1	17050	2.90	2.4	424	177	1.3
CO3CS2	17450	2.97	3.18	559	176	1.3
CO3CS3	18000	3.06	3.85	668	174	2.1
CO3CS4	18550	3.15	4.1	710	173	2.3
CO3CS5	18850	3.21	4.22	731	173	1.3
CO3CS6	19400	3.30	4.22	730	173	2.3
CO3CS7	19950	3.39	4.25	736	173	2.3
CO3CS8	20500	3.49	4.26	736	173	2.3
CO3CS9	20950	3.56	4.28	739	173	1.9
CO3CS10	22000	3.74	4.3	740	172	4.5
CO3CS11	23050	3.92	4.42	761	172	4.6
CO3CS12	24100	4.10	4.5	809	180	4.7
CO3CS13	25150	4.28	4.69	838	179	4.9
CO3CS14	26350	4.48	4.59	809	176	5.5
CO3CS15	28450	4.84	4.22	684	162	8.9
CO3CS16	29500	5.02	3.77	597	158	4.0
CO3CS17	31550	5.37	2.98	454	152	6.1
CO3CS18	32980	5.61	2.52	378	150	3.6
CO3CS19	33525	5.70	2.32	350	151	1.3
CO3W1	34635	5.89	1.81	281	155	2.0
CO3W2	37735	6.42	0.918	170	185	2.8
CO3W3	40565	6.90	0.692	128	185	2.0
CO3W4	43500	7.40	0.407	102	251	1.2
CO3W5	46620	7.93	0.378	103	272	1.2
CO3W6	50500	8.59	0.331	92.4	279	1.3
CO3W7	54150	9.21	0.303	91.8	303	1.1
CO3W8	58150	9.89	0.312	99.8	320	1.2
CO3W9	61220	10.41	0.282	96.4	342	0.9
CO3W9	63270	10.76	0.271	92	339	0.6
CO3W10	69280	11.78	0.266	87.4	329	1.6
CO3W11	72920	12.40	0.293	85.5	292	1.1
CO3W12	76655	13.04	0.331	81.6	247	1.2
			TOTAL mg Sr EXTRACTED			89.7

4.3.3 Potassium Chloride/Bicarbonate Column

The KB column had two sampling ports in addition to the final column effluent. These were called the A port and the B port. The entire column had three parts, each of which was a column ½ meter in length, with a sampling port between the columns. The total weight of sediment in the column was 50 kg, so each ½ -meter column contained about 17 kg, but these individual weights were not determined. It took 12.05 L to fill the entire column and three samples of 50 mL each at Ports A and B yielding a pore volume of about 12 L and a residence time of 96 hours at a little more than 2 mL/min. To fill to Port A, about 30 hours was required or 3,600 mL as pore volume for the first column. To fill to Port B, another 30 hours was needed or 3,600 mL pore volume for the second column. The dead space in columns KB-A and KB-B was estimated at 1,610 mL each and 1,830 mL in column KB-C.

At the column effluent, the first solution breaking through from the preliminary AGW influent contained 1.87 mg/L Sr. The Sr concentration in the effluent fell to 0.156 mg/L after 1.1 PV and then rose abruptly to 0.44 mg/L. The reason for the abrupt rise in Sr level from 0.156 mg/L to 0.44 mg/L was attributed to an error in the preparation of one batch of AGW. Apparently the weight of chemicals calculated for preparing 52 liters of AGW was used to prepare 16 L; all of the cation concentrations in the effluent rose, reflecting this error. By the time the error was discovered, most of that batch of AGW had already been introduced into the column.

At this point, the third section of the column was decommissioned because it plugged up. Thereafter, the B port was used as the column effluent position. At this time, the KCl solution was entering the third column and the brass needle valves were fouling. The valves were replaced with plastic fittings, and flow was maintained in the first two columns but was never recovered in the third column. The brass fittings experienced some leaking prior to failure; therefore, a small amount of solution was lost at Port A and at Port B.

Note that the accounting of pore volumes differs for Columns 1a and 1b. For fluids passing Port A, the effective PV is for the first half meter of column; at Port B, the effective PV is for the full meter of column. The volume of the pore space up to Port A (= PV_A) is only one half the volume of the pore space up to Port B (= PV_B). Therefore, each PV_B equals two PV_A.

The initial Sr level at Port A (see Figures 4-4 and 4-5 and Table 4-3) was 0.64 mg/L with the AGW influent of 0.015 mg/L Sr. The Port A Sr concentration dropped to 0.12 mg/L after 5.42 PV_A. The concentration of Sr rose again precipitously to 0.45 mg/L because of the error in AGW preparation mentioned above. Before the concentration of Sr could recover to a low value by introduction of new AGW, the lixiviant solution was already introduced and caused the Sr level to jump to almost 28 mg/L within 0.2 PV of breakthrough. After about 10 PV_A of lixiviant, the Sr level had dropped to 0.18 mg/L and after 17 PV_A was at 0.02 mg/L.

Wash was introduced after that and brought the Sr concentration to 0.003 mg/L after 8 PV_A. The lixiviant solution was first prepared by dissolving 476 g KCl and 63.5 g $KHCO_3$ in 12.7 liters of AGW. Subsequently, 0.5M KCl and 0.05M $KHCO_3$ batches of 18 L and 6.4 L were each prepared.

At Port B (see Figures 4-6 and 4-7 and Table 4-4), the initial Sr level was 1.06 mg/L, dropping to 0.139 mg/L after 2.2 PV_B before rising to about 0.55 mg/L because of the error in preparation of influent AGW as mentioned above. At breakthrough of the lixiviant, the Sr concentration rose to

34.1 mg/L and immediately dropped off, reaching 0.08 mg/L after 9 pore volumes of lixiviant flow. AGW wash was introduced and decreased the Sr concentration to 0.005mg/L after 4 PV_B.

Table 4-3. Potassium chloride/bicarbonate column (Port A).

SAMPLE #	VOL EFF	NUM PV	Sr (mg/L)	Ca (mg/L)	Ca/Sr	WEIGHT Sr
CO1AG0	0	0.00	0.015	21.8	1453	(INFLUENT)
CO1AG1	50	0.01	0.64	113	177	0.0
CO1AG2	3750	1.04	0.278	49	176	1.0
CO1AG3	7500	2.08	0.186	33.2	178	0.7
CO1AG4	12000	3.33	0.168	30.2	180	0.8
CO1AG5	13250	3.68	0.167	30.4	182	0.2
CO1AG6	14500	4.03	0.172	31.2	181	0.2
CO1AG7	15750	4.38	0.157	28.7	183	0.2
CO1AG8	17000	4.72	0.135	24.5	181	0.2
CO1AG9	18250	5.07	0.127	23.2	183	0.2
CO1AG10	19500	5.42	0.12	22.3	186	0.2
CO1AG11	20750	5.76	0.13	23.9	184	0.2
CO1AG12	22850	6.35	0.441	78.4	178	0.9
CO1AG13	24100	6.69	0.457	79.8	175	0.6
CO1AG14	30745	8.54	0.415	73.5	177	2.8
CO1AKB1	36824	10.23	1.09	194	178	6.6
CO1AKB2	37003	10.28	6.95	1250	180	1.2
CO1AKB3	37182	10.33	19.7	3430	174	3.5
CO1AKB4	37420	10.39	27.7	4830	174	6.6
CO1AKB5	37718	10.48	25.7	4080	159	7.7
CO1AKB6	38100	10.58	19.5	3020	155	7.4
CO1AKB7	38457	10.68	13.5	1710	127	4.8
CO1AKB8	39143	10.87	7.38	636	86	5.1
CO1AKB9	45050	12.51	1.28	69.9	55	7.6
CO1AKB10	48050	13.35	0.92	68.2	74	2.8
CO1AKB11	51000	14.17	0.56	131	234	1.7
CO1AKB12	55600	15.44	0.44	24.7	56	2.0
CO1AKB13	58340	16.21	0.36	18.6	52	1.0
CO1AKB14	61840	17.18	0.28	14.6	52	1.0
CO1AKB15	70590	19.61	0.18	20.8	116	1.6
CO1AKB17	79250	22.01	0.3	21.2	71	2.6
CO1AKB18	85325	23.70	0.24	22.9	95	1.5
CO1AKB19	91400	25.39	0.08	7.48	94	0.5
CO1AKB20	93400	25.94	0.038	3.37	89	0.1
CO1AKB21	99070	27.52	0.02	3.25	163	0.1
CO1AW1	105190	29.22	0.005	0.96	192	0.0
CO1AW2	129300	35.92	0.003	0.71	237	0.1

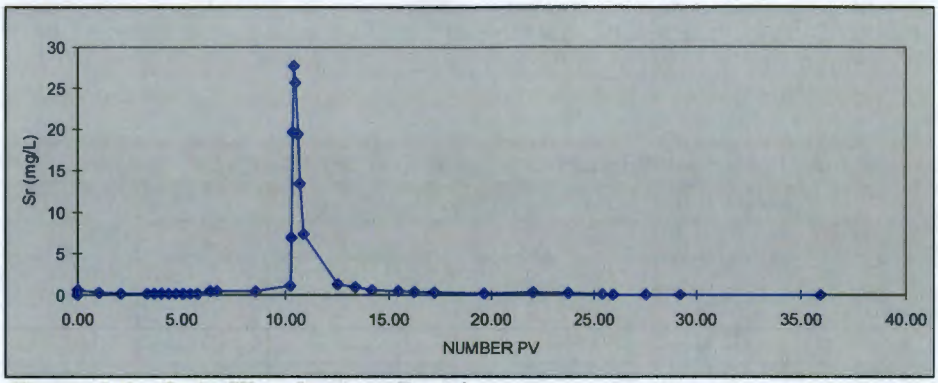

Figure 4-4. Sr in Kb column at Port A.

