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Radionuclide Reactions With Groundwater and Basalts From Columbia River Basalt Formations

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ABSTRACT

Chemical reactions of radionuclides with geologic materials found in Columbia River basalt formations were studied. The objective was to determine the ability of these formations to retard radionuclide migration from a radioactive waste repository located in deep basalt. Reactions that can influence migration are precipitation, ion-exchange, complexation, and oxidation-reduction. These reactions were studied by measuring the effects of groundwater composition and redox potential (Eh) on radionuclide sorption on fresh basalt surfaces, a naturally altered basalt, and a sample of secondary minerals associated with a Columbia River basalt flow. In addition, radionuclide sorption isotherms were measured for these materials and reaction kinetics were determined. The radionuclides studied were ^{137}Cs, ^{85}Sr, ^{75}Se, ^{95m}Tc, ^{237}Np, ^{241}Am, ^{226}Ra and ^{237}Pu. The Freundlich equation accurately describes the isotherms when precipitation of radionuclides does not occur. In general, sorption increased in the order: basalt < altered basalt < secondary minerals. This increase in sorption corresponds to increasing surface area and cation exchange capacity. The Eh of the system had a large effect on technetium, plutonium, and neptunium sorption. Technetium(VII), Pu(VI), and Np(V) are reduced to Tc(IV), Pu(IV), and Np(IV), respectively, under Eh conditions expected in deep basalt formations.

The kinetics of radionuclide sorption and basalt-groundwater reactions were observed over a period of 18 weeks. Most sorption reactions stabilized after about four weeks. Groundwater composition changed the least in contact with altered basalt. Contact with secondary minerals greatly increased Ca, K, and Mg concentrations in the groundwater.

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INTRODUCTION

The suitability of Columbia River basalts as a site for disposal of high-level radioactive wastes depends partly on the ability of these formations to retard radionuclide migration. The host rock formation is the final barrier to migration if engineered barriers are breached. The flow path for contaminated groundwater from a basalt high-level waste repository would likely include fissures and porous interbeds. The dissolved radionuclide would interact with basalt and minerals lining the fissures and in the interbeds retarding their movement by sorption or precipitation.

Studies of radionuclide sorption on Columbia River basalts and related geologic solids found in these formations are reviewed and summarized by Smith, et al. (1980). Effects of temperature, redox potential, and different sources of basalt on radionuclide distribution between groundwaters and basalts are reported. Much additional information is required to understand and predict radionuclide behavior in these complex systems.

The objective of the present study is to determine the effects of chemical and physical parameters on sorption of key radionuclides on basalt, naturally altered basalt, and secondary minerals found in basalt formations. These parameters include groundwater compositions, redox potential, radionuclide concentration, and rates of sorption/desorption and rock-groundwater reactions. This information can be used to better understand reactions and mechanisms controlling sorption. Mechanistic information which can be derived from this work includes the following:

- Competition for sorption sites between radionuclides and major ions in the groundwater.
- Formation of complexes between groundwater components and radionuclides.
- Oxidation states of multi-valent radionuclides.
- Precipitation limits for insoluble compounds of the radionuclides.
- Bonding of the radionuclide on the solid by ion exchange or

coordination.

- o Dissolution and precipitation of components of the solid-groundwater system.

In this paper, radionuclide sorption/desorption reactions will be described by studying the effects of groundwater components and Eh on sorption, measurement of radionuclide sorption isotherms, and studying the kinetics of sorption and solid-groundwater reactions. The radionuclides chosen for study are those shown previously (Barney and Wood, 1980) to be the most significant over the long time periods required for disposal (Pu, Am, Np, Tc, Cs, Sr, Ra, and Se).

EXPERIMENTAL

Materials

Basalt from the Grande Ronde formation was selected for use in these experiments. The Grande Ronde is considered a possible location for construction of a repository. The sample was obtained from an outcropping at Sentinel Gap, Washington and was crushed and sieved to 20-50 mesh. The characteristics of this material have been described by Ames (1978). It is a fine-grained, glassy basalt with three major mineral phases - labradorite, augite, and magnetite.

Samples of naturally altered basalt were obtained during mining operations at the Hanford Near Surface Test Facility (NSTF). They are from the top of the Pomona basalt flow and contain roughly 40 percent by volume vesicles and vugs. These openings are filled with a distinctive secondary mineral assemblage. Vugs are filled with either a light brown tuff or a clay-rich alteration (a yellow to red-brown "nontronite"). Vesicles are filled with tuff, yellowish-brown clays, or, most abundant, a yellowish-white "clay" which may be a mixture of kaolinite, silica, and smectite. The basalt consists of plagioclase and clinopyroxine phenocrysts in a groundmass largely altered to red-brown clay. Samples of this material were crushed and wet sieved to 0.5-10 mm particle size.

The secondary mineral sample was obtained from a large vug in the Pomona basalt flow during excavation of the NSTF. Basalt fragments were removed from the clay vug-filling and the remainder was homogenized and freeze-dried. The main crystalline component of this blue-green material appears to be a smectite clay. Characteristics of these three materials are summarized in Table I.

TABLE I. Characteristics of Geologic Materials

Charateristic	Basalt	Altered Basalt	Secondary Minerals
1. Particle size	0.3-0.9mm	0.5-1.0mm	<0.002mm
2. Surface area, m^2/g			
BET	2.5	--	--
Glycerol	10.3	--	646 ± 19
3. Cation exchange capacity, meq/100g	4.7 ± 0.2	23.7 ± 2.3	75.6 ± 0.7
4. Color	black	yellow-brown	blue-green
5. Major minerals	labradorite augite andesine ilmenite nontronite magnetite	plagioclase pyroxine clay tuff	smectite clay

Synthetic groundwaters were prepared, based on analyses of two groundwater types. The first is a sodium bicarbonate groundwater typical of the upper aquifers, but greatly simplified (no Si or anions other than HCO_3^-). The second has a composition similar to that of samples obtained from the Grande Ronde basalt formation. Their compositions are given in Table II.

Radioactive tracers were used to measure the distribution of radionuclides between groundwaters and solids. Cesium-137, ^{85}Sr, and ^{75}Se, were obtained from New England Nuclear as analyzed isotopic standards. Plutonium-237, ^{238}Pu, and ^{95m}Tc were prepared

TABLE II. Composition of Synthetic Groundwaters

Component	Concentration, mg/l, Upper Aquifer	Concentration, mg/l, Grande Ronde #2
Na^+	100	246
K	0.5	2.51
Ca^{2+}	0.4	1.01
$CO_3^{2-}+HCO_3^-$	265	65.4
$H_3SiO_4^-$	0	82
Cl^-	0	152
SO_4^{2-}	0	108
F^-	0	37.1
	pH=8.2	pH=10.0

by Argonne National Laboratory. Neptunium-237 and ^{241}Am were obtained through Rockwell Standards Laboratory and analyzed by alpha and gamma spectroscopy for isotopic purity. The ^{226}Ra was purchased from Amersham as a standardized solution.

Procedures

Batch equilibrations of groundwaters, tracers, and geologic solids were used to measure radionuclide distribution. The experimental procedure used for measuring distribution was similar for studying effects of groundwater composition and measuring sorption isotherms. Details of the procedure are as follows: a one gram sample (1.00 ± 0.03 g, 2.00 ± 0.1 g for isotherm measurement) of the geologic solid was added to a 50 ml polycarbonate centrifuge tube. Thirty milliliters of the appropriate unspiked solution was added to the tube and the mixture was gently shaken overnight to pre-equilibrate the system. The tube was then centrifuged and the supernate discarded. This pre-equilibration was repeated and the tube + solid + solution weighed to estimate the volume of residual solution. A spiked groundwater solution was prepared by dissolving a measured amount of solid tracer (obtained by evaporating stock tracer solution) in the solution. The spiked solution was filtered through a 0.3 μm Millipore filter to remove any undissolved solids and then analyzed for tracer concentration. Thirty milliliters of the spiked solution was added to the tube and the mixture was sealed and shaken gently for 14 days. The tube was then centrifuged and the supernate filtered through a 30 Ångstrom Amicon 50A ultra-filter.

Filtrates and, when appropriate, solids were analyzed for tracers using standard counting techniques. Cesium-137, ^{85}Sr, and ^{75}Se were analyzed by gamma spectroscopy using a GeLi detector and ^{95m}Tc and ^{237}Pu by gamma spectroscopy using a NaI well detector. Plutonium-238, ^{241}Am, ^{237}Np and ^{226}Ra were analyzed by measuring total alpha and alpha energy analysis.

The kinetics experiments were performed similarly, except that larger volumes of solutions (300 ml) were used and more of the solids (20 g). Also, the equibrations were carried out for longer time periods. Five milliliter samples were withdrawn weekly from the bottles and filtered through 30 Ångstrom Amicon 50A ultra-filters. Filtrates were analyzed for tracer concentration. Groundwater-geologic solids mixtures without tracers were also equilibrated and sampled as above, but the filtrates were analyzed for metal ion and anion concentrations using an inductively coupled plasma emission spectrometer (Applied Research Laboratory Model 137) and a liquid ion chromatograph (Dionex, Model 10).

RESULTS AND DISCUSSION

Radionuclide sorption reaction mechanisms were studied by determining the effects of groundwater components on sorption, measuring sorption isotherms, and determining the kinetics of sorption/desorption reactions as well as solid-groundwater reactions. The results of these studies are discussed in detail below.

Effects of Groundwater Composition and Redox Potential

The major components of groundwaters found in the Grande Ronde basalt formation are Na^+, Ca^{2+}, K^+, Mg^{2+}, Cl^-, F^-, CO_3^{2-}, HCO_3^-, and SO_4^{2-}. Contaminated groundwater from a deep basalt repository will have a variable chemical composition and redox potential (Eh) as it moves along the flow path. Aquifers at various depths have been observed to have large differences in composition. To accurately model sorption reactions and radionuclide migration, it is necessary to understand the effects of chemical components and Eh on sorption and solubility of key radionuclides.

Because of the large number of variables to be studied, it was necessary to use statistical methods to design the experiments. An efficient design for screening nine variables is the 20-run Plackett-Burman design (Plackett and Burman, 1946). This is a fractional, 2-level, factorial design which is used to identify significant variables. The effect of Eh was examined by adding a chemical redox buffer, hydrazine, as a variable. Hydrazine lowered the Eh from about +0.2 volts (air saturated solution) to about -0.8 volts at pH ≈10.

The Plackett-Burman design requires a high and low value for each parameter. The values were chosen to cover the range of concentrations found in the Grande Ronde formation. Table III compres the values used in the experiment to those actually found in the Grande Ronde aquifers. The design requires preparation of twenty solutions, each with a different combination of components. These compositions are shown in Table IV along with the pH values of each solution. The silicate was added to each solution so that equilibrium silicate concentrations would be approached more rapidly during equilibration. Since the geologic solid will control [SiO_3^{2-}], it was not possible to study it as a variable.

TABLE III

COMPARISON OF EXPERIMENTAL AND MEASURED PARAMETERS

Concentration Parameter	Experimental Range	Measured Range*
Na^+	0.002 to 0.0222 M	0.009 to 0.016 M
K^+	0 to 0.0005 M	0.00001 to 0.0004 M
Ca^{2+}	0 to 0.0001 M	0.00002 to 0.0001 M
Mg^{2+}	0 to 0.00002 M	<0.0000002 to 0.00001 M
Cl^-	0.001 to 0.011 M	0.001 to 0.008 M
F^-	0 to 0.002 M	0.001 to 0.002 M
SO_4^{2-}	0 to 0.003 M	0.0008 to 0.002 M
CO_3^{2-}	0 to 0.001 M	0 to 0.001 M
HCO_3^-	0 to 0.001 M	0 to 0.001 M
SiO_3^{2-}	0.001 M	0.001 to 0.002 M

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*Based on unpublished analyses of Grande Ronde groundwater by T. E. Jones, Rockwell Hanford Operations, Richland, Washington

TABLE IV

TWENTY-RUN SCREENING DESIGN

Concentration (moles/l) of

Soln.*	[NaCl]	[NaF]	$[Na_2SO_4]$	$[Na_2CO_3]$	$[NaHCO_3]$	$[CaCl_2]$	$[MgCl_2]$	[KCl]	$[N_2H_4]$	pH
1	0.01	0.002	0	0	0.001	0.0001	0.00002	0.0005	0	10.3
2	0.01	0	0	0.001	0.001	0.0001	0.00002	0	0.05	10.8
3	0.001	0	0.003	0.001	0.001	0.0001	0	0.0005	0	10.5
4	0.001	0.002	0.003	0.001	0.001	0	0.00002	0	0.05	10.8
5	0.01	0.002	0.003	0.001	0	0.0001	0	0.0005	0	10.9
6	0.01	0.002	0.003	0	0.001	0	0.00002	0	0	10.3
7	0.01	0.002	0	0.001	0	0.0001	0	0	0	10.9
8	0.01	0	0.003	0	0.001	0	0	0	0	10.4
9	0.001	0.002	0	0.001	0	0	0	0	0.05	11.0
10	0.01	0	0.003	0	0	0	0	0.0005	0.05	10.6
11	0.001	0.002	0	0	0	0	0.0002	0.0005	0	10.7
12	0.01	0	0	0	0	0.0001	0.00002	0	0.05	10.9
13	0.001	0	0	0	0.001	0.0001	0	0.0005	0.05	10.6
14	0.001	0	0	0.001	0.001	0	0.00002	0.0005	0	10.6
15	0.001	0	0.003	0.001	0	0.0001	0.00002	0	0	10.9
16	0.001	0.002	0.003	0	0.001	0.0001	0	0	0.05	10.7
17	0.01	0.002	0	0.001	0.001	0	0	0.0005	0.05	10.7
18	0.01	0	0.003	0.001	0	0	0.00002	0.0005	0.05	10.9
19	0.001	0.002	0.003	0	0	0.0001	0.00002	0.0005	0.05	10.7
20	0.001	0	0	0	0	0	0	0	0	10.9

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*In addition, each solution contained 0.001 M Na_2SiO_3.

