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Strontium-85 and Plutonium–239 Sorption in Rock Samples from the Semipalatinsk Test Site, Kazakhstan

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ABSTRACT

The adsorption and desorption of strontium and plutonium were studied as a function of rock type and simulated ground waters from the Semipalatinsk Test Site (STS). Seven different rock types were obtained from the Balapan Region of the STS and were subjected to x-ray diffraction analyses. Two different ground waters were simulated using data supplied by the National Nuclear Center. The results indicate the sorption of strontium is strongly dependent on the minerals present in the rock species and on the total ionic strength of the ground water whereas, in all cases, plutonium was strongly irreversibly sorbed.

INTRODUCTION

The STS was used by the Soviet Union for testing nuclear devices for forty years The STS includes about 20,000 km^2 of the vast steppe in eastern Kazakhstan with semi arid plains with scattered ridges and rounded hills. In the northeast the elevations are about 300 m above sea level with intermittent drainage to the Irtysh River via the Shagan River. The annual rainfall of 22cm arrives as summer thunderstorms. The ground is frozen and snow covered for 6 months of the year. Ground water occurs as interstitial water in permeable zones in unconsolidated deposits but in the impermeable bedrock it is restricted to weathered zones and fractures. Pore space in the hard dense rocks is low and not significant for ground water movement. The water table in the unconsolidated materials occurs at depths of less than a meter to tens of meters and is hydraulically continuous with fracture water in the underlying rocks. The area around Shagan River is covered by alluvium and other unconsolidated sediments. No outcropping bedrock is visible.

There are three areas which were used for nuclear tests: for atmospheric tests, for tunnel horizontal shots (Degelen Mountain) and for vertical shaft shots (Balapan Lake) as shown in Figure 1.

No work has been reported on the subsurface movement of radionuclides although there are several surface studies (1,2,3). These surface studies show elevated surface radionuclide (Pu, Sr and Cs) contamination around the three testing areas. Subsurface movement is governed by many factors including rock structure, porosity, and ground water composition. The main rock types in the Shagan river area are sedimentary and volcanic including sandstone, shale, limestone, marl, welded tuff and flow rocks.

The retardation of radionuclide migration is an important feature in assessing the movement from the STS into the Shagan River and nearby Irtysh River and from there, eventually, through sediment transport, contributing to contamination in the Arctic.

We report here the sorption characteristics of seven of the main rock types found in the Shagan area of the test site where vertical underground shots were performed using the composition of two local ground waters. Strontium and plutonium were chosen as representative of radionuclides with different characteristics that present health problems when present at sufficiently elevated concentrations.