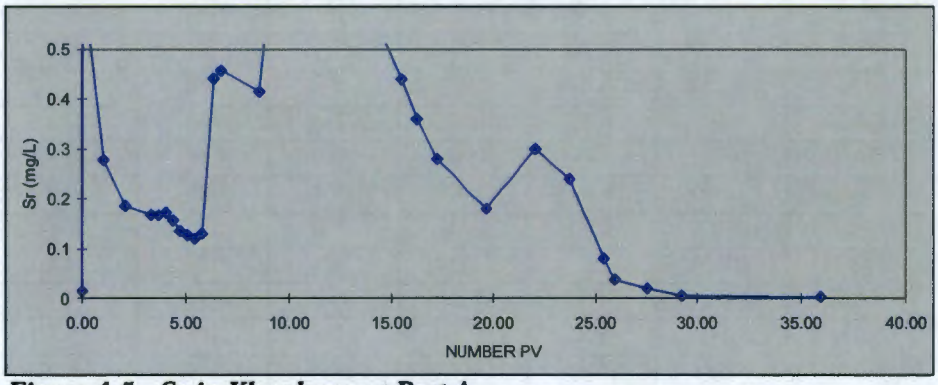

Figure 4-5. Sr in Kb column at Port A.

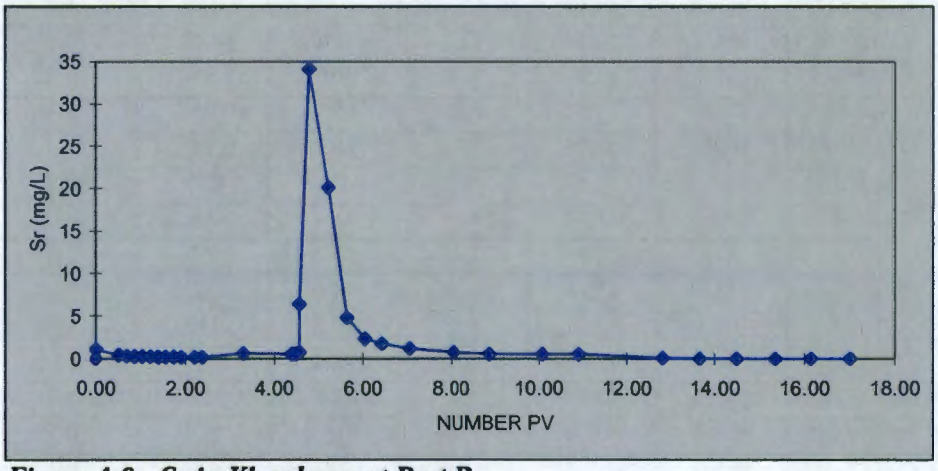

Figure 4-6. Sr in Kb column at Port B.

The integrated graph of Sr concentration in the effluent vs. volume of effluent yielded 178 mg Sr at Port B. The total Sr calculated from analysis of all the aggregated effluents and individual samples was 169 mg, a discrepancy of approximately 5%.

Table 4-4. Potassium chloride/bicarbonate column (Port B).

SAMPLE #	VOL EFF	NUM PV	Sr (mg/L)	Ca (mg/L)	Ca/Sr	WEIGHT Sr
CO1BG0	0	0.00	0.015	21.8	1453	(INFLUENT)
CO1BG1	50	0.01	1.06	183	173	0.1
CO1BG2	3750	0.52	0.375	66.1	176	1.4
CO1BG3	5000	0.69	0.3	53.5	178	0.4
CO1BG4	6250	0.87	0.259	46.8	181	0.3
CO1BG5	7500	1.04	0.232	42.2	182	0.3
CO1BG6	8750	1.22	0.202	37	183	0.3
CO1BG7	10000	1.39	0.194	35.1	181	0.2
CO1BG8	11250	1.56	0.179	32.8	183	0.2
CO1BG9	12500	1.74	0.166	30.3	183	0.2
CO1BG10	13750	1.91	0.151	27.7	183	0.2
CO1BG11	15850	2.20	0.139	25.1	181	0.3
CO1BG12	17100	2.38	0.156	28.2	181	0.2
CO1BG13	23750	3.30	0.586	102	174	3.9
CO1BKB1	31612	4.39	0.52	89.3	172	4.1
CO1BKB2	31850	4.42	0.539	93.1	173	0.1
CO1BKB3	32100	4.46	0.546	93.8	172	0.1
CO1BKB4	32420	4.50	0.576	99	172	0.2
CO1BKB5	32790	4.55	0.74	127	172	0.3
CO1BKB6	32860	4.56	6.38	1120	176	0.4
CO1BKB7	34490	4.79	34.1	5490	161	55.6
CO1BKB8	37540	5.21	20.1	2290	114	61.3
CO1BKB9	40540	5.63	4.8	301	63	14.4
CO1BKB11	43440	6.03	2.32	131	56	6.7
CO1BKB12	46190	6.42	1.72	101	59	4.7
CO1BKB13	50790	7.05	1.16	71.4	62	5.3
CO1BKB14	57900	8.04	0.75	42.5	57	5.3
CO1BKB16	63810	8.86	0.54	31.7	59	3.2
CO1BKB18	72475	10.07	0.48	24.7	51	4.2
CO1BKB19	78550	10.91	0.48	32	67	2.9
CO1BKB20	92330	12.82	0.08	6.34	79	1.1
CO1BW1	98380	13.66	0.01	1.42	142	0.1
CO1BW2	104330	14.49	0.003	0.48	160	0.0
CO1BW3	110570	15.36	0.004	0.56	140	0.0
CO1BW4	116210	16.14	0.007	1.04	149	0.0
CO1BW5	122500	17.01	0.005	0.94	188	0.0
CO1BW6	131380	18.25				

At Port B, the Ca/Sr ratio was consistently about 178 (standard deviation = 5), quite close to the ratio (i.e., 177) in the ground water we were mimicking with our AGW. After the lixiviant broke through, the ratio dropped to a low of 51 and an average of 75 (not a weighted average). It is evident from the graph of Figure 4-8 that a considerable amount of the calcium has been left in the column even though the amount of Sr mobilzed is comparable to that released by the citrate.

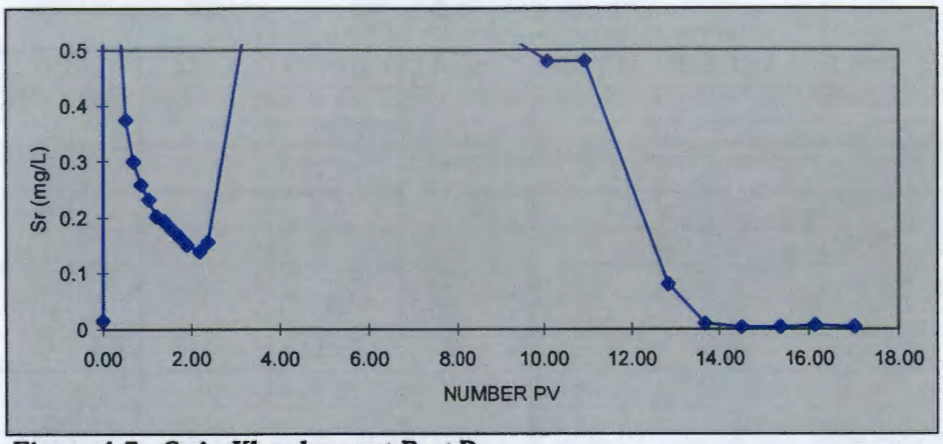

Figure 4-7. Sr in Kb column at Port B.