The experimental design requires 20 measurements of radionuclide distribution for each radionuclide-geologic solid combination. The distribution parameter measured, in most cases, was K_d which is defined as,

$$K_d = \frac{\text{activity in the solid phase/g}}{\text{activity in the groundwater/ml}}$$

The K_d values were used in a statistical analysis of the sorption data. The objective of this analysis was to calculate a value of the "factor effect" for each variable and compare this value with the calculated error. If the absolute value of the factor effect was greater than the error, the corresponding variable was significant.

A factor effect for a given variable is simply the difference between the average K_d value observed when the variable has its high value and the average K_d value when the variable is at its low value. For each variable, there are 10 K_d values corresponding to the high value and 10 K_d values corresponding to the low value. In addition to factor effects, the Plackett-Burman design yields a pooled standard deviation for factor effects which is used to determine significance. The standard deviation is multiplied by the appropriate t value (2.23 for 10 degrees of freedom at the 95% confidence level). This gives the minimum absolute value for the factor effect to be significant at the desired significance level.

Measured K_d values for ^{137}Cs, ^{85}Sr, ^{237}Np, ^{238}Pu, ^{241}Am, ^{95m}Tc, ^{75}Se, and ^{226}Ra are given in Tables 5-12. Initial and final concentrations are also included.

TABLE V

Sorption Data for ^{137}Cs*

Solution	Initial Conc.,μCi/l	Basalt Final Conc.μCi/l	 K_d,ml/g	Altered Basalt Final Conc.μCi/l	 K_d,ml/g	Secondary Minerals Final Conc.μCi/l	 K_d ml
1	779	132	145	6.3	3654	11.7	1927
2	782	102	200	2.5	9133	24.9	890
3	758	121	158	3.5	6432	7.7	2882
4	752	93.5	209	3.1	7318	9.6	2286
5	777	150	124	6.2	3650	13.8	1657
6	732	55.5	362	4.6	4775	8.3	2559
7	759	47.1	449	3.9	5808	6.3	3489
8	769	50.8	424	3.6	6218	10.1	2186
9	806	89.8	236	3.0	7924	9.5	2450
10	760	177	98.5	4.2	5396	48.8	427
11	735	96.3	197	5.3	4154	6.2	3525
12	782	92.6	221	2.6	8890	12.7	1814
13	785	187	95.6	5.7	4131	10.1	2277
14	758	102	189	5.1	4446	4.2	5355
15	764	40.0	537	2.8	8155	4.5	5062
16	796	154	123	4.2	5628	37.4	593
17	796	174	107	3.0	7773	14.6	1603
18	795	187	94.5	4.2	5619	26.3	873
19	798	174	107	3.5	6810	13.0	1773
20	680	21.0	941	2.4	8577	2.8	7360

*To convert cesium concentration to moles/l, multiply by 8.39 x 10^{-11} moles/μCi

TABLE VI

Sorption Data for ^{85}Sr*

		Basalt		Altered Basalt		Secondary Minerals	
Solution	Initial Conc.μCi/l	Final Conc.μCi/l	K_d,ml/g	Final Conc.μCi/l	K_d,ml/g	Final Conc.μCi/l	K_d,ml
1	14810	2141	175	365	1187	559	763
2	15120	1534	250	153	2877	365	1196
3	15870	1696	250	208	2236	299	1470
4	15460	1395	296	184	2418	397	1127
5	16190	2381	174	157	3063	593	756
6	15120	2025	188	431	1022	762	563
7	16180	1508	291	197	2409	385	1192
8	14460	1582	241	400	1054	652	618
9	13290	363	1068	41.7	9253	181	2147
10	17610	2224	194	480	1049	772	643
11	13380	388	984	79.4	4832	145	2736
12	19980	2416	216	90.6	6585	510	1141
13	15060	918	444	84.8	5297	116	3642
14	14200	642	621	67.3	6289	78.2	5258
15	18430	1320	388	188	2553	318	1706
16	6238	1810	74.9	255	696	463	370
17	13510	1219	293	174	2254	358	1097
18	16430	2062	199	340	1391	591	768
19	17300	2200	198	327	1511	488	1029
20	8857	76.2	3200	18.2	14425	37.0	7149

*To convert strontium concentration to moles/l, multiply by 2.09×10^{-10} mole/μCi

TABLE VII

Sorption Data for ^{237}Np*

		Basalt		Altered Basalt		Secondary Minerals	
Solution	Initial Conc. μCi/l	Final Conc. μCi/l	K_d, ml/g	Final Conc. μCi/l	K_d, ml/g	Final Conc. μCi/l	K_d, ml/g
1	0.94	0.79	5.4	0.43	35	0.48	26
2	1.1	0.16	173	0.0054	6081	0.35	56
3	1.0	0.79	7.7	0.50	29	0.50	27
4	0.83	0.14	148	0.0074	3335	0.26	58
5	0.96	0.71	10.3	0.34	54	0.36	47
6	1.0	0.80	7.2	0.52	27	0.53	23
7	0.99	0.71	11.5	0.26	84	0.43	36
8	1.0	0.79	7.5	0.45	36	0.51	25
9	0.97	0.14	174	0.0062	4572	0.13	191
10	0.99	0.11	240	0.0040	7179	0.25	81
11	1.0	0.80	7.2	0.42	40	0.45	35
12	0.93	0.12	202	0.0032	8688	0.25	75
13	0.94	0.13	185	0.0072	3886	0.11	219
14	1.1	0.82	9.8	0.51	34	0.48	37
15	0.99	0.83	5.4	0.40	43	0.46	31
16	0.77	0.14	135	0.0062	3696	0.28	44
17	0.87	0.25	73	0.0063	4072	0.29	49
18	0.93	0.11	223	0.0094	2938	0.20	101
19	0.70	0.068	278	0.0042	4970	0.14	114
20	0.98	0.77	7.7	0.38	46	0.42	39

*To convert neptunium concentration to moles/l, multiply by 5.99×10^{-6} moles/μCi

TABLE VIII

Sorption Data for ^{238}Pu*

		Basalt		Altered Basalt		Secondary Minerals	
Solution	Initial Conc.μCi/l	Final Conc.μCi/l	K_d,ml/g	Final Conc.μCi/l	K_d,ml/g	Final Conc.μCi/l	K_d,ml/g
1	0.20	0.074	50	0.026	198	0.0019	3125
2	0.11	0.013	220	0.00063	4913	0.00036	8612
3	0.64	0.23	52	0.021	867	0.0046	4059
4	0.13	0.027	110	0.0018	2136	0.00070	5480
5	0.35	0.095	79	0.0080	1269	0.001	9417
6	0.51	0.19	50	0.031	463	0.0037	4060
7	0.45	0.14	66	0.016	797	0.0014	9064
8	0.73	0.33	35	0.029	703	0.0042	5180
9	0.37	0.067	131	0.0043	2526	0.0010	10777
10	0.66	0.11	148	0.0057	3446	0.0011	17442
11	0.56	0.24	39	0.12	107	0.015	1066
12	0.036	0.0016	645	<0.0003	>3570	0.00055	1873
13	0.078	0.018	97	0.0011	2036	0.0087	226
14	0.73	0.14	125	0.032	647	0.0060	3545
15	0.48	0.10	113	0.027	498	0.0057	2351
16	0.035	0.0066	125	<0.0004	>2380	<0.0003	>3430
17	0.15	0.045	68	0.0029	1683	<0.0004	>10782
18	0.24	0.099	41	0.0024	2969	<0.0004	>17273
19	0.057	0.011	124	0.00053	3133	0.00056	2988
20	0.67	0.26	46	0.075	237	0.037	486

*To convert plutonium concentration to moles/l, multiply by 2.47×10^{-10} moles/μCi

TABLE IX

Sorption Data for ^{241}Am

		Basalt		Altered Basalt		Secondary Miner	
Solution #	Initial Conc.μCi/l	Final Conc.μCi/l	K_d,ml/g	Final Conc.μCi/l	Fraction Sorbed	Final Conc.ml/g	Frac Sorb
1	0.011	0.0014	205	0.00066	0.940	<0.0005	>0.95
2	0.013	0.00026	1470	<0.0010	>0.923	<0.0003	>0.97
3	0.024	0.0032	191	0.0031	0.987	<0.0002	>0.09
4	0.012	0.0033	78	0.00055	0.954	<0.0003	>0.97
5	0.038	0.0033	315	0.00074	0.981	<0.0003	>0.99
6	0.012	0.0024	118	<0.00060	>0.950	0.00031	0.97
7	0.046	0.0067	176	0.0010	0.978	<0.0003	>0.99
8	0.025	0.0093	50	0.00062	0.975	0.00035	>0.98
9	0.020	0.0033	167	0.00069	0.966	<0.0004	>0.98
10	0.023	0.0079	56	0.00091	0.960	<0.0003	>0.98
11	0.0087	0.00092	246	<0.0004	>0.954	<0.0002	>0.97
12	0.0015	<0.0003	>120	<0.0003	>0.800	<0.0003	>0.80
13	0.0086	0.0020	99	0.00044	0.949	<0.0003	>0.96
14	0.018	0.0035	124	0.0011	0.939	0.00031	0.98
15	0.010	0.0012	220	0.00031	0.969	<0.0002	>0.98
16	0.0056	0.0033	20	0.00050	0.911	<0.0003	>0.94
17	0.016	0.0050	66	0.00044	0.973	<0.0003	>0.98
18	0.0076	0.00071	288	0.00052	0.932	<0.0003	>0.96
19	0.025	0.0046	129	0.0022	0.912	0.00051	0.93
20	0.026	0.0034	197	0.00060	0.977	0.00055	0.97

TABLE X

Sorption Data for ^{95m}Tc*

		Basalt		Altered Basalt		Secondary Mineral	
Solution #	Initial Conc.μCi/l	Final Conc.μCi/l	K_d,ml/g	Final Conc.μCi/l	K_d ml/g	Final Conc.μCi/l	K_d ml
1	88	85	-0.29	<14	>155	77	2.9
2	86	<13	>170	<10	>230	<11	>206
3	96	86	-0.65	< 8	>295	83	0.45
4	94	<11	>206	< 6	>404	<10	>230
5	89	87	1.0	80	1.6	82	0.83
6	89	76	3.3	75	3.8	78	2.5
7	86	80	1.6	80	1.6	69	6.8
8	94	86	-0.65	76	3.3	82	0.83
9	82	<10	>230	<11	>206	<11	>206
10	90	<10	>230	39	36	<11	>206
11	79	71	5.8	84	0.07	79	5.8
12	84	17	123	< 6	>404	<12	>187
13	85	<10	>230	< 8	>295	<12	>187
14	90	75	3.8	73	4.8	70	6.3
15	80	78	2.5	71	5.8	83	0.95
16	84	< 6	>404	< 6	>404	<10	>230
17	89	<11	>206	<11	>206	<6.2	>390
18	86	<12	>187	< 6	>404	<11	>206
19	83	<10	>230	< 9	>259	<10	>230
20	76	81	1.2	90	-2.0	72	5.3

*To convert technetium concentration to moles/ℓ, multiply by 4.8×10^{-18} mole/μCi.