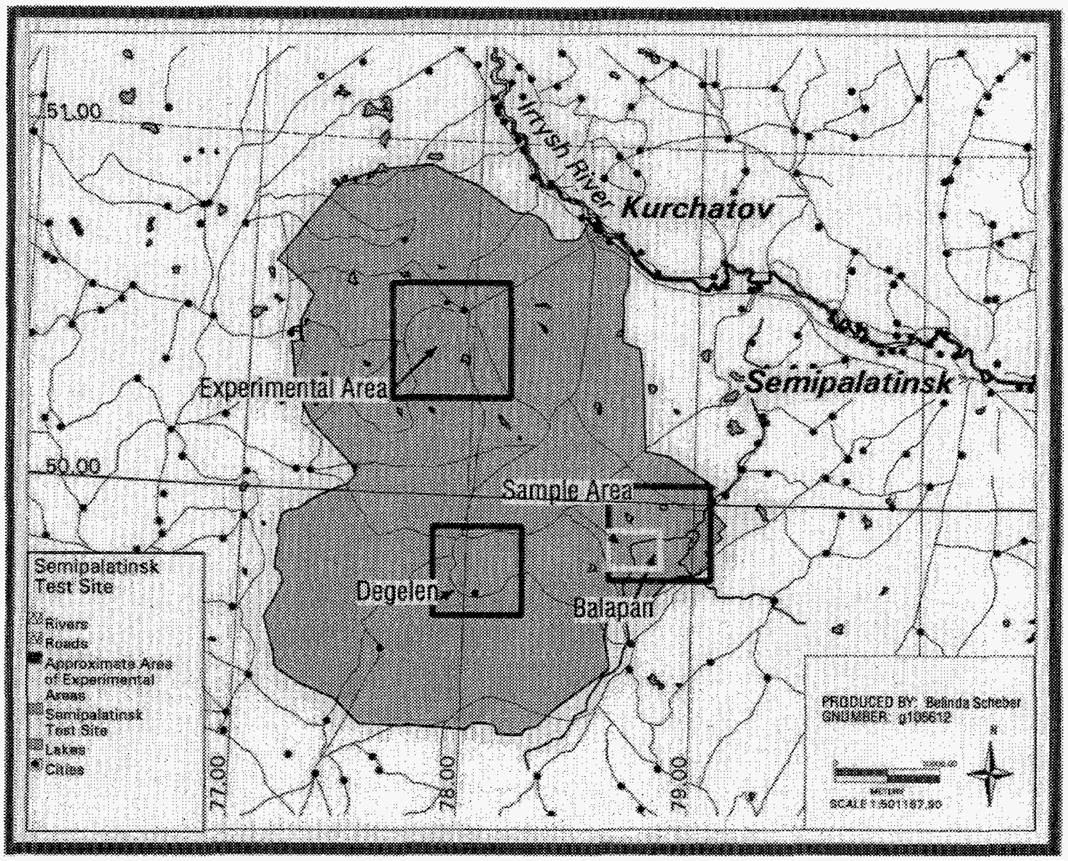


Figure 1.
Semipalatinsk Test Site, Kazakhstan showing the three test areas.

MATERIALS AND METHODS

Rock Samples

Seven rock samples were obtained from the Balapan Lake area from bore holes that were drilled for the geologic characterization of the area for nuclear weapons tests. These are listed in Table I.

Table I.
Rock Samples supplied by National Nuclear Center, Republic of Kazakhstan

Number	core hole number	depth m	Description	water table m
1	4076	91	tuff	37
2	4076	94	silt	37
3	4100	103.4	sand	13.6
4	4027	64.5	sandstone	?
5	4048	88.5	porphyrite	11.3
6	4041	76	sandstone	2
7	4035	92	tuff/silt	14.4

The locations are given in Figure 2. The core samples obtained were all south of the river except for 4076 that is in a region adjacent to the river that seasonally becomes marsh.

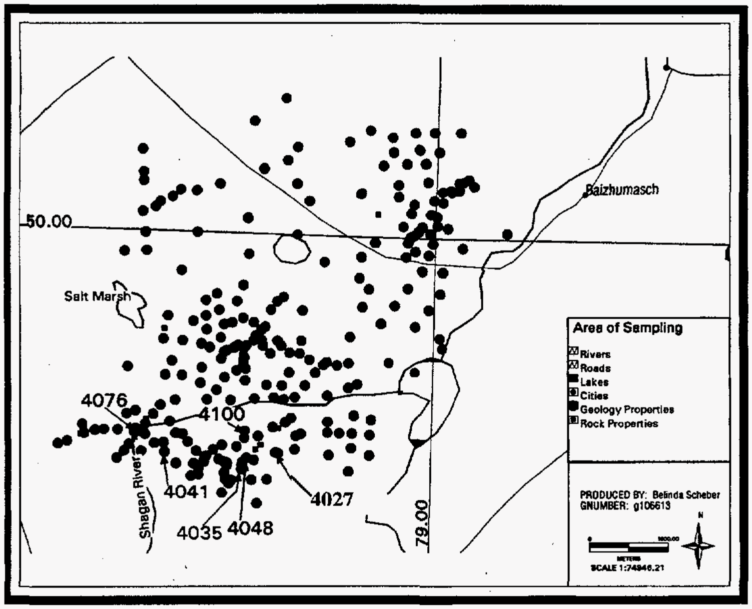


Figure 2.
Locations of Bore Holes in the Balapan area. The numbers show the bore holes from where the core samples were obtained.

Table II gives the geologic profiles of the six core samples.

4027		4035		4041		4048		4076		4100	
Start strata m	Description	Start strata m	Description	Start strata m	Description	Start strata m	Description	Start strata m	Description	Start strata m	Description
0	Sand	0	Sand	0	Sand Gravel	0	Sand Loam	0	Sand	0	Sand
6	Clay	2.3	Clay Sand	6	Tuff	5	Clay	3	Gravel	7.5	clay
17.5	Slate	3.5	Clay Sand	32	Silt	15.5	Sandstone	7	Sand	56.4	granite
25	Slate	25	Clay Sand	36	Tuff	30.2	Basalt porphyrites	9.5	Clay	61.2	
32	Slate	36	Tuff/ Sandstone	47	Tuff	75	Basalt porphyrites	74.9	Sandstone Silt	85.5	granite
47	Slate	60.7	Argillite	53	Tuff, Sandstone, Silt	**88**	**Basalt porphyrites**	80	Tuff	**88**	**sand**
68	**Tuff/sandstone**	**66**	**Tuff/Sandstone/Silt**	**63.5**	**Tuff/Sandstone/Silt**	100	Basalt porphyrites	**81**	**Sandstone/Silt**	105.2	
		95	Tuffobreccia	80.6	Tuff/Sand stone/Silt	106.5	Basalt porphyrites	95	Tuff		