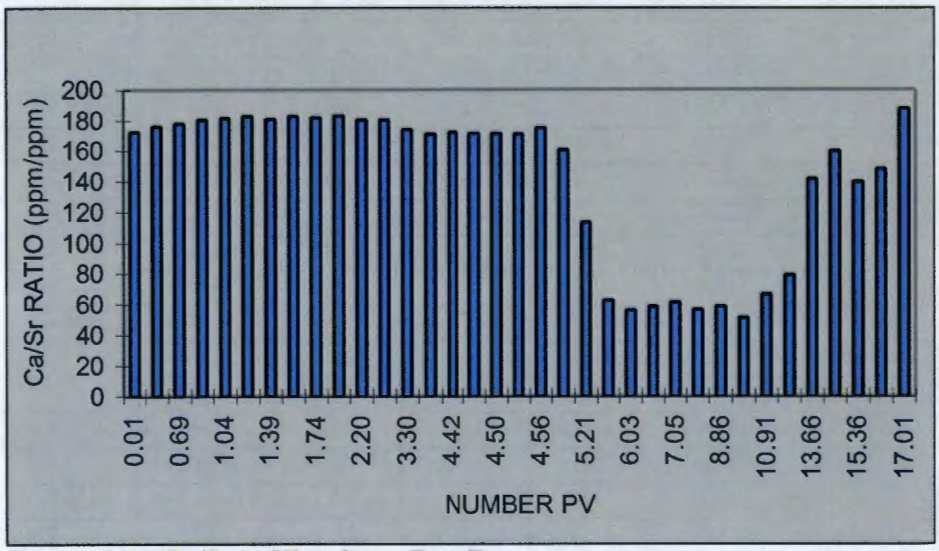

Figure 4-8. Ca/Sr in Kb column Port B.

Dividing the integrated calcium (sum of Ca concentration times PV increment) by the integrated Sr gives approximately 119, which shows about 1/3 of the calcium exchanged was precipitated in the column. However, a considerable fraction of the calcium came out along with the Sr peak at PV 4.79. The reduction of calcium in the effluent is what was anticipated to happen by the inclusion of bicarbonate with the potassium chloride. Figures 4-9a and 4-9b and Table 4-5 show the concentration of bicarbonate at Ports A and B as a function of PV.

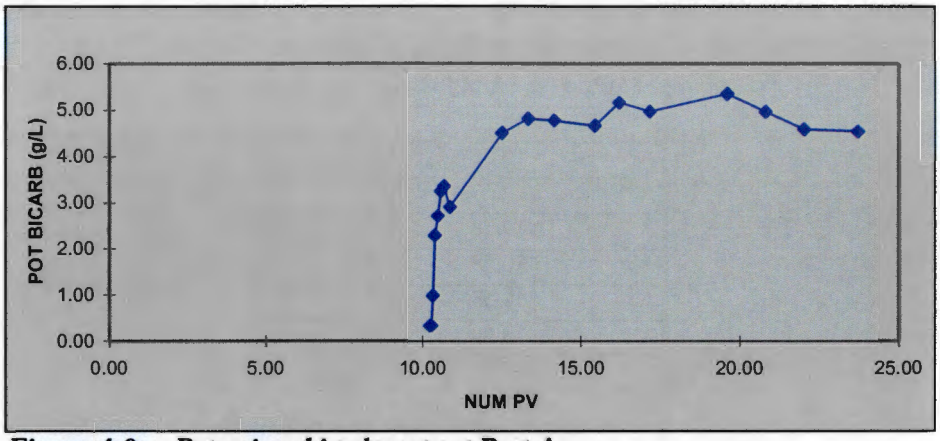

Figure 4-9a. Potassium bicarbonate at Port A.

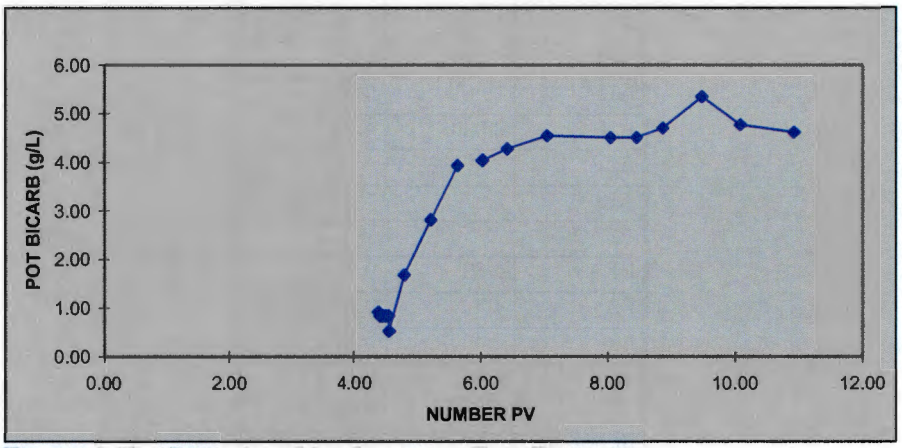

Figure 4-9b. Potassium bicarbonate at Port B.

Table 4-5. Bicarbonate data.

SMPL #	NUM PV	KB (g/L)
A1	10.23	0.34
A2	10.28	0.34
A3	10.33	0.99
A4	10.39	2.29
A5	10.48	2.71
A6	10.58	3.24
A7	10.68	3.36
A8	10.87	2.90
A9	12.51	4.50
A10	13.35	4.81
A11	14.17	4.77
A12	15.44	4.66
A13	16.21	5.15
A14	17.18	4.96
A15	19.61	5.34
A16	20.80	4.96
A17	22.01	4.58
A18	23.7	4.54
B1	4.39	0.92
B2	4.42	0.84
B3	4.46	0.84
B4	4.50	0.84
B5	4.55	0.84
B6	4.56	0.53
B7	4.79	1.68
B8	5.21	2.82
B9	5.63	3.93
B10	5.83	
B11	6.03	4.04
B12	6.42	4.27
B13	7.05	4.54
B14	8.04	4.50
B15	8.45	4.50
B16	8.86	4.69
B17	9.47	5.34
B18	10.07	4.77
B19	10.91	4.62

5. EXCHANGEABLE CATIONS IN RINGOLD "E" SEDIMENT

5.1 PURPOSE

As described above, column tests to mobilize adsorbed Sr were run on < 2 inch Ringold-type sediment from the bank of the Columbia River outside the contaminated zone. These tests released between 5.0 and 5.7 mg Sr per kg sediment. Additional tests were conducted in order to estimate 1) the total exchangeable Sr and other cations on the original sediment materials and 2) the exchangeable Sr and other cations on the residue from one of the column tests. From these data, it was possible to compute the fraction of exchangable Sr removed in the column tests.

5.2 MATERIALS

Exchangeable cation tests are generally run on small samples (2 to 10 grams) of finely divided soil. MSE was interested, however, in working with samples containing large cobbles (up to 2 inch diameter) as well as clay-sized particles, so it was necessary to use larger samples to achieve adequate sampling. Since one cobble could weigh more than 150 grams, total sample size had to greatly exceed this in order to ensure representative sampling. Thus, a sample size of 2000 g was chosen; however, roughly a 20% bias in calculated values (just by the random misplacement of one cobble) could still be expected. This is because the cobble would contribute precious little in the way of exchangeable cations, while the sand and clay it replaced would contribute 1 to 2 mg of Sr, as well as other cations. Thus for the first test run on virgin Ringold sediment, 2,000 gram samples were used.

Procedurally, it is more difficult and time consuming to work with large samples than with small samples primarily because of the problem of laboratory filtration of the large volume of wet, unsorted soil. Consequently, when additional tests were run, the samples were separated into two fractions—those that passed ¼ inch (sand) and those that did not (cobbles). For the smaller size fraction, nominally 100 g samples were used for the exchangeable cations test; for the larger size fraction, 2–3 kg were used because it was assumed that the large cobbles would filter rapidly.

The ratio of weight of sand to weight of cobbles was determined for the samples as an aid in estimating the exchangeable Sr content of a given sample.

Ammonium acetate solution (1M) was prepared by mixing 1.75 L of 2M acetic acid with 1.75 L of 2M ammonium hydroxide, each prepared from the concentrated reagents. The pH of the final solution was shown to lie between 6 and 8 as verified by pH paper. Measurements were made with a 1,000 mL graduated cylinder.

5.3 PROCEDURE

This procedure for the determination of exchangeable cations is adapted from the procedure published in Reference 3. The adaptation was necessary because of the large sample and particle size.

For samples containing large particles, 2–3 kg of sample was weighed to the nearest 0.02 kg and placed into a 1 gallon plastic wide-mouthed jug with sealable lid. For virgin sediment samples, a preliminary wash with distilled water was made to remove soluble salts. This was accomplished by

adding 1,000 mL of distilled water to the sample in the jug and rolling overnight. The sample mix was then filtered and the residue weighed. For this washed residue and for residues from the column tests, 1,000 mL (or so) of 1M ammonium acetate solution was added, the jug sealed shut, and the mixture rolled overnight. The jug was removed from the roller and allowed to settle (sometimes for over a day) before filtration. The mixture was then filtered through a 0.45-micron acetate filter by removing supernatant solution with a pipet, with the filtrate being collected for assay and weighed, and the residue saved for further treatment. The residue was weighed and then treated with approximately 1,000 mL of 1M ammonium acetate and rolled again overnight, settled, filtered, etc. The filtrate was again saved for assay and the residue was again weighed and treated with 1,000 mL of ammonium acetate solution. This third treatment was filtered, the filtrate saved for assay, and the residue discarded. From these data and the assays, the exchangeable cations and Sr content of the sample could be calculated. Filtrates were sent to MSE-HKM laboratory in Butte, Montana for ICP assay of Ca, Mg, Na, K, and Sr.