TABLE XI

Sorption Data for ^{75}Se

		Basalt		Altered Basalt		Secondary Minera	
Solution #	Initial Conc. μCi/l	Final Conc. μCi/l	K_d, ml/g	Final Conc. μCi/l	K_d, ml/g	Final Conc. μCi/l	K_d,m
1	582	488	5.6	349	19.2	299	26.0
2	591	540	2.7	489	6.0	405	8.5
3	606	542	3.3	427	12.3	388	14.3
4	542	441	6.5	351	15.7	387	7.0
5	572	454	7.7	444	8.0	359	15.2
6	545	444	6.5	424	8.1	336	16.2
7	552	507	2.5	478	4.3	182	58.6
8	565	491	4.4	430	8.9	369	13.5
9	569	506	3.4	425	9.7	422	5.4
10	581	520	3.4	330	22.5	384	10.6
11	602	531	3.8	450	9.7	426	10.1
12	600	496	6.1	329	24.4	395	11.1
13	618	412	14.7	279	35.8	395	13.1
14	567	528	2.1	425	9.7	402	10.1
15	584	532	2.8	406	12.8	380	13.6
16	580	448	8.6	316	24.7	362	13.2
17	613	559	2.8	395	16.3	401	11.2
18	571	473	6.0	320	22.9	354	13.5
19	565	498	3.9	315	23.6	196	51.5
20	620	582	1.8	447	11.2	466	7.8

TABLE XII

Sorption Data for ^{226}Ra

		Basalt		Altered Basalt		Secondary Mineral	
Solution #	Initial Conc.μCi/l	Final Conc.μCi/l	K_d,ml/g	Final Conc.μCi/l	K_d,ml/g	Final Conc.μCi/l	K_d,ml/g
1	1.0	0.027	1081	0.0067	4403	0.0023	12,883
2	1.1	0.0034	9676	0.0017	19382	0.024	1341
3	0.85	0.013	1894	0.0044	5765	0.018	1385
4	0.75	0.0091	2394	0.0026	8623	0.022	988
5	1.2	0.018	1912	0.0050	7099	0.028	1241
6	0.92	0.012	2225	0.0062	4335	0.019	1407
7	1.3	0.0097	3951	0.0020	19277	0.018	2093
8	0.81	0.0076	3167	0.0026	9224	0.012	1916
9	0.37	0.00054	20123	<0.001	>11070	0.0042	2609
10	1.5	0.017	2591	0.0086	5202	0.044	979
11	0.40	0.0024	4825	0.0030	3970	0.0042	2770
12	1.6	0.0079	5986	0.0012	39574	0.026	1776
13	1.2	0.0054	6571	0.0045	7891	0.0084	4253
14	0.70	0.0062	3324	0.0017	12201	0.0024	8632
15	1.3	0.0087	4453	0.0049	7850	0.015	2568
16	1.3	0.014	2756	0.0019	20293	0.026	1451
17	0.75	0.0068	3279	0.0036	6158	0.019	1127
18	1.4	0.024	1686	0.0089	4689	0.052	766
19	1.2	0.022	1606	0.0031	11355	0.028	1252
20	0.35	0.0049	2113	0.00073	14072	0.0032	3186

Factor effects for each of the nine variables studied were calculated for each radionuclide-geologic solid combination. For ^{238}Pu sorption, factor effects were calculated using the fraction sorbed and for ^{95m}Tc sorption, final concentrations were used rather than K_d values. In these two cases, the error was smaller and the results more definitive than when using K_d.

Significant variables for sorption of each radionuclide on basalt, altered basalt, and secondary minerals are given in Table XIII. They are listed in order of decreasing significance and + and - signs indicate whether sorption is increased or decreased, respectively.

For cesium sorption, both KCl and N_2H_4 are significant in most cases. Both decrease sorption of cesium, apparently by competing for similar sorption sites on the solids. Competition between K^+ and Cs^+ ions for sorption sites on mica-like minerals is well known. However, displacement of Cs^+ by hydrazine was surprising since N_2H_4 should exist mainly as the neutral species at pH 9-10. A small amount (0.0005 to 0.005M) will be protonated and apparently competes with Cs^+. Amonium ion is known to compete effectively with Cs^+ for mineral sorption sites. These ions can displace each other because of similar ion sizes. Effective ion diameters in aqueous solution have been calculated by Kielland (1937). Table XIV shows calculated values for Cs^+, K^+, NH_4^+, and Rb^+ and also an estimated value for $N_2H_5^+$ (based on the calculated value for an analogous ion, $CH_3NH_3^+$).

TABLE XIII

Significant Variables for Radionuclide Sorption*

Radionuclide	Basalt	Altered Basalt	Secondary Minerals
^{137}Cs	KCl (-) N_2H_4 (-)	KCl (-) $N_2H_4^{**}$ (-)	N_2H_4 (-) NaCl (-) Na_2SO_4 (-)
^{85}Sr	Na_2SO_4 (-) NaCl (-) $CaCl_2^{**}$ (-)	Na_2SO_4 (-) NaCl (-) $NaHCO_3^{**}$ (-)	NaCl (-) Na_2SO_4 (-) NaF (-)
^{237}Np	N_2H_4 (+) $NaHCO_3$ (-)	N_2H_4 (+)	N_2H_4 (+)
^{238}Pu	N_2H_4 (+) $CaCl_2^{**}$ (+)	N_2H_4 (+) Na_2SO_4 (+)	Na_2CO_3 (+) NaCl (+)
241Am	$MgCl_2$ (+) $NaHCO_3$ (-) Na_2SO_4 (-)		
^{95m}Tc	N_2H_4 (+)	N_2H_4 (+)	N_2H_4 (+)
^{75}Se	Na_2CO_3 (-) $N_2H_4^{**}$ (+)	N_2H_4 (+) Na_2CO_3 (-) KCl (+)	$CaCl_2^{**}$ (+)
^{226}Ra	Na_2SO_4 (-) KCl (-) NaCl (-)	KCl (-) Na_2SO_4 (-) NaCl (-)	Na_2SO_4 (-) NaCl (-) $NaHCO_3$ (+)

*Variables are listed in order of decreasing significance. Sign in parentheses indicate whether variable increased (+) or decreased (-) sorption.

**Significant at the 90% confidence level.

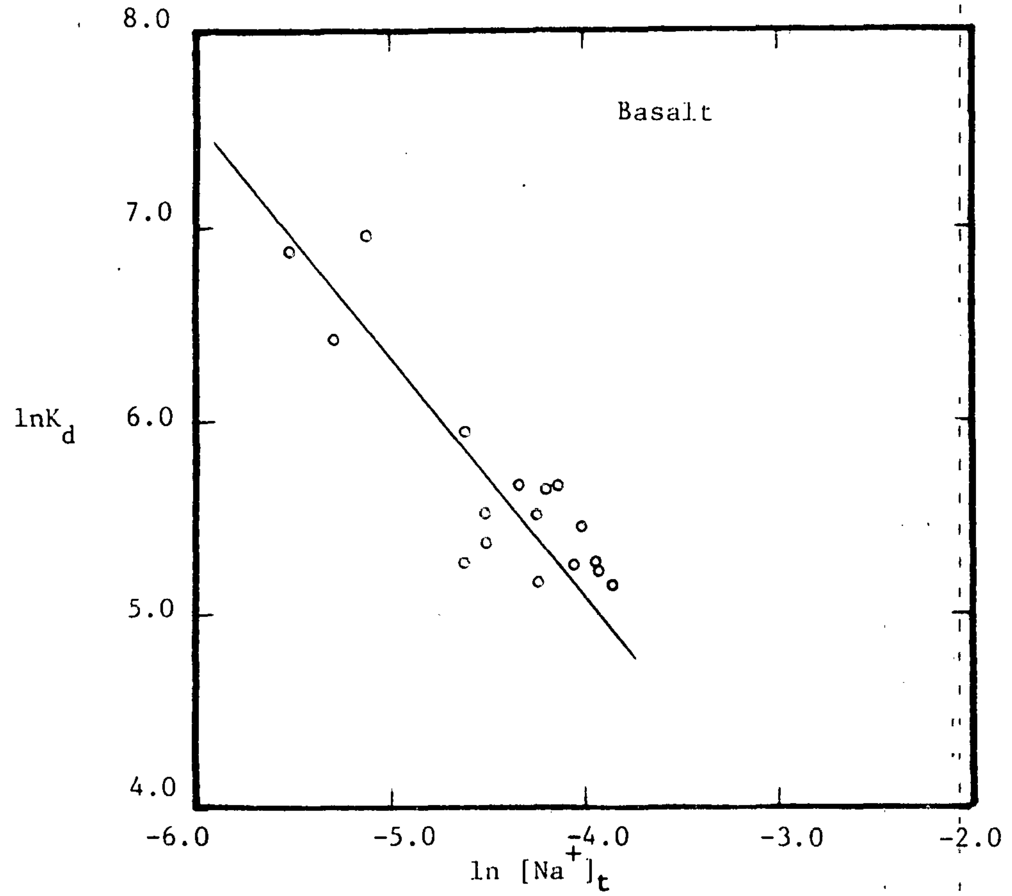
TABLE XIV

Effective Ion Diameters

Ion	Effective Diameter, Å
Cs^+	2.5
K^+	3.0
Rb^+	2.5
NH_4^+	2.5
$N_2H_5^+$	3.5 (estimated)
Na^+	4
Li^+	6

Although it is slightly larger than Cs^+, $N_2H_5^+$ has a diameter near that of Cs^+, K^+, Rb^+, and NH_4^+ and may compete with these ions for sorption sites. For secondary minerals, Na^+ appears to be more effective than K^+ for displacing Cs^+. Reasons for this unique behavior of secondary minerals will require further study but may be due to dissolution of K^+ from the secondary minerals. If enough K^+ is dissolved, K^+ concentration would obviously not vary with solutions 1 to 20. A concentration of about 7 ppm (0.00018 M) K^+ dissolved from secondary minerals has been observed during contact with a synthetic Grande Ronde groundwater. This concentration approaches the 0.0005 M concentration of the solutions used in these experiments.

Table XIII shows that sodium salts significantly reduce strontium sorption. Those sodium salts which contribute the largest concentration of Na^+ to the solution (NaCl and Na_2SO_4) are the most significant. Strontium sorption appears to be mainly a simple ion-exchange reaction with the solids. The K_d values obtained in these experiments appear to be a function of the total Na^+ concentration. Plots of ln K_d versus ln $[Na^+]_t$ are linear as shown in Figure 1. The scatter in the basalt plot is probably due to variable Ca^{2+} concentrations. Calcium chloride was significant at the 90% confidence level for Sr sorption on basalt. The similar size, ionic charge, and chemical behavior of Sr^{2+} and Ca^{2+} would suggest that they could compete for sorption sites.



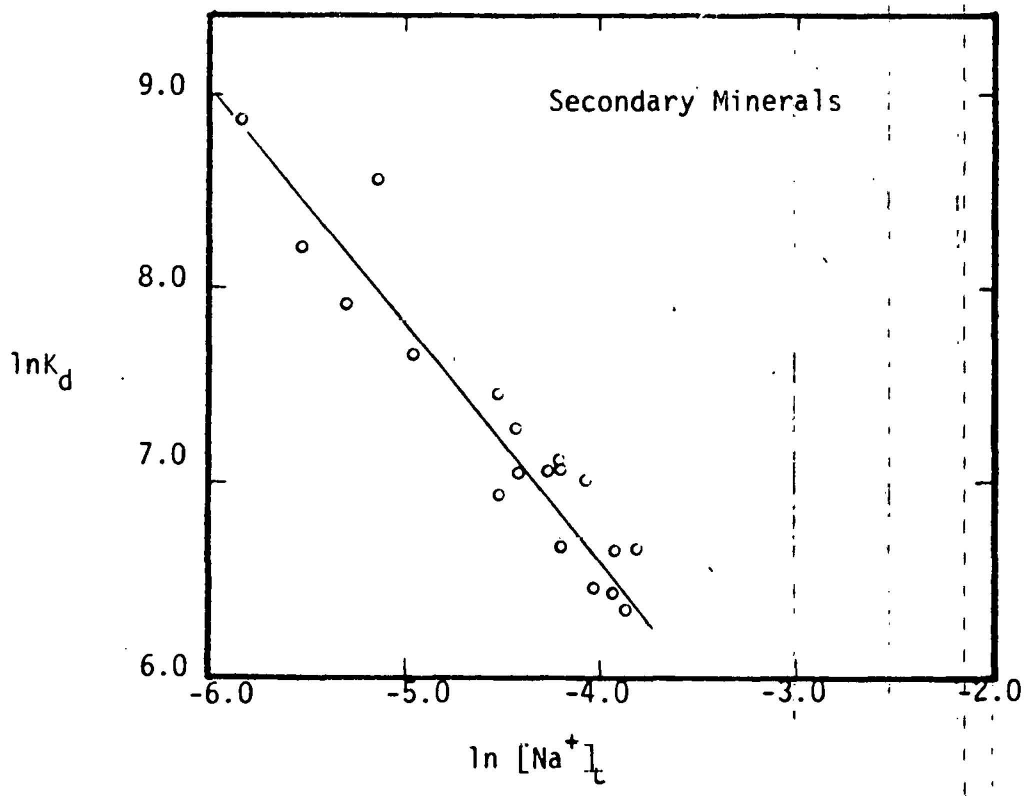


Figure 1. - Ln K_d versus ln $[Na+]_t$ (total sodium ion concentration) for strontium sorption on basalt and secondary minerals.

Sorption of Np is greatly increased when hydrazine is present. The only other groundwater variable found to be significant is $NaHCO_3$. The effect of hydrazine is to reduce Np(V) to Np(IV) (Allard _et al_, 1980) which is sorbed much more completely.

The effect of $NaHCO_3$ is to decrease sorption due to formation of carbonate complexes by Np(IV). Carbonate complexation does not appear to be significant for Np(V). A neutral or anionic species is probably formed which will not sorb as strongly as positively-charged, non-complexed Np(IV). Possible species include $Np(CO_3)_x^{+(4-2x)}$ by analogy with Pu(IV) carbonate complexes.

Plutonium sorption is also strongly affected by hydrazine. Since hydrazine greatly increases Pu sorption on basalt and altered basalt, it appears that Pu exists in the air-saturated solutions as Pu(V) or Pu(VI) and is reduced to Pu(III) or Pu(IV) by hydrazine. According to Eh-pH diagrams given by Allard _et al_ (1980), Pu(III) is the stable oxidation state at a pH of 10 and Eh of -0.8 volts.

The effect of significant calcium and sodium salts is to increase sorption of Pu. It appears that these salts cause precipitation of insoluble Pu compounds. In most cases, the spiked solutions 1 through 20 were saturated with Pu. Many of the filtered solutions had Pu concentrations less than that added initially, indicating that some Pu-containing solids were filtered out. A Plackett-Burman analysis of Pu solubilities for the twenty solutions gave N_2H_4, $CaCl_2$, and NaF as significant factors affecting solubility. Each of the significant variables cause precipitation of Pu. A close examination of the data indicates that the solubility of Pu in the lower oxidation state (reduced by N_2H_4) is strongly lowered by Ca^{2+} and F^-. Slightly soluble double salts of PuF_4 are known, including $CaPuF_6$ and $NaPuF_5$ (Cleveland, 1970), but it is questionable whether these compounds would be formed under high pH conditions (≃10) of these experiments.

Hydrazine is the only significant parameter for ^{95m}Tc sorption at the 95% confidence level. This is true for basalt, altered basalt, and secondary minerals. Hydrazine causes Tc to be removed from solution by either sorption or precipitation.

Hydrazine is known to reduce TcO_4^- by the following reaction (Anders, (1960):

$$4H_2O + 3N_2H_4 + 4TcO_4^- = 4TcO_2 \cdot 2H_2O + 3N_2 + 4OH^-$$

This reaction may be occurring during the sorption experiments. It seems more likely that a Tc(IV) species is sorbing on the geologic materials since the starting concentrations (after filtering the spiked solution through 0.45 µm filters) were not affected by hydrazine. Gorski and Koch (1969) have proposed the species TcO^{2+} at pH 1 for Tc(IV).

Because americium was sorbed so strongly, the activity left in solution after contacting the solids was near the detection limit for measurement. The best data was obtained using basalt as the sorbent since it sorbed the least amount of Am. The significant parameters were MgCl, $NaHCO_3$, and Na_2SO_4. Magnesium increases Am sorption on basalt, apparently by forming an insoluble compound. As will be shown later, Mg^{2+} significantly lowers the solubility of Am in Grande Ronde groundwater. Bicarbonate and $SO_4^=$ decrease sorption by complexing Am^{3+}. Possible species are $AmCO_3^+$ and $AmSO_4^+$. Analysis of the sorption data for altered basalt and secondary minerals yielded no significant parameters (at the 90% confidence level) because of very extensive sorption on these solids.

Table XIII shows that the significant parameters for Se sorption are Na_2CO_2, N_2H_4, and $CaCl_2$. Carbonate decreases sorption while N_2H_4 and $CaCl_2$ increase sorption. Selenium is present in these experiments as SeO_3^{2-}. Since the anion exchange capacity of the solid is very low at pH 8-10, SeO_3^{2-} will not sorb appreciably by anion exchange. Sorption reactions are probably chemisorption or precipitation. Since calcium increases sorption, it appears likely that a Ca-Se compound forms on the solid surface. The effect of CO_3^{2-} is to make calcium unavailable for reaction with SeO_3^{2-} due to formation of complexes such as $CaHCO_3^+$ and $CaCO_3^\circ$. Hydrazine may promote sorption by partially reducing SeO_3^{2-} to Se°, although this reaction cannot be extensive.

Significant parameters for Ra sorption are Na_2SO_4, KCl, and NaCl. Each of these variables decrease sorption by ion exchange reactions similar to those of Sr. The effective ion diameter of Ra^{2+} (5Å) is near that of Na^+ so that competition for similar sites should occur. However, K^+ is smaller (3 Å) and an explanation for its significance is not apparent.

The Eh of Grande Ronde groundwater is likely controlled by the magnetite/hematite couple. Plots of Eh versus pH for magnetite/hematite, H_2/H_2O, and hydrazine/N_2 are shown in Figure 2. Hydrazine is a powerful reducing agent and should reduce Np(IV), Pu(VI), Pu(V), Tc(VII), and Se(V), as shown by the standard half-cell potentials in Table XV.

TABLE XV

Standard Half-Cell Potentials

Reaction	E°, volts
$N_2H_4 + 4OH^- = N_2+4H_2O+4e^-$	1.16
$2Fe_3O_4 + H_2O = 3Fe_2O_3 + 2H^++2e^-$	-0.22
$Np^{4+} + 2H_2O = NpO_2^+ + 4H^+ + e^-$	-0.74
$Pu^{4+} + 2H_2O = PuO_2^+ + 4H^+ + e^-$	-1.15
$Pu^{4+} + 2H_2O = PuO_2^{2+} + 4H^+ + 2e^-$	-1.04
$TcO_2 + 2H_2O = TcO_4^- + 4H^+ + 3e^-$	-0.738
$Se + 3H_2O = SeO_3^{2-} + 6H^+ + 4e^-$	-0.740

Although SeO_3^{2-} should be reduced by hydrazine, sorption of Se was only slightly affected by hydrazine. If SeO_3^{2-} is reduced to Se°, sorption should increase due to the slight solubility of Se°.

The solubilities of Pu, Am, and Ra are also controlled by solution parameters. Statistical analyses of the 20 solutions using the initial concentrations of these radionuclides (after filtration through 0.3 µm filters) as solubility parameters identified the parameters which signi-

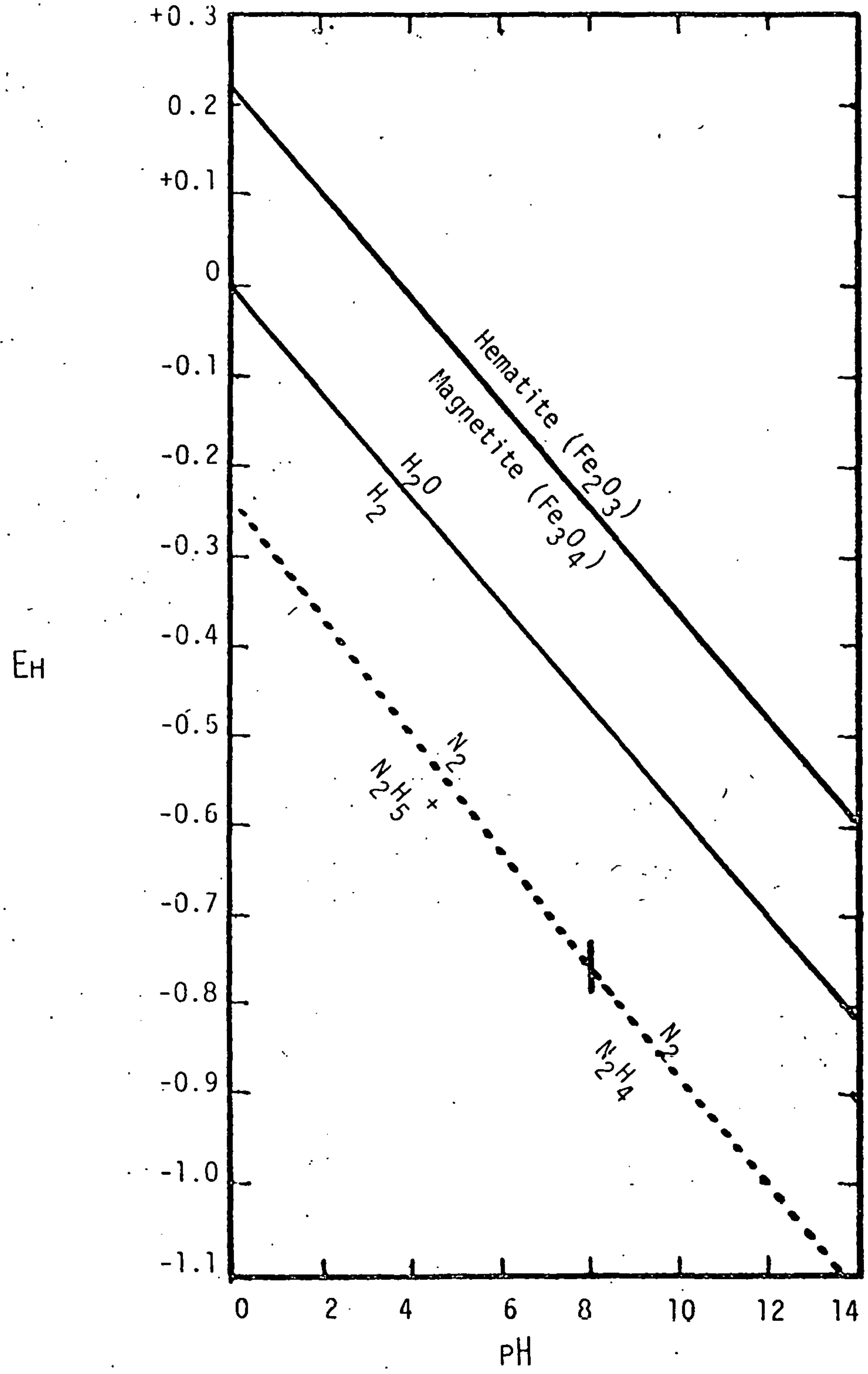


Figure 2 - Eh-pH Curves for Magnetite/Hematite, H_2/H_2O, and N_2H_4/N_2 (0.1 $\underline{M}$ N_2H_4)

ficantly affect solubility. These are listed in order of decreasing importance in Table XVI.

TABLE XVI

Significant Factors for Pu, Am, and Ra Solubility*

Pu	Am	Ra
N_2H_4(-)	$MgCl_2$(-)	NaCl (+)
$CaCl_2$(-)	N_2H_4(-)	Na_2SO_4(+)
NaF(-)		N_2H_4(+)

*A (+) or (-) sign indicates that the factor increases or decreases solubility.

Values of K_d are summarized in Table XVII. These are averages of K_d when the two most significant components are at the high or low concentrations shown. They are the averages of five K_d values. In most cases the order of increasing sorption is: basalt < secondary minerals < altered basalt. Although the secondary minerals have the largest surface area and cation exchange capacity, altered basalt is a more effective sorbent except for Pu. This is especially true for Np(IV). This suggests that Np(IV) is sorbed by a chemisorption mechanism rather than by ion exchange.

It was hoped that hydrazine, used as a redox buffer, would not interfere with radionuclide sorption reactions. Results with Tc, Pu and Np sorption show that hydrazine is an effective redox buffer and does not complex these radionuclides. Since hydrazine will not complex or reduce Cs or Sr it should have no effect on their sorption unless it somehow alters the solid or competes for sorption sites. Although there is little evidence for alteration of the geologic solids, the small amount of $N_2H_5^+$ present at pH 9-10 effectively competes with Cs for sorption sites.