For samples not containing cobbles, a much smaller sample size could be used. Thus, 100-gram samples of sediment treated with 50 mL solution were used. Otherwise, the procedure was quite similar to that described above for the cobbles.

5.4 CALCULATIONS

Two values for each sample were calculated from the data: the amount of exchangeable strontium (Sr_{ex}) in mg Sr/kg sediment and the CEC in milliquivalent (meq)/100 g. For both of these quantities, a related value was calculated for the first treatment with ammonium acetate. Using this value and the measured amount of residual solution remaining in the sample for the next treatment, the amount of cation in the sample prior to the next ammonium acetate treatment could be determined. Then, more ammonium acetate solution was added and some of the solution collected by filtration; the residual solution still wetting the residue contained an amount of cation determined from the cation assay and the weight of the residual. Thus, for each new treatment, the cation value contributed by that treatment could be calculated. The total of the values for each of the three treatments then gives the total in the sample.

The total exchangeable Sr in mg Sr/kg, is referred to as Sr_{ex}, the sample weight W_s, the weight of the residual solution W_{rn}, the weight Sr released in treatment n Sr_n, the weight of Sr in solution n S_n, and the weight of Sr in the residual in treatment n R_n. Furthermore, V_{an} is the volume of solution added in treatment n, V_{rn} ($=W_{rn}$) is the volume of residual solution left after filtration n, and V_{tn} is the total volume of solution in treatment n. Then,

$$S_n = Sr_n + R_n$$

and $$R_n = S_{n-1}(V_{rn-1}/V_{tn-1})$$

Thus,

$$Sr_n = S_n - S_{n-1}(V_{rn-1}/V_{tn-1})$$

and

$$Sr_{ex} = \Sigma Sr_n/W_s.$$

By a similar development, the CEC of a sample is given by:

$$CEC = \Sigma M_n/W_s \text{ , where}$$

$M_n = \Sigma(C_{in}/G_i)$ and is the sum of the cation charge milliequivalents of all the cationic species (Ca, Mg, Sr, Na, K) when C_{in} is the concentration of the individual cation in mg/L contributed by a given treatment and G_i is the equivalent weight of the cation. For each individual species,

$$C_{in} = C_{imn} - C_{imn-1}(V_{rn-1}/V_{tn-1}) \text{ ,}$$

where the m subscript indicates the concentration of that particular analyte measured in the treatment solution.

Values of solution concentrations and calculated values of CEC and Sr_{ex} are shown in Table 5-1 for unfractioned virgin sediment, in Tables 5-2a and 5-2b for fractioned virgin sediment, and in Table 5-3a and 5-3b for fractioned residue from Column 1a.

Table 5-1. Exchangeable cations in virgin Ringold sediment, < 2 inch.

WEIGHT SAMPLE (grams) 2000									
	WATER WASH		**AM ACETATE 1**		**AM ACETATE 2**		**AM ACETATE 3**		
ELEMENT	**PPM**	**MEQ/L**	**PPM**	**MEQ/L**	**PPM**	**MEQ/L**	**PPM**	**MEQ/L**	
Ca	34.5	1.73	939	46.95	528	26.40	333	16.65	
Mg	15.3	1.26	319	26.23	160	13.16	82.2	6.76	
Sr	0.189	0.00	6.9	0.15	4.22	0.09	2.49	0.06	
Na	9.85	0.43	20.1	0.87	14.3	0.62	10.5	0.46	
K	10.5	0.27	114	2.92	78.6	2.01	50.2	1.28	
MEQ/L SUM		3.68		77.13		42.28		25.21	
V added (mL)	1000		1000		1000		100		
V residue (mL)	640		700		840				
V total (mL)	1000		1640		1700		1840		
MILLIEQ		3.68		124.13		17.89		10.86	CEC
MEQ/100 g		0.18		6.21		0.89		0.54	7.64
									EXCH Sr
Sr(mg/kg)			5.60		1.17		0.52		7.29
Ca (mg/kg)			759		120		85		
Ca/Sr			136		103		163		

Exchangeable cations and cation exchange capacity (CEC) for virgin Ringold sediment, minus 2 inch. CEC in meq/100g; exchangeable Sr and Ca in mg/kg.

Table 5-2a. Exchangeable cations in virgin Ringold sand < 0.25 inch.

WEIGHT SAMPLE (grams) 80.84									
	WATER WASH		AM ACETATE 1		AM ACETATE 2		AM ACETATE 3		
ELEMENT	PPM	MEQ/L	PPM	MEQ/L	PPM	MEQ/L	PPM	MEQ/L	
Ca	36.3	1.82	1410	70.50	533	26.65	269	13.45	
Mg	16.7	1.37	394	32.40	97.5	8.02	42.8	3.52	
Sr	0.209	0.00	8.1	0.18	3.39	0.08	1.73	0.04	
Na	9	0.39	13.2	0.57	6.85	0.30	4.07	0.18	
K	13	0.33	132	3.38	56.1	1.43	29.3	0.75	
MEQ/L SUM		3.92		107.03		36.48		17.93	
V added (mL)	50		50		50		50		
V residue (mL)	20		21		32		17.4		
V total (mL)	50		70		71		82		
MILLIEQ		0.20		7.41		0.34		0.30	CEC
MEQ/100 g		0.24		9.17		0.42		0.38	9.97
									EXCH Sr
Sr(mg/kg)			6.96		0.87		0.41		8.25
Ca (mg/kg)			1212		102		62		
Ca/Sr			174		117		150		

Exchangeable cations and cation exchange capacity (CEC) for virgin Ringold sediment, sand fraction (minus 0.25 inch). CEC in meq/100g; exchangeable Sr and Ca in mg/kg.

Table 5-2b. Exchangeable cations in virgin Ringold sand, 0.25 inch - 2 inch.

WEIGHT SAMPLE (grams): 2500							
	WATER WASH		AM ACETATE 1		AM ACETATE 2		
ELEMENT	PPM	MEQ/L	PPM	MEQ/L	PPM	MEQ/L	
Ca	25.8	1.29	1340	67.00	612	30.60	
Mg	11.4	0.94	392	32.24	161	13.24	
Sr	0.143	0.00	8.77	0.19	5.21	0.12	
Na	11.8	0.51	27.7	1.20	21.4	0.93	
K	6.67	0.17	117	2.99	75.2	1.92	
MEQ/L SUM		2.91		103.63		46.81	
V added (mL)	1000		1000		500		
V residue (mL)	220		380				
V total (mL)	1000		1220		880		
MILLIEQ		2.91		125.79		1.81	CEC
MEQ/100 g		0.12		5.03		0.07	5.10
							EXCH Sr
Sr(mg/kg)			4.27		0.50		4.77
Ca (mg/kg)			652		12		
Ca/Sr			153		23		

Exchangeable cations and cation exchange capacity (CEC) for virgin Ringold sediment, cobble fraction (0.25 –2 inch). CEC in meq/100g; exchangeable Sr and Ca in mg/kg.

Table 5-3a. Exchangeable cations in 1A residue sand, < 0.25 inch.

WEIGHT SAMPLE (grams): 93.08							
	AM ACETATE 1		AM ACETATE 2		AM ACETATE 3		
ELEMENT	PPM	MEQ/L	PPM	MEQ/L	PPM	MEQ/L	
Ca	813	40.65	222	11.10	81	4.05	
Mg	118	9.70	29.5	2.43	8.5	0.70	
Sr	3.7	0.08	1.08	0.02	0.563	0.01	
Na	19	0.83	5.74	0.25	2.28	0.10	
K	2670	68.29	916	23.43	264	6.75	
MEQ/L SUM		119.55		37.23		11.61	
V added (mL)	50		50		50		
V residue (mL)	12		11.9		17.4		
V total (mL)	50		62		61.9		
MILLIEQ		5.98		0.87		0.28	CEC
MEQ/100 g		6.42		0.94		0.30	7.66
							EXCH Sr
Sr(mg/kg)	1.99		0.24		0.24		2.47
Ca (mg/kg)	437		43		25		
Ca/Sr	220		178		108		

Exchangeable cations and cation exchange capacity (CEC) for Column 1 residue, sand fraction (minus 0.25 inch). CEC in meq/100g; exchangeable Sr and Ca in mg/kg.

Table 5-3b. Exchangeable cations in 1A residue sand, 0.25 Inch – 2 Inch

Weight Sample (Grams): 2400					
	AM ACETATE 1		AM ACETATE 2		
ELEMENT	PPM	MEQ/L	PPM	MEQ/L	
Ca	698	34.90	481	24.05	
Mg	71	5.84	59	4.85	
Sr	2.48	0.06	2.04	0.05	
Na	23.7	1.03	22.6	0.98	
K	1780	45.52	1220	31.20	
MEQ/L SUM		87.35		61.13	
V added (mL)	1000		500		
V residue (mL)	181		11.9		
V total (mL)	1000		681		
MILLIEQ		87.35		25.82	CEC
MEQ/100 g		3.64		1.08	4.72
					EXCH Sr
Sr(mg/kg)	1.03		0.39		1.43
Ca (mg/kg)	291		84		
Ca/Sr	281		214		

Exchangeable cations and cation exchange capacity (CEC) for Column 1 residue cobble fraction (0.25 - 2 inch). CEC in meq/100g; exchangeable Sr and Ca in mg/kg.