TABLE XVII

K_d Values (ml/g) for Cs, Np, Pu, Am, Tc, Se, and Ra Sorption

	Factor				
Radionuclide	#1	#2	Basalt	Altered Basalt	Secondary Minerals
^{137}Cs	KCl	N_2H_4			
	+	+	101 ± 6	5946 ± 1395	
	+	-	163 ± 30	4467 ± 1150	
	-	+	198 ± 44	7779 ± 1408	
	-	-	543 ± 231	6707 ± 1610	
	N_2H_4	NaCl			
	+	+			1121 ± 572
	+	-			1876 ± 761
	-	+			2364 ± 712
	-	-			4837 ± 1748
^{85}Sr	Na_2SO_4	NaCl			
	+	+	199 ± 25	1516 ± 878	670 ± 89
	+	-	241 ± 116	1883 ± 776	1140 ± 509
	-	+	245 ± 50	3062 ± 2064	1079 ± 181
	-	-	1263 ± 1113	8019 ± 3972	4186 ± 2030
^{237}Np	N_2H_4	N_2HCO_3			
	+	+	159 ± 47	4083 ± 1024	103 ± 73
	+	-	240 ± 38	6945 ± 1870	90 ± 21
	-	+	8.1 ± 2.2	44 ± 20	32 ± 8
	-	-	7.5 ± 0.4	43 ± 4	37 ± 2
^{238}Pu	N_2H_4	Na_2SO_4			
	+	+	110 ± 41	2813 ± 542	
	+	-	232 ± 238	2946 ± 1309	
	-	+	66 ± 31	760 ± 328	
	-	-	65 ± 35	397 ± 305	
	Na_2CO_3	NaCl			11030 ± 3583
	+	+			5242 ± 3291
	-	+			6336 ± 6326
	-	-			1639 ± 1473

*A (+) sign indicates the high value of the variable and a (-) sign, the low value.

TABLE XVII (Continued)

K_d Values (ml/g) for Cs, Np, Pu, Am, Tc, Se, and Ra Sorption

Radionuclide	Factor #1	Factor #2	Basalt	Altered Basalt	Secondary Minerals
^{241}Am	MgCl	$NaHCO_3$			
	+	+	131 ± 53		
	+	-	221 ± 67		
	-	+	85 ± 66		
	-	-	182 ± 92		
^{95m}Tc	N_2H_4				
	+		>150	>160	>170
	-		1.6 ± 2.3	2.4 ± 2.6	3.3 ± 2.5
^{75}Se	Na_2CO_3	N_2H_4			
	+	+	4.3 ± 1.8	13.4 ± 6.5	9.1 ± 3.2
	+	-	2.7 ± 0.5	9.4 ± 3.0	13.3 ± 2.2
	-	+	5.5 ± 2.4	26.2 ± 5.4	12.1 ± 1.4
	-	-	4.4 ± 1.8	9.5 ± 1.3	14.7 ± 7.0
^{226}Ra	Na_2SO_4	KCl			
	+	+	1940 ± 380	6800 ± 2700	1100 ± 250
	+	-	3000 ± 890	10100 ± 6000	1600 ± 600
	-	+	3600 ± 2000	6900 ± 3300	4200 ± 3200
	-	-	8400 ± 7100	23000 ± 11000	2200 ± 700

Sorption Isotherms

Sorption isotherms for sorption of ^{137}Cs, ^{85}Sr, ^{65}Se, ^{237}Np, ^{241}Am, and ^{237}Pu on the three geologic materials were measured at 23 ± 2°C using Grande Ronde #2 groundwater. Sorption data are plotted according to the Freundlich adsorption isotherm in Figure 3. The Freundlich equation,

$$\frac{x}{m} = k \, C_f{}^{1/n},$$

where $\frac{x}{m}$ is the quantity of radionuclide adsorbed per gram of solid, k and n are empirical constants, and C_f is the equilibrium concentration of the radionuclide in moles per liter, describes the sorption data quite well, except when precipitation occurs. Precipitation was observed for strontium sorption on basalt and altered baslat, neptunium sorption on each of the geologic material, and americium sorption on basalt.

Freundlich constants and K_d values for the sorption reactions studied are given in Table XVI. When 1/n is equal to one, the isotherm is linear and can be described by a single value of K_d $(\frac{x}{m} / C_f)$. Strontium sorption on secondary minerals and americium sorption on altered basalt and secondary minerals are the only sorption reactions which have nearly linear isotherms. Most values of 1/n are less than one in which case K_d decreases as C_f increases. Values of 1/n that are greater than one indicate precipitation.

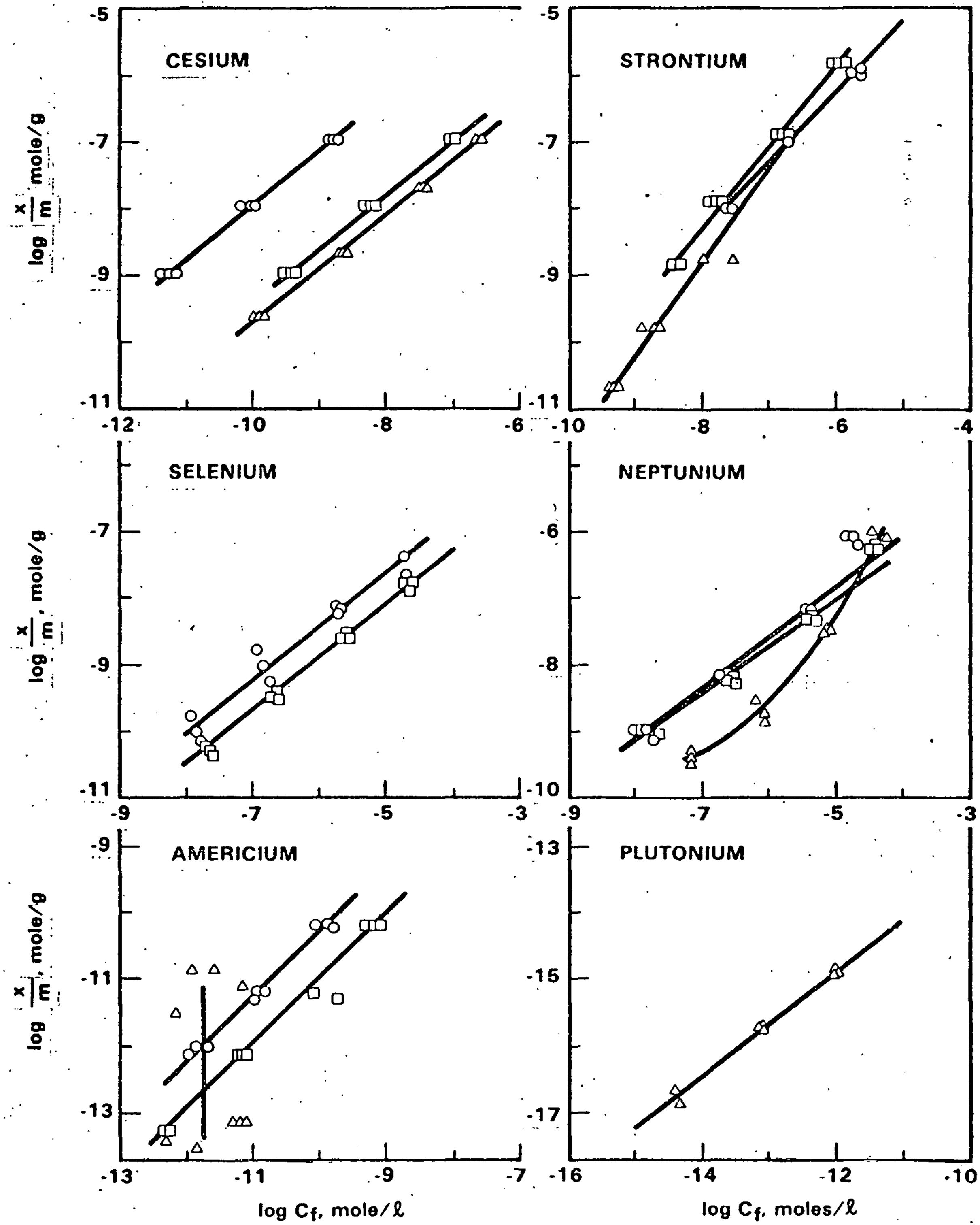


Figure 3. Sorption Isotherms for Sorption Reactions of Cesium, Strontium, Selenium, Neptunium, Americium, and Plutonium on Basalt (Δ), Altered Basalt (□), and Secondary Minerals (0)

TABLE XVI

Freundlich Constants and K_d Ranges for Fission Product Sorption on a Molar Basis

Radio-nuclides	Geological Material	k	1/n	r^2	K_d range,ml/g	pH
Cs	basalt	0.0363	0.83	0.995	500-1900	8.6
Cs	altered basalt	0.0631	0.82	0.995	960-3200	8.3
Cs	secondary minerals	2.26	0.83	0.994	60,000-150,000	8.2
Sr	basalt	186	1.39	0.977	40-450	8.6
Sr	altered basalt	12.8	1.16	0.989	400-1400	8.5
Sr	secondary minerals	0.873	1.02	0.998	600-800	8.3
Se	altered basalt	0.00012	0.82	0.996	0.60-3.0	8.8
Se	secondary minerals	0.00029	0.81	0.954	1.4-10	8.1
Np	basalt	---	---	---	2-20	8.6
Np	altered basalt	0.00115	0.78	0.992	17-70	9.5
Np	secondary minerals	0.00039	0.71	0.986	13-80	8.5
Am	basalt	---	---	---	12-9000	8.6
Am	altered basalt	0.0162	0.92	0.897	80-140	9.4
Am	secondary minerals	0.175	0.96	0.990	520-590	8.4
Pu	basalt	0.000015	0.83	0.989	1.4-5.8	8.6

In general, sorption of each radionuclide increases in the order: basalt < altered basalt < secondary minerals, the same order for increasing surface area and cation exchange capacity. It appears, therefore, that the extent of radionuclide sorption is related to these two parameters.

Very low values of K_d for plutonium were observed compared to previous measurements at higher Pu concentrations. It is likely that at the high pH (approximately 8.6) and oxidizing conditions of these experiments, negatively-charged complexes of Pu(V) or Pu(VI) are the dominant species. (Rai and Serne, 1978). One possible complex which may exist in the bicarbonate groundwater is $PuO_2CO_3OH^-$. This negatively-charged species would not be expected to sorb strongly on the negatively charged rock surface.

Americium solubility in the Grande Ronde #2 groundwater is much greater than in the sodium bicarbonate groundwater even though the pH of the Grande Ronde is higher. Americium must be forming a relatively soluble complex with anions other than carbonate (F^-, SO_4^{2-}, Cl^-, or $H_3SiO_4^-$).

Reaction Kinetics

In addition to radionuclide sorption reactions, the geologic solids react with the groundwater by hydroloysis, dissolution, precipitation, oxidation, or mineral transformation. Since the products of these reactions will influence radionuclide sorption mechanisms, it is necessary to measure the extent and rate of reaction.

The surfaces of the solids are chemically altered by the groundwater. In addition, the composition of the groundwater will change. Ions which compete for sorption sites will be introduced into the solutions. These reactions are generally quite slow at the temperature of the sorption experiments (23 ± 5°C). It was necessary to follow these reactions over long time periods (≈20 weeks) to identify reactions. Dissolution and precipitation reactions were followed by measuring changes in groundwater composition over the reaction period. Concentrations of major groundwater components versus time for groundwater equilibration with basalt, altered basalt, and secondary minerals are given in Figures 4-6. Only these elements with concentrations greater than ≈1 ppm are plotted, although others were measured (Ba, Zn, Cu, Al, Fe, B, P, and Cr). Values of pH for basalt, altered basalt, and secondary minerals beveled out at 8.8, 9.4, and 8.4, respectively. The upper aquifer groundwater composition was used to equilibrate with basalt. Grande Ronde #2 groundwater was used with altered basalt and secondary minerals.