5.5 RESULTS OF EXCHANGEABLE STRONTIUM TESTS

An initial test was performed on a sample of Ringold E sediment. The analysis yielded 7.3 mg/kg exchangeable Sr. However, it was unknown what the distribution of exchangeable Sr was between the sands and cobbles in the sample. Therefore, an additional sample of Ringold E was screened to separate the sand fraction (< ¼ inch) from the cobble fraction (> ¼ inch). The size distribution showed 32% sand and 68% cobbles by weight. Separate tests were performed on each of the fractions. These tests showed 8.25 mg/kg Sr in the < ¼ inch fraction and 4.77 mg/kg Sr in the > ¼ inch fraction. (The > ¼ inch fraction actually contained about 10% fines showing after washing and tumbling during the procedure). Therefore, the sand fraction contributed 8.25 × 0.32 = 2.64 mg/kg Sr, and the cobbles contributed 4.77 × 0.68 = 3.24 mg Sr for a total of 5.88 mg/kg Sr in the second sample.

To cross-check the first analysis, the first sample was dried and screened. The screening showed that the original sample contained 62% sand and 38% cobbles by weight. Using the values of Sr concentrations as found for the second sample, that would yield 8.25 × 0.62= 5.12 mg/kg Sr plus 4.77 × 0.38 = 1.81 mg/kg Sr for 6.93 mg/kg Sr total, about 5% lower than the previous measurement (7.3 mg/kg).

The dry weight of the sediment in Column 1a was found to be 16.4 kg. The size distribution in Column 1a showed 35% sand and 65% cobbles. For Column 1a, the expected Sr content was 8.25 × 0.35 = 2.89 mg/kg Sr plus 4.77 × 0.65 = 3.10 mg/kg Sr for a total of 5.99 mg/kg Sr in the column. Therefore, Column 1a should have contained 16.4 kg × 5.99 mg/kg Sr = 98.2 mg exchangeable Sr before being flushed with the lixiviant solution. The sum of the effluent concentrations times volume increments for Column 1a showed 73.4 mg Sr removed. From these measurements, the calculated removal efficiency of the lixiviant is 74.7%.

A test was performed on the residue from Column 1a in an attempt to cross-check the calculated removal efficiency. The residue from Column 1a showed 2.47 mg/kg Sr in the sand and 1.43 mg/kg Sr in the cobbles. Thus the fines contributed 2.47 × 0.35 = 0.86 mg/kg Sr, and the cobbles contributed 1.43 × 0.65 = 0.93 mg/kg Sr for a total of 1.79 mg/kg Sr in the residue. That would make the 1.79 mg/kg residue represent 1.79/5.99 = 29.9% of the Sr left behind by the treatment, for a removal efficiency of 70.1%.

The residue from Column 1b was then dried and screened. The dry weight of the sediment was approximately 16.5 kg with size distribution of 38% sand and 62% cobbles. By using the previously determined exchangeable Sr concentrations for these size fractions, the estimated total for Column 1b would be: 8.25 × 0.38 = 3.13 mg/kg Sr plus 4.77 × 0.62 = 2.96 mg/kg Sr for a total of 6.09 mg/kg. Therefore, the estimated total exchangeable Sr in Column 1b would be 6.09 mg/kg × 16.5 kg = 100.5 mg Sr. The sum of the effluent concentrations times volume increments for Column 1b showed 104.7 mg Sr removed. Thus, the calculated removal efficiency for the lixiviant in Column 1b is 104.2%.

5.6 CONCLUSIONS

The determination of exchangeable Sr and lixiviant removal efficiency for Ringold E sediments are challenging tasks due to the wide range of particle size present. Given the agreement of values for exchangeable Sr found by the whole sample and size fractionated methods, we feel confident that the

values of exchangeable Sr for sand and cobbles are representative of our samples as a whole. Also, good agreement was found by two separate methods for determining the lixiviant removal efficiency for Column 1a.

The lixiviant had a calculated removal efficiency of 89.5% for the whole of Column 1. The cause of the variation in removal efficiency between Column 1a and 1b is unknown. However, it is not unreasonable to suspect that zones of low flow could have occurred within the columns due to the heterogeneity of particle size in the samples. Lixiviant contact within a low-flow zone would be less, thereby lowering the removal efficiency.

6. TOTAL ANALYSIS OF COLUMN INFLUENTS AND EFFLUENTS

6.1 INTRODUCTION

Two influent solutions and two effluent solutions from a column leaching test of Ringold formation sediment were submitted for total analysis to MSE-HKM Laboratory in Butte, Montana. The influent solutions were:

AGW –artificial groundwater used to wash the column before and after lixiviant addition,

KB –the influent lixiviant solution,

SC1B18 –a composite of effluent samples taken close to the Sr peak, and

SC1BW28 –a composite of effluent samples taken near the end or tail of the wash cycle.

Each of the samples was analyzed by ICP for a suite of metals and individually for various major anions, including chloride, nitrate, sulfate, and alkalinity.

6.2 CHARGE BALANCE

Results of the analyses were examined in several perspectives. First, the cation vs. anion charge balance was calculated by converting all mg/L measurements to meq/L and summing the cation charges separately from the anion charges. Cations considered were Na, K, Ca, Mg, and Sr. These were compared to chloride, nitrate, sulfate, and alkalinity. Table 6-1 summarizes the results of this comparison, although it is not as good agreement as is desired. Each of the solutions shows a negative charge imbalance varying from 8% to 17% error.

Table 6-1. Hanford Column 1 total analysis (charge balance).

	AGW		KB INF		PEAK		TAIL	
CATIONS	**mg/L**	**meq/L**	**mg/L**	**meq/L**	**mg/L**	**meq/L**	**mg/L**	**meq/L**
Ca	28.8	1.440	2.84	0.142	513	25.650	4.79	0.240
Mg	3.84	0.316	3.24	0.266	291	23.931	0.3	0.025
Na	3.29	0.143	3.91	0.170	14.2	0.617	0.837	0.036
K	1.75	0.045	18900	484.615	16100	412.821	399	10.231
Sr	0.017	0.000	0.007	0.000	6.68	0.154	0.022	0.001
ANIONS								
Cl	4	-0.113	17000	-478.873	18000	-507.042	30	-0.845
SO4	14	-0.286	78	-1.592	48	-0.980	15	-0.306
NO3	0.52	-0.008	0.59	-0.010	1.19	-0.019	0	0.000
HCO3	92	-1.840	2240	-44.800	226	-4.520	561	-11.220
IMBALANCE		-0.303		-40.081		-49.389		-1.839
CATION TOTAL		1.944		485.194		463.172		10.532
% IMBALANCE		-15.57		-8.26		-10.66		-17.46

Major ionic constituents of solutions for Column 1. AGW is the artificial groundwater wash influent, KB INF is the potassium chloride/bicarbonate lixiviant, and PEAK and TAIL are effluent samples.

6.3 SULFUR ANALYSIS

Next, the sulfate analysis was compared to the total dissolved sulfur value from the ICP. The ICP value is multiplied by 96/32 (=3) to convert to sulfate equivalents; the converted ICP value should be at least as high as the sulfate value since the ICP detects sulfur in all forms, not just sulfate. Table 6-2 shows this not to be the case; ICP estimates of total sulfur are far lower than expected from sulfate analysis.

Table 6-2. Comparison of ICP and chemical sulfate analysis of Column 1 solutions (mg/L).

	ICP	ICP	CHEM
Solution	Sulfur	Sulfate	Sulfate
Agw	2.88	8.64	14
Wash Eff	2.57	7.71	15
Kb Inf	2.67	8.01	78
Leach Eff	2.91	8.73	46

6.4 ARTIFICIAL GROUND WATER ANALYSIS

Artificial ground water was prepared in the laboratory to have the composition shown as "PREP" in Table 6-3 and is reported by the analysis to have the composition shown as "FOUND" in Table 6-3.

Table 6-3. Artificial groundwater assay vs. target composition (mg/L).

SOLUTE	PREP	FOUND
Ca	23	28.8
Mg	4	3.84
Na	3.3	3.29
K	1.6	1.75
Sr	0	0.017
Cl	1	< 5
NO3	2.8	0.52
SO4	8.6	14
ALK	75	92

6.5 LIXIVIANT INFLUENT ANALYSIS

The KB lixiviant solution was prepared in the laboratory to be 0.500M in KCl and 0.050M in $KHCO_3$, yielding a total potassium concentration of 0.550M (21,505 mg/L), chloride concentration of 0.500M (17,730 mg/L), and bicarbonate concentration of 0.050M (2500 mg/L as $CaCO_3$). A small amount of Ca, Mg, Na, and Sr was also present. Analytical values are compared to these values in Table 6-4.