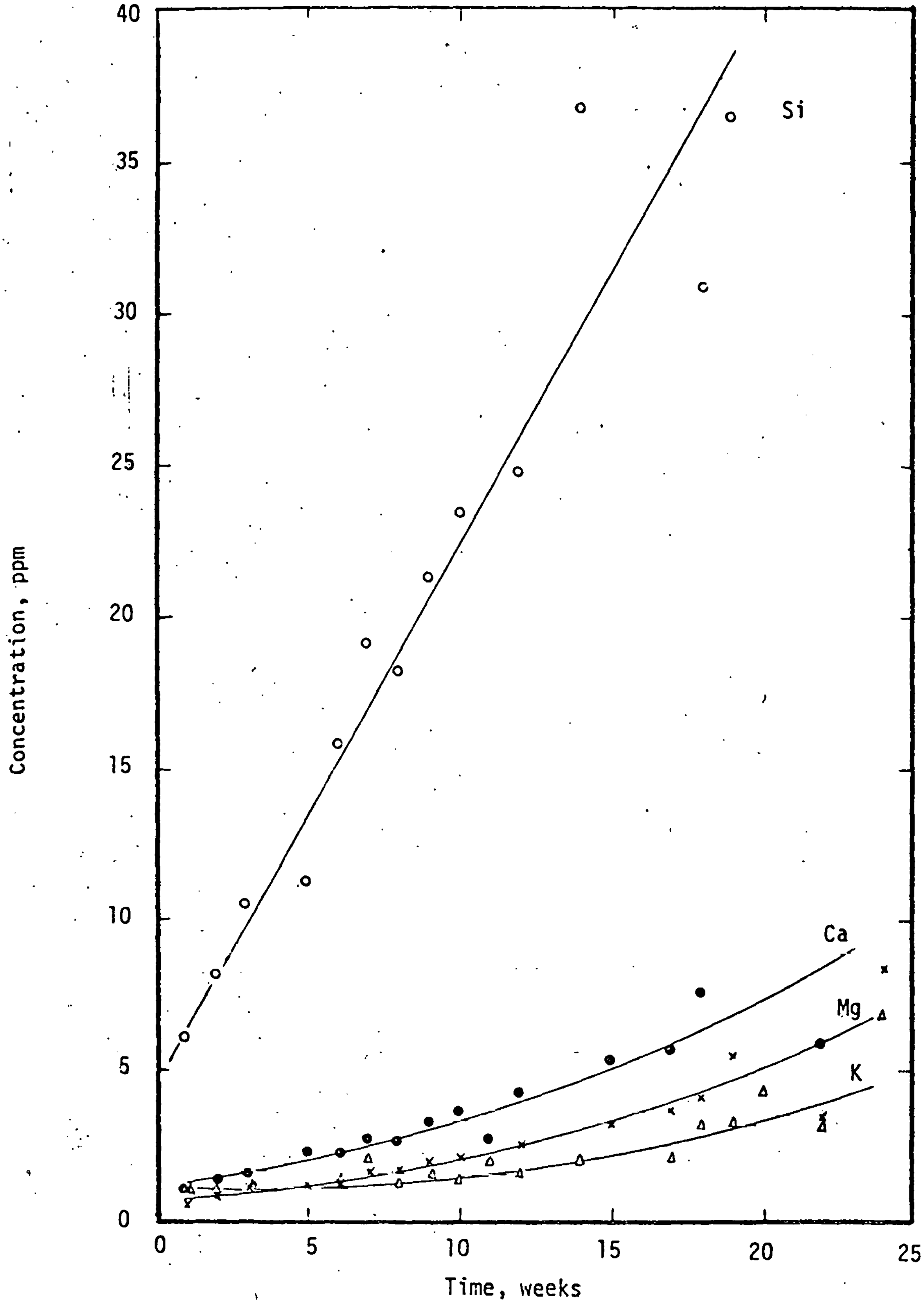


Figure 4 - Dissolution of Basalt in Groundwater

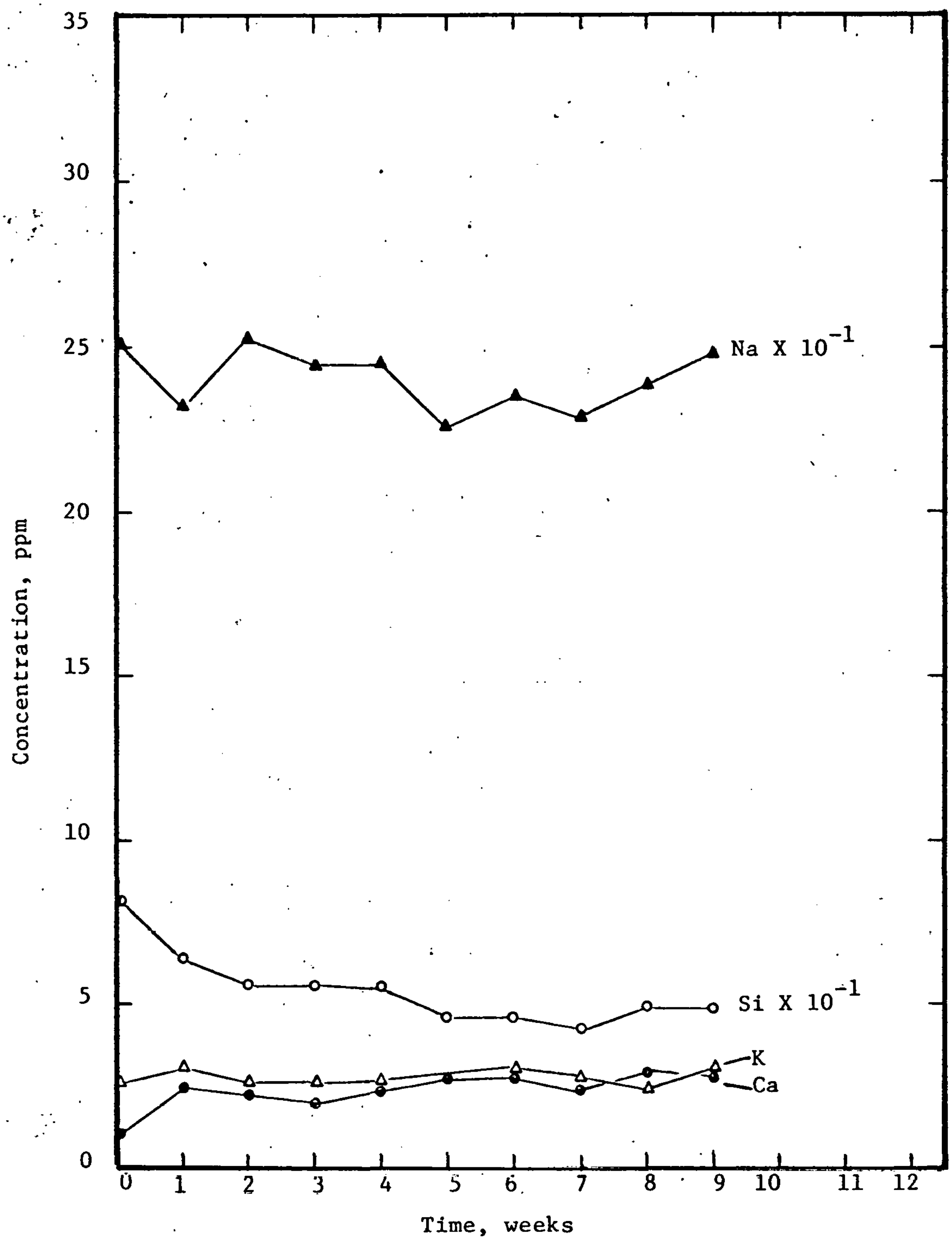


FIGURE 5 - Dissolution of Altered Basalt in Grande Ronde #2 Groundwater

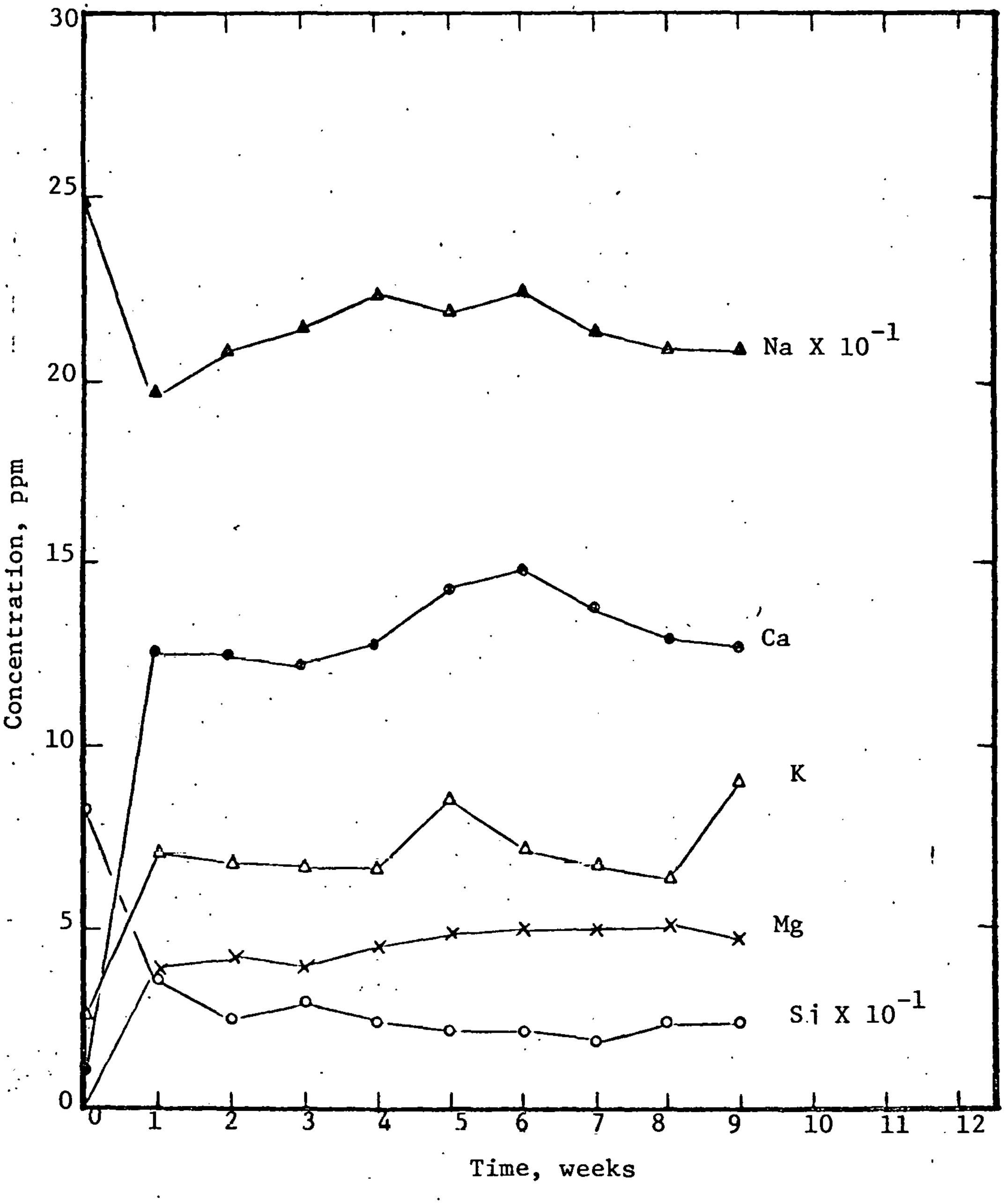


FIGURE 6 - Dissolution of Secondary Minerals in Grande Ronde #2 Groundwater

The curves for basalt dissolution show silicon as the major element going into solution. The rapid dissolution and high concentration of Si is consistent with dissolution of the glassy phase of the basalt. The minor amounts of Ca, Mg, and K could also be from the glassy phase. Dissolution of ions which compete with radionuclides for sorption sites is very slow. Basalt dissolution is accompanied by formation of colloidal solids which contain Si, Fe, Ca, and Al. These colloids are not totally filtered out even with 0.3 µm filters. Several radionuclides were found to be associated with these colloids.

Relatively minor composition changes were observed for groundwater in contact with altered basalt. The initial Grande Ronde #2 groundwater composition appear to be in near equilibrium with the altered basalt. The greatest change was the Si concentration which decreased from 82 ppm to 50 ppm.

Contact with secondary minerals greatly changes the composition of Grande Ronde #2 groundwater. These secondary minerals are, therefore, not representative of the minerals in the flow path of Grande Ronde aquifers. Concentrations of Ca, K, Mg, and Sr increase and Si and Na decrease in the first few weeks. After this time, concentrations stabilize.

Radionuclide concentrations versus time are shown in Figures 7-9 for the three geologic solids. For basalt, Cs and Np concentrations stabilize after ≈4 weeks. Strontium concentrations, however, continue to increase over 25 weeks after the initial rapid sorption. This is consistent with slow dissolution of Ca and Mg from basalt which will compete with Sr for sorption sites. The large increase in Si due to basalt dissolution does not affect radionuclide sorption.

Sorption of Cs, Sr, and Np on altered basalt approaches equilibrium after several weeks. Plutonium, however, continues to sorb over many weeks.

Radionuclide sorption reactions with secondary minerals stabilize after several weeks, except for Cs. There is a slow sorption reaction of Cs^+ with the minerals which may be diffusion of cesium ions into the hydrated layer of the smectite clay structure.