Table 6-4. Column 1 lixiviant assay vs. target composition. (mg/L).

SOLUTE	PREP	FOUND
K	21500	18900
Cl	17730	17000
ALK	2500	2240

6.6 LIXIVIANT INFLUENT VS. EFFLUENT

Comparison of influent potassium chloride-bicarbonate lixiviant solution to effluent leachate at the peak of leaching activity (Table 6-5) showed the effluent to be slightly decreased in potassium ion and slightly increased in chloride ion, while the effluent was greatly depleted of bicarbonate ion. The decrease in potassium is reasonable as the potassium ion was displacing calcium, magnesium, sodium, barium, lithium, and Sr from the exchange sites on the clays as seen by the increases in the concentrations of these cations. The decrease in bicarbonate is reasonable from the standpoint that calcium and magnesium mobilized from the clays were free to react with the bicarbonate forming insoluble salts. This led to the overall decrease in ionic charge of the effluent compared to the influent.

Table 6-5. Column 1 assays of influent lixiviant compared to leach solution effluent (mg/L).

SOLUTE	INF LIX	EFF LEACH
Ca	2.84	513
Mg	3.24	291
Na	3.91	14.2
K	18900	16100
Sr	<0.007	6.68
Cl	17000	18000
NO3	0.59	1.19
SO4	78	46
ALK	2240	228
CAT EQ	485	463
Fe	0.14	0.11
Ce	<0.15	0.25
Sn	0.2	<0.12
Tl	<0.08	0.1
V	<0.017	0.025
Si	0.15	11.5

The trace elements cerium, thallium, and vanadium also appeared in the effluent and were absent in the influent, while tin was present in the influent but absent in the effluent. As expected, silicon appeared in the effluent at greater concentration than at the influent as the influent was made up from laboratory chemicals and the effluent contacted siliceous materials in the column. Notably, iron appeared at quite similar levels in the influent and effluent.

6.7 WASH INFLUENT VS. EFFLUENT

Comparing the AGW influent to the column wash effluent (Table 6-6) shows the effluent ions to be largely potassium bicarbonate and some chloride. The total charge of cations is 6 times greater in the effluent than in the influent. The lowered values of calcium, magnesium, sodium, and Sr show that these cations in the influent are being displaced by potassium ions on the clay sites. I do not know why the bicarbonate is so much higher than the chloride; I expected the ratio of chloride to bicarbonate to increase, as it did for the effluent during active leaching, since the wash should still be releasing some lixiviant solution from the interstices of the particles.

Table 6-6. Column 1 assays of wash influent compared to wash effluent (mg/L).

SOLUTE	INF (AGW)	EFF
Ca	28.8	4.79
Mg	3.84	0.3
Na	3.29	0.837
K	1.75	399
Sr	0.017	0.022
Cl	< 5	30
NO3	0.52	< 0.06
SO4	14	15
ALK	92	561
CAT EQ	1.94	10.5
Fe	0.014	0.014
Cu	0.003	< 0.002
Zn	0.039	< 0.01
As	< 0.03	0.1
Pb	< 0.02	0.03
Li	< 0.0009	0.002
Sn	< 0.02	0.09
V	< 0.003	0.026
Ba	0.002	0.03
P	0.08	1.4
Si	< 0.009	17.9

Some trace elements (Al, Cu, Zn) were seen in the influent but absent in the effluent. In addition, some trace elements (As, Pb, Li, Sn, and V) were seen in the effluent but not seen in the influent. Ba, P, and Si were increased in the effluent over the influent. Strontium in the effluent was slightly greater than Sr in the influent in this composite; discreet samples taken at the end of the wash cycle showed effluent Sr to be much lower than influent Sr.

7. ESTIMATION OF DESORPTION ISOTHERM

7.1 INTRODUCTION

The column tests described above were designed to measure the effectiveness of mobilizing strontium adsorbed on the sediments. Both potassium salts effectively eluted the great majority of alkaline earth metals (i.e., calcium, magnesium, and strontium) on the exchange sites. The column tests were not designed with the goal of deriving a complete desorption isotherm from the effluent data. In the following discussion, an estimate of the desorption isotherm is attempted from the available data. Also, an estimate is made of the exchange constants for these reactions based on the analysis of the effluent solutions.

The calculations made herein follow the recommendations of Griffloen, et al (Ref. [4]); however, it is necessary to state that there was no intention of applying this method of calculation when the column test parameters were designed, so the columns do not exactly meet the criteria specified by Griffloen. In particular, we were seeking only the elution and tracking of strontium from the column, though calcium, magnesium, and potassium were also tracked. The mathematical development by Griffloen assumed a binary system (one chemical species displacing another); however, we had at least three elements being displaced by the potassium. Consequently, all the eluted cations were aggregated to obtain an isotherm descriptive of all the alkaline earth elements instead of strontium alone.

The development by Griffloen also assumed a constant normality of eluant and eluate at all points in the column. That is, after the initial washing, the influent potassium concentration was assumed constant, and no other side reactions took place to affect the total solution concentration of the eluted metals. This was not followed exactly by our procedure because the influent concentration varied somewhat and the final few pore volumes used influent formation water to wash out the column. Furthermore, in the column with the bicarbonate, the bicarbonate was intentionally added to precipitate the calcium, reducing the normality of the eluate as that precipitation occurred. Because of the nonconformity of the calcium ion behavior to the stated criterion, an estimated calcium concentration was calculated that would be expected if there had been no precipitation. This was done by computing an average ratio of calcium concentration to strontium concentration in the effluent of the citrate column (502 on a molar basis) and multiplying each individual strontium concentration in the bicarbonate column by that ratio to estimate the probable calcium concentration. While this practice is not highly defensible, it was the one recourse we saw for estimating the isotherm given the deviations from ideality that were experienced.

7.2 CALCULATION OF THE ISOTHERM

Griffloen defined *isotherm* as the graph of adsorbed concentration vs. aqueous concentration of the same chemical species. To simplify the procedure, Griffloen defined the concentrations in relative terms with the following: $\alpha = c/c_T$ expressing the aqueous concentration as the ratio of the measured normal concentration to the normality of the influent solution (assuming ionic normality is constant throughout the exchange process); β expresses the adsorbed concentration of the same chemical species compared to the CEC of the medium with the added simplification that the adsorbed concentration was in terms of effective aqueous concentration if all were desorbed. That is, $q_T = CEC\ \rho/\theta$, where q_T is the effective solution concentration in eq/L, if all adsorbed ions went into solution; CEC is the cation exchange capacity in eq/Kg; ρ is the bulk density of the soil; and θ is the porosity of the soil.

Griffloen performed calculations of the isotherm both with and without the consideration of dispersion. It is a superior technique to consider dispersion in the calculations; however, there was not enough information for us to do so. Consequently, we used the development that excluded dispersion as an option.

The nondispersion equations of relevance here are

1) $n = (q_T/c_T)(\partial\beta/\partial\alpha)$,

where n is the number of pore volumes after breakthrough of the eluant, q_T is the adsorption limit described above, and c_T is the normality of the eluate.

2) $\beta = \beta_o + c_T/q_T \int n d\alpha = \beta_o + 1/q_T \int n dc$,

where c is the sum of the normal concentrations of the alkaline earth ions, and β_o is the original adsorbed amount of alkaline earth ions (assumed to saturate the exchanger and so = q_T). β represents the amount adsorbed at any particular value of n; therefore, the integral term represents the amount of previously adsorbed material that has been eluted or flushed from the column.

3) $K = [\beta(1-\alpha)]/[\alpha(1-\beta)]$,

where K is the cation exchange selectivity coefficient for the alkaline earth elements compared to potassium.

Our data consisted of measurements of mg/L concentrations of Ca, Mg, Sr, and K vs n (number of pore volumes). To carry out the previous calculations, our concentrations were converted to meq/L by dividing by equivalent weights; adding the Ca, Mg, and Sr into one lump SUM EQ; converting the potassium values to meq/L and adding that to the SUM EQ to obtain our "constant" normality for each pore volume sample; and then computing α by dividing SUM EQ by the constant normality.

To conduct the integration required by Equation 2, the difference in SUM EQ (= Δc) between two successive pore volume measurements was computed and multiplied times the pore volume number (since breakthrough). Those products were added over the entire range of pore volumes for which the potassium salt was the influent. To obtain q_T (= β_o), 100% efficiency in removal of the alkaline earth cations was assumed and added SUM EQ over the entire range of measurements, including the washes.

7.3 RESULTS OF ISOTHERM ESTIMATION

Calculations of the isotherm and selectivity coefficient for the citrate column are shown in Table 7-1. The isotherm itself is plotted in Figure 7-1a, and the corresponding elution curve is shown in Figure 7-1b.

Calculations of the isotherm and selectivity coefficient for the chloride/bicarbonate column are shown in Table 7-2. The isotherm is plotted in Figure 7-2a, and the corresponding elution curve is shown in Figure 7-2b.

Table 7-1. Potassium citrate effluent concentrations, etc.