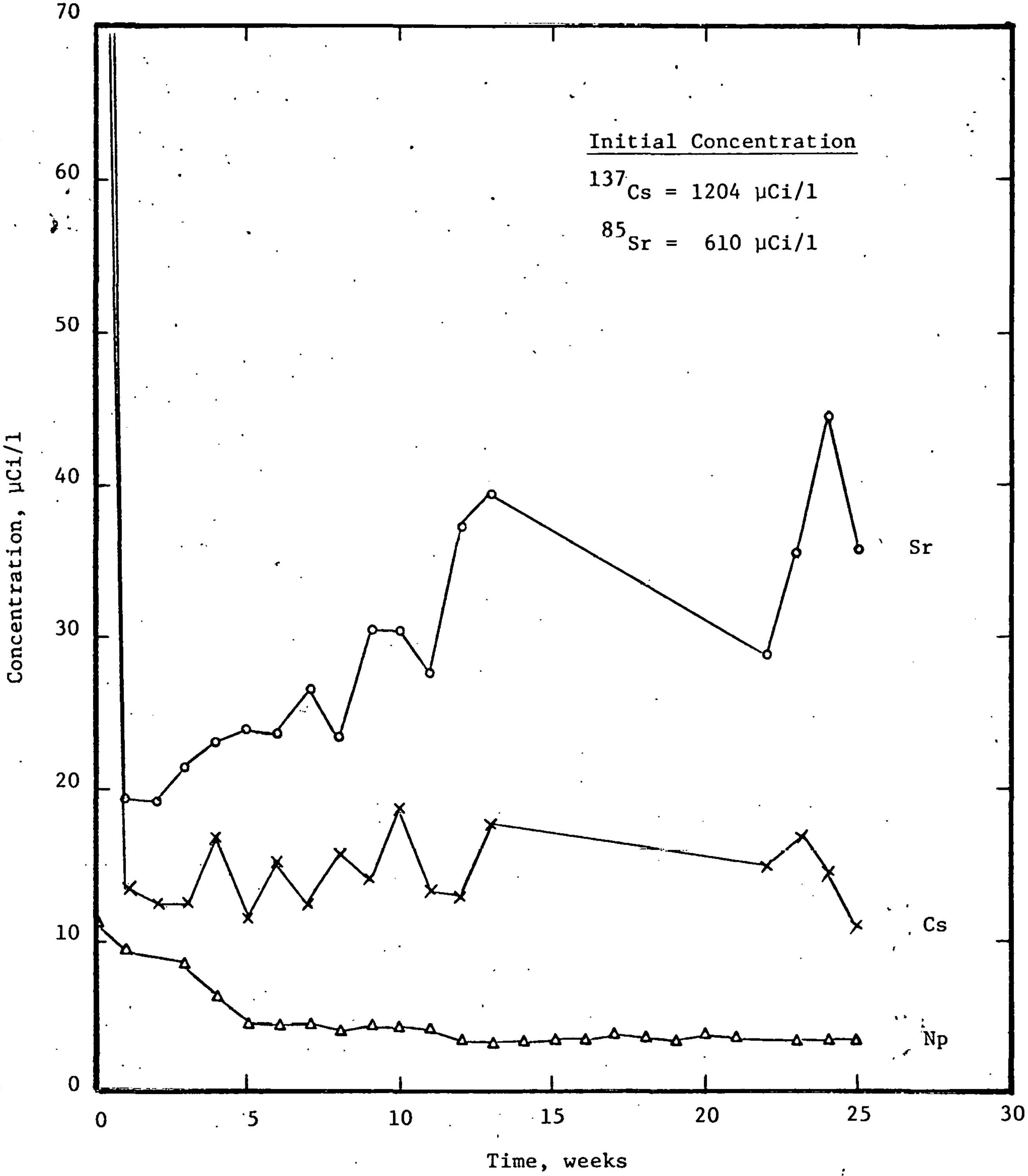


FIGURE 7 - Radionuclide Concentrations Versus Time For Sorption Reactions With Basalt

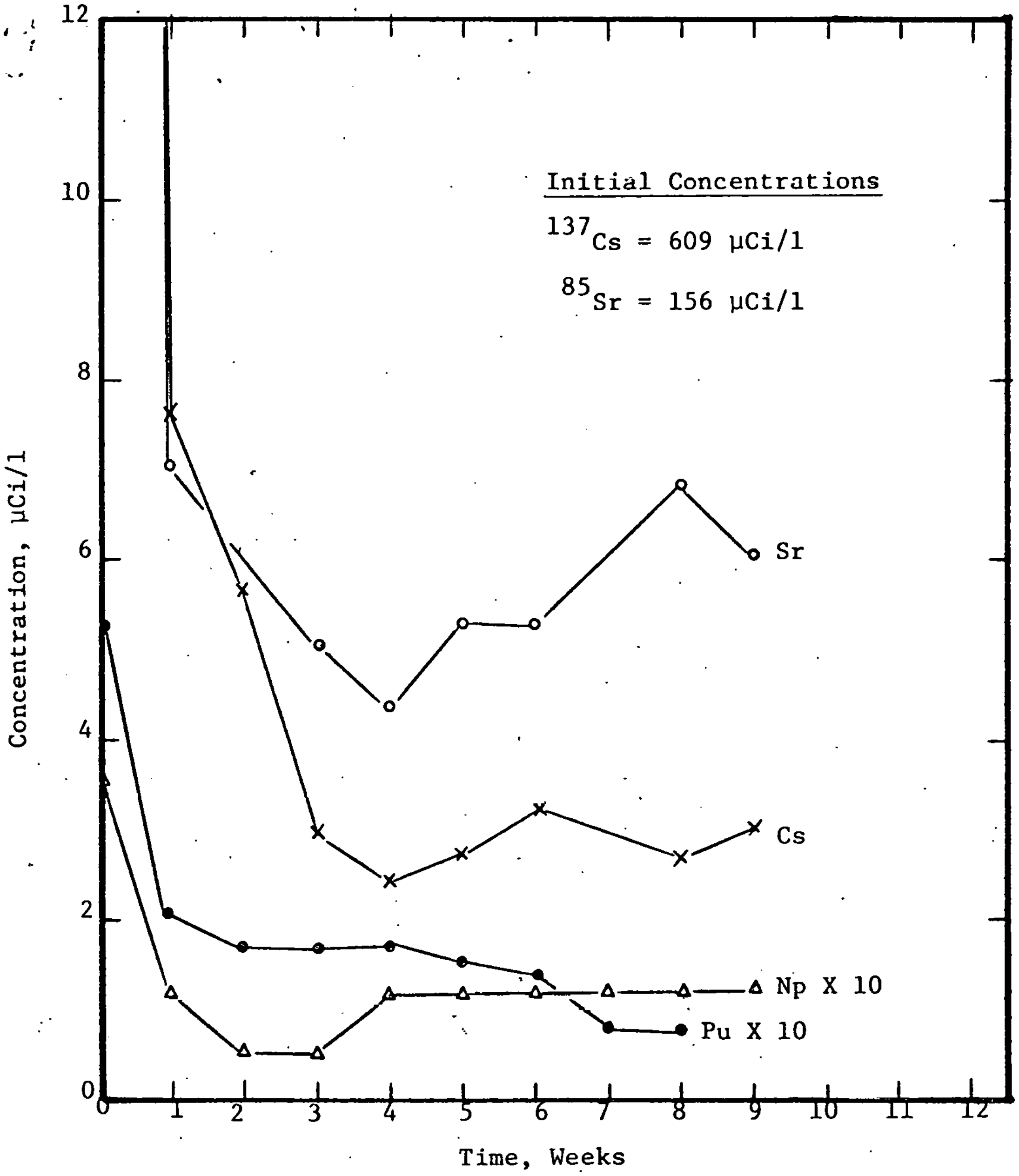


FIGURE 8 - Radionuclide Concentration Versus Time For Sorption Reactions With Altered Basalt

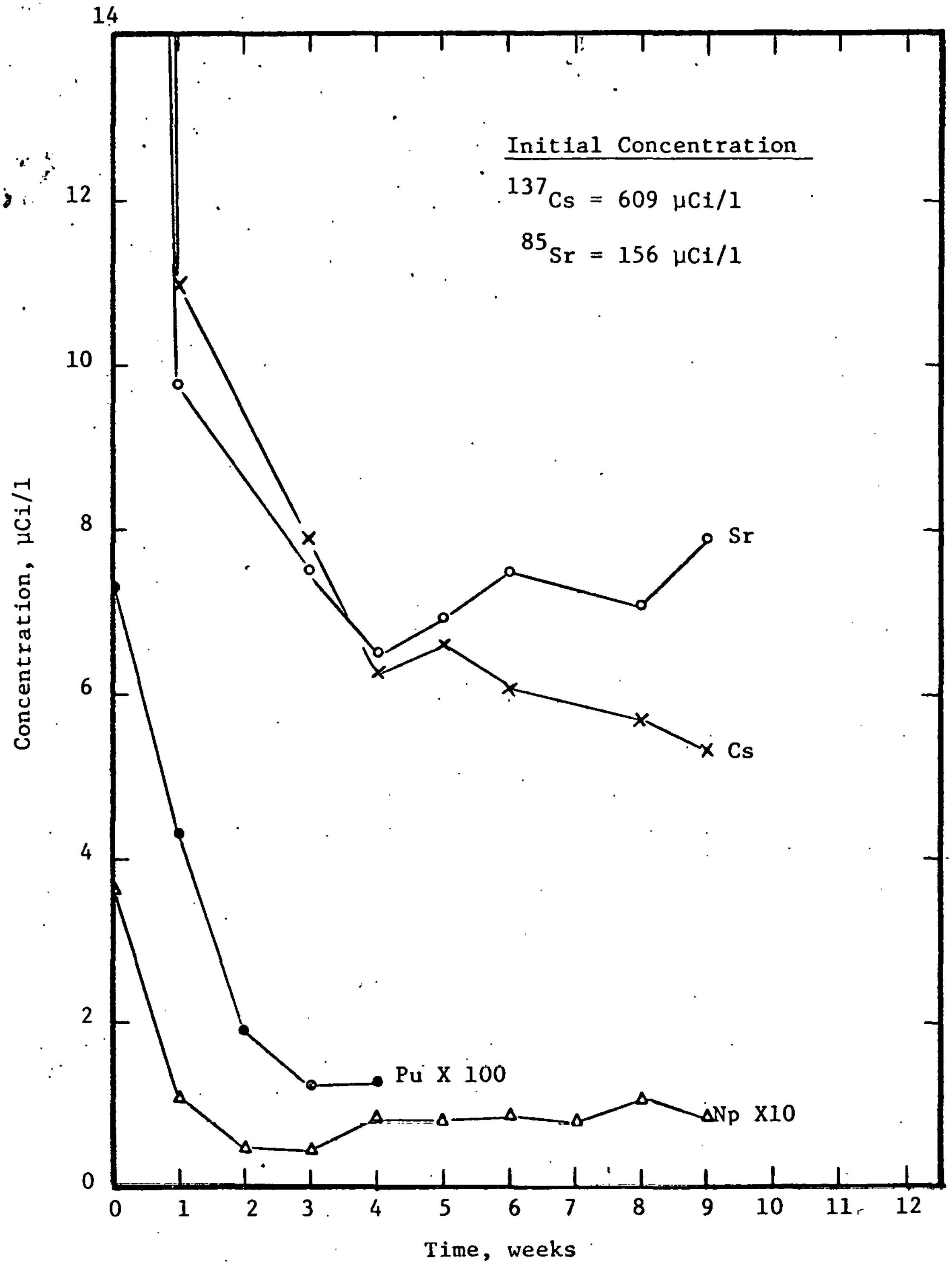


FIGURE 9 - Radionuclide Concentration Versus Time for Sorption Reactions With Secondary Minerals

Grande Ronde groundwater contains significant amounts of the anions, F^-, Cl^-, and SO_4^{2-}. The concentrations of these anions can affect the chemical species of radionuclides and therefore their sorption characteristics. Because of this, the stability of anion concentrations over the period required for sorption experiments must be known. The concentrations of F^-, Cl^-, and SO_4^{2-} in synthetic Grande Ronde groundwater equilibrated with altered basalt and secondary minerals over a period of 12 weeks have been measured. The effect of hydrazine (0.075 M̲) was also determined. Plots of F^- and Cl^- concentrations versus time are shown in Figure 10 and SO_4^{2-} concentration versus time in Figure 11. Anion concentrations were quite stable for solutions in contact with altered basalt. The greatest change for these solutions was an increase of approximately 10 ppm Cl^- (only a 7% change). The solutions in contact with secondary minerals were not as stable. Flouride concentration decreased from 37 to 25 ppm, Cl^- and SO_4^{2-} concentrations increased by 20 and 15 ppm, respectively. The greatest changes were observed for those solutions containing hydrazine.

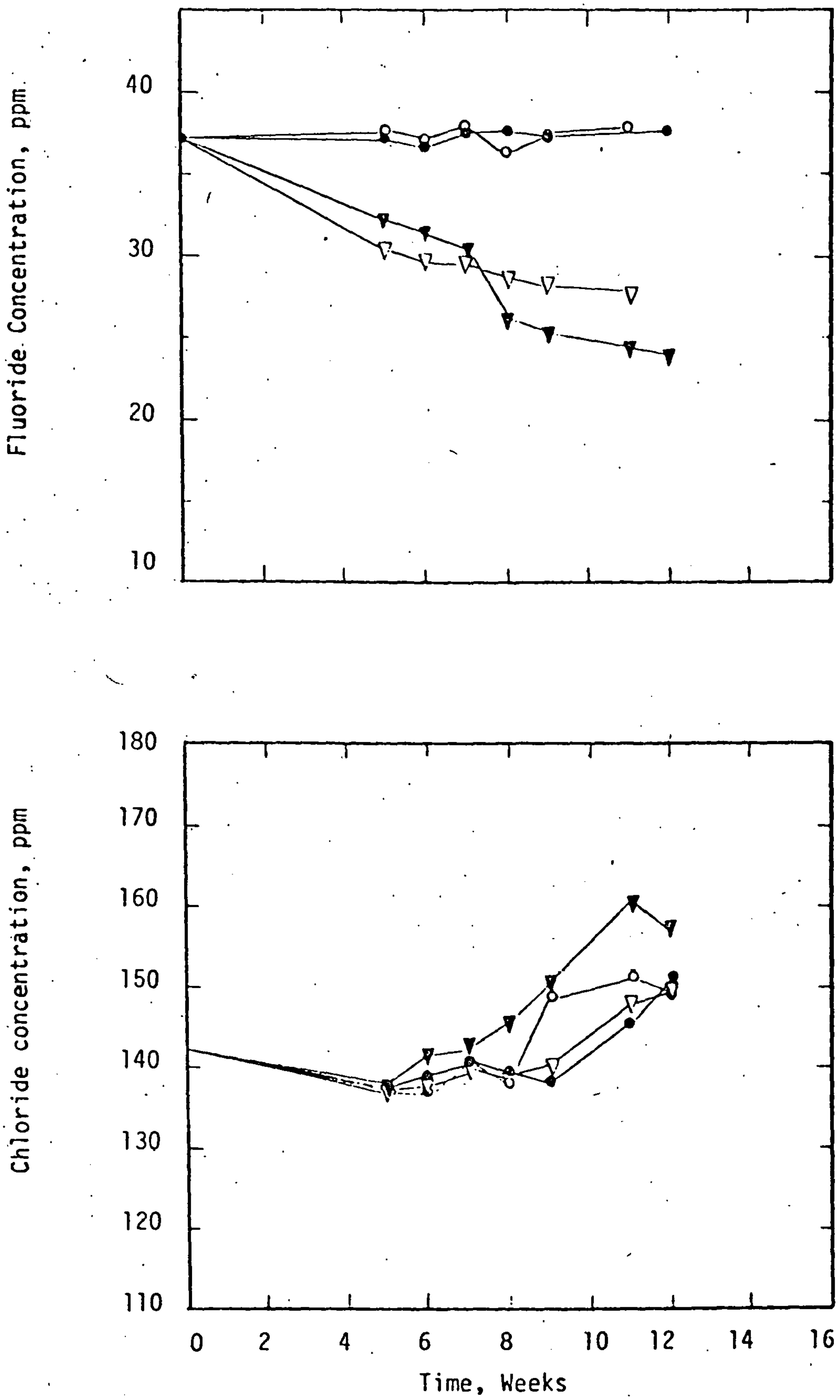


Figure 10 - Chloride and fluoride concentrations versus time for Grande Ronde groundwater in contact with altered basalt (circles) and secondary minerals (triangles). Closed circles and triangles indicate the presence of hydrazine.

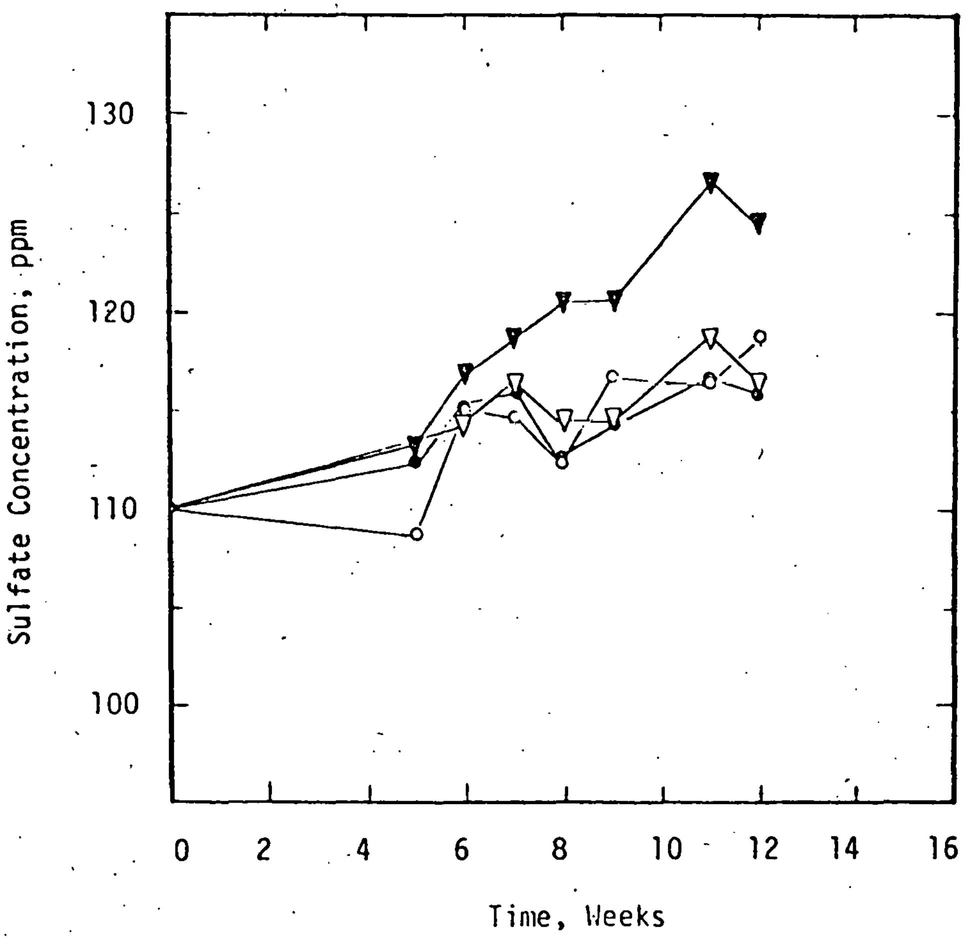


Figure 11 - Sulfate concentrations versus time for Grande Ronde groundwater in contact with altered basalt (circles) and secondary minerals (triangles). Closed circles and triangles indicate the presence of hydrazine.

CONCLUSIONS

Several conclusions can be made concerning the mechanisms of radionuclide sorption reactions in Columbia River basalt formations. Cesium sorption on the solids is by ion exchange with possibly some Cs^+ "fixed" in mica-like minerals. Both K^+ and $N_2H_5^+$ ions can replace part of the sorbed Cs. Sorption is very extensive for both altered basalt and secondary minerals. A slow diffusion of Cs^+ into secondary mineral sorption sites continues over many weeks after an initially rapid sorption reaction.

Strontium sorption appears to be strictly a simple ion exchange reaction, except when Sr concentrations are high and Sr is precipitated. Sodium and Ca^{2+} ions effectively complete with Sr for sorption sites. In Grande Ronde groundwater Na^+ concentration is much higher than Ca^{2+} and therefore, Na^+ dominates the exchange reactions. Because of slow dissolution of Ca^{2+} and Mg^{2+} from basalt, Sr is slowly desorbed over a period of ≈20 weeks.

Under the Eh conditions of Grande Ronde basalt formations, Np should exist as Np(IV). Using a hydrazine Eh buffer, Np(IV) was found to sorb much more strongly than Np(V). Bicarbonate decreases sorption by forming $Np(CO_3)_x^{+(4-2x)}$ complexes. Large differences in Na^+, K^+, or Ca^{2+} concentration had no effect on Np sorption indicating that sorption is not by ion exchange. Additional evidence for this conclusion is the fact that Np(IV) sorption on secondary minerals (which had the highest ion exchange capacity) was the weakest of the solids measured. Neptunium(IV) must be chemisorbed on the mineral surfaces.

The oxidation state of Pu in basalt is probably Pu(IV). Plutonium(IV) is much more strongly sorbed than the higher oxidation states. Calcium and sodium salts increase sorption by formation of insoluble Pu compounds. These may be slightly soluble double salts such as $CaPuF_6$ or $NaPuF_5$. As for Np, no evidence for ion exchange of Pu on minerals surfaces was found.

Americium solubility and sorption are strongly influenced Mg^{2+}. The solubility is lowered and sorption is increased when Mg^{2+} is present. It appears that Am forms an insoluble compound with Mg. Bicarbonate and SO_4^{2-} decrease sorption due to formation of complexes such as $AmCO_3^+$ and $AmSO_4^+$.

Technetium probably exists in the +4 oxidation state under the reducing conditions of a basalt formation. A possible species is TcO^{2+} which is strongly sorbed on the three solids studied. The only significant parameter found was the Eh buffer, hydrazine, which reduced TcO_4^- to Tc(IV).

Selenite ion, SeO_3^{2-}, was not reduced to Se° by hydrazine as expected from the standard half-cell potentials. Selenium does not sorb by anion exchange, but by chemisorption or precipitation. Calcium increases sorption probably by formation of a CaSe compound. Carbonate decreases sorption by making Ca^{2+} unavailable by forming complexes such as $CaHCO_3^+$ and $CaCO_3^\circ$.

As might be expected, Ra sorption is similar to that of Sr. Cation exchange is the main sorption mechanism. Sodium ion and K^+ both compete with Ra for sorption sites.

All sorption reactions studied thus far can be accurately described using the Freundlich isotherm, except when precipitation occurs. These isotherms can be used to quantify sorption and to determine at which point precipitation becomes important for various radionuclide-groundwater-solid systems.

Kinetics studies show that most sorption reactions are relatively fast. However, some groundwater-geologic solid reactions are slow and can influence sorption by dissolution of solid components. These are most important for reactions with secondary minerals which are not near equilibrium with Grand Ronde groundwater. Altered basalt, however, comes very close to being in equilibrium with this groundwater.

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REFERENCES

1. Allard, B., H. Kipatsi, and J. O. Liljenzin (1980), "Expected Species of Uranium, Neptunium, and Plutonium in Neutral Aqueous Solutions", J. Inorg. Nucl. Chem., 42, 1015-1027.

2. Ames, L. L. (1978), "Controlled *Sample Program, Publication No. 1 - Characterization of Rock Samples*". PNL-2797, Battelle, Pacific Northwest Laboratory, Richland, Washington

3. Anders, E. (1960), "Radiochemistry of Technetium", USAEC Report, NAS-NS-3021.

4. Barney, G. S. and B. J. Wood (1980), "Identification of Key Radionuclides in a Nuclear Waste Repository in Basalt", U. S. Department of Energy Report RHO-BWI-ST-9, Rockwell International, Richland, Washington, May, 1980.

5. Cleveland, J. M. (1970), "The Chemistry of Plutonium", Gordon and Breach Science Publishers, New York, N.Y.

6. Gorski, B. and H. Koch (1969), "The Chemistry of Technetium in Aqueous Solution", *J. Inorg. Nucl. Chem.*, *31*, 3565-71.

7. Kielland, J. (1937), "Individual Activity Coefficients of Ions in Aqueous Solutions", *J. Am. Chem. Soc.*, *59*, 1675-1678.

8. Plackett, R. L. and J. P. Burman (1946), "The Design of Optimum Multifactorial Experiments", *Biometrika*, *33*, 305-325.

9. Smith, M. J. *et al.* (1980), "Barrier Development for a Nuclear Waste Repository in Basalt, on Integration of Current Knowledge", U. S. Department of Energy Report RHO-BWI-ST-7, Rockwell International, Richland, Washington, August 1980.