SAMPLE	INF VOL	n	Sr (ppm)	Ca (ppm)	Mg (ppm)	K (ppm)	Sr EQ	Ca EQ	Mg EQ	K EQ	SUM EQ	DEL SUM	N (DEL SUM)	INTEGRAL		BETA	ALPHA	BETA	K	N	ALPHA
CO2KC1	17700	3.07	24.6	4360	1780	779	0.559	218	146.4	20.0	364.9										
CO2KC2	18270	3.17	23.3	3860	1720	1290	0.530	193	141.4	33.1	335.0	-30.0	-5.0	5.0	365.0	0.987	0.910	0.987	7.23	0.07	0.910
CO2KC3	18850	3.27	24.4	3870	1760	2210	0.555	193.5	144.7	56.7	338.8	3.8	1.0	4.0	366.0	0.989	0.857	0.989	15.43	0.17	0.857
CO2KC4	19150	3.32	24.3	3310	1650	3870	0.552	165.5	135.7	99.2	301.7	-37.0	-11.8	15.8	354.2	0.957	0.753	0.957	7.38	0.27	0.753
CO2KC5	19700	3.41	23.7	2310	1320	10700	0.539	115.5	108.6	274.4	224.6	-77.2	-32.0	47.7	322.3	0.871	0.450	0.871	8.25	0.32	0.450
CO2KC6	20250	3.51	18.8	1990	711	15500	0.427	99.5	58.5	397.4	158.4	-66.2	-33.7	81.5	288.5	0.780	0.285	0.780	8.89	0.41	0.285
CO2KC7	20800	3.60	14	1710	481	15800	0.318	85.5	39.6	405.1	125.4	-33.0	-20.0	101.4	268.6	0.726	0.236	0.726	8.55	0.51	0.236
CO2KC8	21350	3.70	11.4	1500	377	17200	0.259	75	31.0	441.0	106.3	-19.1	-13.4	114.8	255.2	0.690	0.194	0.690	9.22	0.60	0.194
CO2KC9	22400	3.88	9.5	1370	292	20000	0.216	68.5	24.0	512.8	92.7	-13.5	-11.9	126.8	243.2	0.657	0.153	0.657	10.61	0.70	0.153
CO2KC10	23450	4.06	7.32	1060	206	16100	0.166	53	16.9	412.8	70.1	-22.6	-24.1	150.8	219.2	0.592	0.145	0.592	8.56	0.88	0.145
CO2KC11	24540	4.25	6.21	913	168	16300	0.141	45.65	13.8	417.9	59.6	-10.5	-13.2	164.0	206.0	0.557	0.125	0.557	8.81	1.06	0.125
CO2KC12	25590	4.44	5.25	784	134	16700	0.119	39.2	11.0	428.2	50.3	-9.3	-13.3	177.3	192.7	0.521	0.105	0.521	9.25	1.25	0.105
CO2KC13	26800	4.64	4.83	722	113	16900	0.110	36.1	9.3	433.3	45.5	-4.8	-8.0	185.2	184.8	0.499	0.095	0.499	9.50	1.44	0.095
CO2KC14	28900	5.01	4.2	628	88.1	17700	0.095	31.4	7.2	453.8	38.7	-6.8	-13.6	198.8	171.2	0.463	0.079	0.463	10.09	1.64	0.079
CO2KC15	29950	5.19	3.81	556	78.2	17500	0.087	27.8	6.4	448.7	34.3	-4.4	-9.7	208.5	161.5	0.436	0.071	0.436	10.13	2.01	0.071
CO2KC16	31580	5.47	3.12	446	65.6	17100	0.071	22.3	5.4	438.5	27.8	-6.6	-16.2	224.7	145.3	0.393	0.060	0.393	10.21	2.19	0.060
CO2KC17	35580	6.17	3.03	386	72.5	17500	0.069	19.3	6.0	448.7	25.3	-2.4	-7.7	232.4	137.6	0.372	0.053	0.372	10.48	2.47	0.053
CO2KC18	37550	6.51	3.45	401	91.9	17400	0.078	20.05	7.6	446.2	27.7	2.4	8.3	224.2	145.8	0.394	0.058	0.394	10.48	3.17	0.058
CO2KC19	39700	6.88	3.12	341	93.3	19300	0.071	17.05	7.7	494.9	24.8	-2.9	-11.2	235.4	134.6	0.364	0.048	0.364	11.41	3.51	0.048
CO2KC20	42200	7.31	1.64	167	42.1	19700	0.037	8.35	3.5	505.1	11.8	-12.9	-55.8	291.2	78.8	0.213	0.023	0.213	11.53	3.88	0.023
CO2KC21	44520	7.72	0.96	124	25.9	19800	0.022	6.2	2.1	507.7	8.4	-3.5	-16.5	307.7	62.3	0.168	0.016	0.168	12.30	4.31	0.016
CO2KC22	47090	8.16	0.76	121	24.2	19700	0.017	6.05	2.0	505.1	8.1	-0.3	-1.5	309.2	60.8	0.164	0.016	0.164	12.32	4.72	0.016
CO2KC23	50020	8.67	0.68	117	23.8	20300	0.015	5.85	2.0	520.5	7.8	-0.2	-1.3	310.6	59.4	0.161	0.015	0.161	12.73	5.16	0.015
CO2KC24	54070	9.37	0.64	116	23.4	20000	0.015	5.8	1.9	512.8	7.7	-0.1	-0.5	311.1	58.9	0.159	0.015	0.159	12.54	5.67	0.015
CO2KC25	55810	9.67	0.48	102	20.7	15100	0.011	5.1	1.7	387.2	6.8	-0.9	-6.2	317.3	52.7	0.142	0.017	0.142	9.44	6.37	0.017
CO2KC26	56750	9.84	0.44	96.1	20.7	12000	0.010	4.805	1.7	307.7	6.5	-0.3	-2.0	319.3	50.7	0.137	0.021	0.137	7.50	6.67	0.021
CO2W1	57300	9.93	0.34	79.5	17.5	8200	0.008	3.975	1.4	210.3	5.4	-1.1	-7.6	326.9	43.1	0.116	0.025	0.116	5.11	6.84	0.025

n = number pore volumes from beginning of test
N = number of pore volumes since breakthrough of potassium citrate
N = n - 3.0
qT = bo = 370

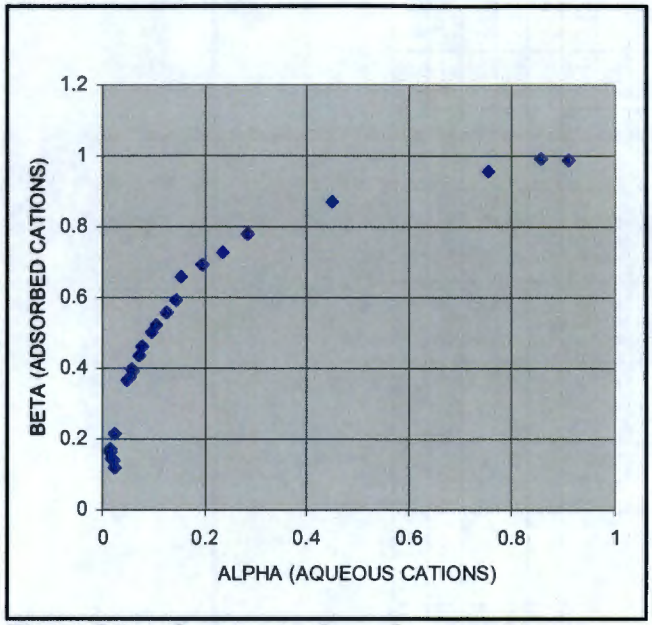

Figure 7-1a. Sorption isotherm for potassium citrate/alkaline earths.

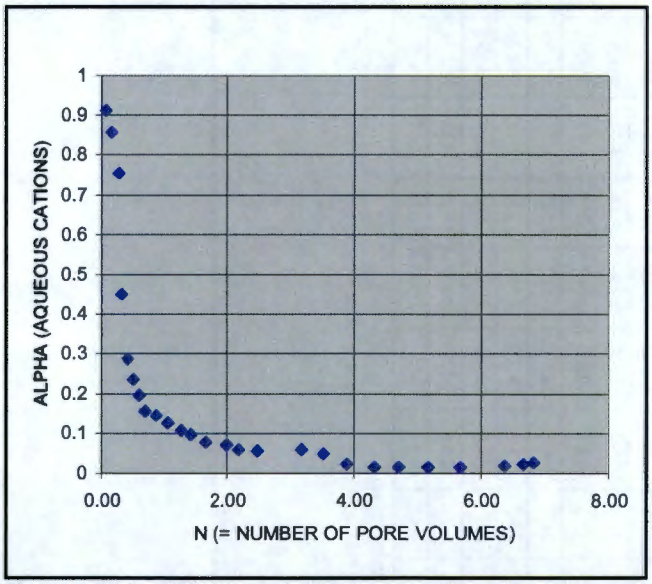

Figure 7-1b. Elution of alkaline earth cations by potassium citrate.

Table 7-2. Potassium chloride column effluent concentrations, etc.

SAMPLE	INF VOL	n	Sr (ppm)	Ca (ppm)	Mg (ppm)	K (ppm)	Sr EQ	Ca EQ	Mg EQ	K EQ	SUM EQ	DEL SUM	N (DEL SUM)	INTEGRAL		BETA	ALPHA	BETA	K	N	ALPHA
CO1BKB6	32860	4.38	6.38	1120	481	35.4	0.145	56	39.56	0.91	72.79										
CO1BKB7	34490	4.60	34.1	5490	1840	182	0.775	274.5	151.32	4.67	389.05	159.73	0.00	0.00	166.00	1.000	0.988	1.000		0.00	0.988
CO1BKB8	37540	5.01	20.1	2290	632	12000	0.457	114.5	51.97	307.69	229.32	174.56	70.75	70.75	95.25	0.574	0.427	0.574	1.8	0.41	0.427
CO1BKB9	40540	5.41	4.8	301	162	16900	0.109	15.05	13.32	433.33	54.76	28.29	22.79	93.54	72.46	0.436	0.112	0.436	6.1	0.81	0.112
CO1BKB11	43440	5.79	2.32	131	75.1	18300	0.053	6.55	6.18	469.23	26.47	6.85	8.16	101.70	64.30	0.387	0.053	0.387	11.2	1.19	0.053
CO1BKB12	46190	6.16	1.72	101	56	17600	0.039	5.05	4.61	451.28	19.62	6.39	9.96	111.66	54.34	0.327	0.042	0.327	11.2	1.56	0.042
CO1BKB13	50790	6.77	1.16	71.4	36.7	17900	0.026	3.57	3.02	458.97	13.23	4.68	10.16	121.82	44.18	0.266	0.028	0.266	12.6	2.17	0.028
CO1BKB14	57900	7.72	0.75	42.5	24.1	17800	0.017	2.125	1.98	456.41	8.56	2.40	7.48	129.29	36.71	0.221	0.018	0.221	15.1	3.12	0.018
CO1BKB16	63810	8.51	0.54	31.7	18.7	20200	0.012	1.585	1.54	517.95	6.16	0.68	2.68	131.97	34.03	0.205	0.012	0.205	21.7	3.91	0.012
CO1BKB18	72475	9.66	0.48	24.7	15.7	18300	0.011	1.235	1.29	469.23	5.48	0.00	0.00	131.97	34.03	0.205	0.012	0.205	22.1	5.06	0.012
CO1BKB19	78550	10.47	0.48	32	14.5	17900	0.011	1.6	1.19	458.97	5.48	4.56	26.80	158.77	7.23	0.044	0.012	0.044	3.8	5.87	0.012
CO1BKB20	92330	12.31	0.08	6.34	2.56	6330	0.002	0.317	0.21	162.31	0.91	0.80	6.16	164.93	1.07	0.006	0.006	0.006	1.2	7.71	0.006
CO1BW1	98380	13.12	0.01	1.42	0.34	456	0.000	0.071	0.03	11.69	0.11	0.11	0.97	165.90	0.10	0.001	0.010	0.001	0.1	8.52	0.010

n = number pore volumes from beginning of test
N = number of pore volumes since breakthrough of potassium chloride
N = n – 4.6
qT =bo = 166

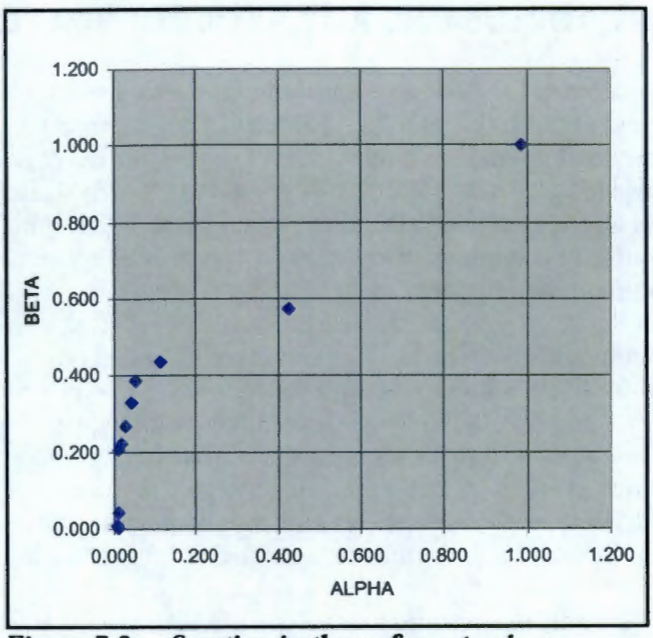

Figure 7-2a. Sorption isotherm for potassium chloride/alkaline earths.

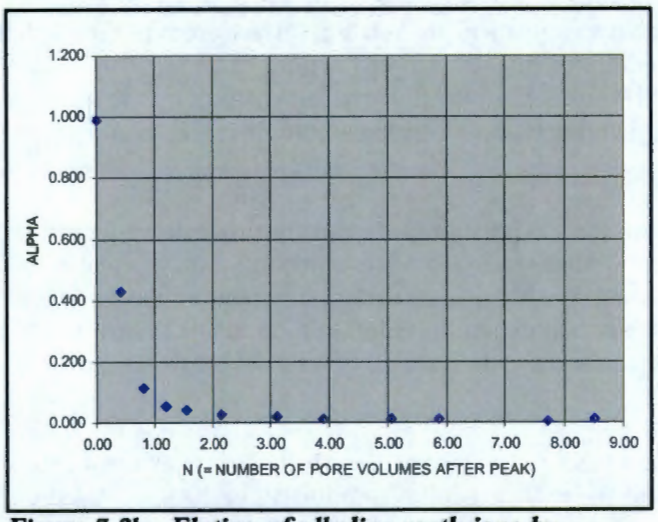

Figure 7-2b. Elution of alkaline earth ions by potassium chloride.

8. CONCLUSIONS AND RECOMMENDATIONS

The Ringold "E" sediments used for these tests appear to have geochemical characteristics that are very similar to those found in the 100-N area. Of particular importance is the fact that the equilibrium concentration of Sr in the column effluents after the first flushes with AGW (approximately 0.2 mg/L) is very similar to Sr concentrations in the 100-N area groundwater. The Ca to Sr ratio in the tests (approximately 180:1) is also very similar to the ratio found in the 100-N groundwater. Therefore, these tests are representative of conditions (with the exception of Sr90 contamination) that will be found within the 100-N groundwater system.

For each of the column tests, relatively higher concentrations of Sr and other cations appeared in the initial effluent. As more AGW was flowed through the columns, the ionic concentrations dropped steadily. This phenomenon is attributed to the presence in the soil samples of soluble salts. Since these sediment samples were taken from an area that was exposed to the atmosphere, it is likely that some weathering of the minerals has transpired, making the salts available to aqueous leaching. These soluble ions are mobilized without the necessity of exchange processes. It would not be expected that soils taken from beneath the water table (within the saturated zone) would exhibit this behavior.

Both potassium lixiviant systems removed exchangeable Sr in the range of 160 mg to 200 mg from the 35 kg of material in their respective columns. Given the fact that the greater than 2-inch material was excluded from the column test, the minus ¾ inch material in the columns makes up 38% of the total. Our estimate of exchangeable Sr in the minus ¾ inch fraction is 9 mg/kg or approximately 120 mg per column. Although the amount of exchangeable Sr on the material between ¾ inch and 2 inches in size was not determined, a rough estimate of the relative surface areas of the particles indicates that an additional 40 mg Sr is contributed by the larger fraction. This calculation does not account for some additional Sr that should be present in the fine-grained coatings on the larger gravels and cobbles. Nonetheless, it appears that nearly all the exchangeable Sr in the columns was removed by the potassium lixiviants.

Both the potassium citrate and the potassium chloride/bicarbonate systems effectively diminished the effluent concentration of Sr after removing a large amount of exchangeable Sr from the sediment. The potassium chloride/bicarbonate system also substantially reduced the amount of calcium mobilized along with the Sr. Of the two systems, the chloride/bicarbonate system is far cheaper to implement, given that potassium citrate is approximately 20 times as expensive as potassium chloride, on an equivalent weight basis.

It is apparent that the ClaStaXP did not act as effectively as the potassium citrate in the removal of Sr and that it did not seal off the exchange sites from further exchange. Based on this test, we would not recommend use of ClaStaXP for remediation of the Sr90 problem at Hanford.

It would be beneficial to do another set of batch tests followed by column tests to see if the potassium chloride/bicarbonate system can be optimized. The citrate system may also be improved by lowering the influent potassium citrate concentration. It would also be of value to test use of both potassium lixiviants in series to determine if those configurations are more efficient.

The purpose of the column tests was to determine the feasibility of mobilizing major amounts of Sr from the soil into the effluent solution with the selected lixiviants and concurrently estimate the fraction of Sr released and the number of pore volumes of lixiviant required to accomplish that task. Therefore, the tests were successful.

9. REFERENCES

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