Table II
Geologic Profiles of the seven core samples used. The actual samples are shown bolded.
(Data supplied by the National Nuclear Center, Kazakhstan)

The chemical composition of the water from bore holes has been extensively analyzed. Table III shows the range of the major cations and anions found from many analyses varying from one (4076) to 56 (4035). The 4035 analyses were taken over a period of five years during all months of the year.

Well Number	Depth m	pH	Na + K mg/l	Ca mg/l	Mg mg/l	NH_4 mg/l	Cl mg/l	SO_4 mg/l	HCO_3 mg/l
4027	25-20	7.9-7.6	2135-872	410-267	279-167	6-0	3230-740	2184-2040	159-104
4035	40	8.3-6.6	1339-767	183-111	199-76	20-0	1749-1101	1225-622	221-28
4041	20	8.4-6.6	1312-809	204-58	194-128	10-0	750-573	2256-1961	322-43
4048	40-20	8.4-6.4	119-815	262-141	159-76	20-0	1446 -817	1552-1187	197-101
4076	?	7.5	2524	494	532	5	4086	2691	439
4100	60	7.3-6.4	1470-58	277-29	221-6	15-0	1558 -36	2996-107	651-92

Table III.
Range of the chemical analyses obtained for ground water from the six bore holes.
(Data supplied by the National Nuclear Center, Kazakhstan)

METHODS

1. X-Ray Diffraction analyses.

All X-ray powder diffraction patterns (XRD) were obtained on a Siemens D500 X-ray powder diffractometer using CuKα radiation, incident- and diffracted-beam Soller slits, and a Kevex Si(Li) solid-state detector. X-ray diffraction runs were conducted from 2 to 50° 2θ, with 0.02° steps and counting times of at least 4 seconds per step.

To prepare the samples, a small portion of each sample (~0.8 g) was mixed with 1.0-µm corundum (Al_2O_3) internal standard in the ratio 80% sample to 20% corundum by weight. Each sample was then ground under acetone in an automatic Brinkmann Micro-Rapid mill (fitted with an agate mortar and pestle) for a time greater than 10 minutes. This produced a sample with an average particle size of less than 5 µm and ensured thorough mixing of sample and internal standard. The fine particle size is necessary to ensure adequate particle statistics and to reduce primary extinction and other sample-related effects

Quantitative XRD analyses for this report employed the internal standard or "matrix-flushing" method of Chung (1974) using synthetic 1.0-µm corundum as the internal standard. The method has been extensively modified, however, to utilize multiple reflections and intensity ratios. Complete outlines of the methods we use for quantitative analyses are provided in Bish and Chipera, 1988; 1989; and Chipera and Bish, 1995.

2. Rocks

Each rock sample was ground to a powder. The powder was successively sieved through a 500-µm and a 75-µm US standard sieves. The samples with particle size ranged from 75 µm to 500 µm were collected and stored for sorption experiments. The methods used for collecting the core samples are unavailable.

3. Solutions

Two synthetic groundwaters, referred to as 4076 (pH 7.5) and 4100 (pH 6.8), and two deionized waters, referred as to DI-4076 (pH 7.5) and DI-4100 (pH 6.7) were used. The 4076 synthetic groundwater consists of 7.2 x 10^{-3} M sodium bicarbonate ($NaHCO_3$), 2.19 x 10^{-2} M magnesium sulfate ($MgSO_4$), 6.33 x 10^{-3} M calcium chloride ($CaCl_2$), 0.103 M sodium chloride (NaCl), and 5.96 x 0^{-3} M calcium sulfate ($CaSO_4$).

The ionic strength of the solution was 0.2405 M. The 4100 synthetic groundwater consists of 1.606 x 10^{-3} M $NaHCO_3$, 2.467 x 10^{-4} M $MgSO_4$, 1.015 x 10^{-3} M NaCl, 9.36 x 0^{-5} M sodium sulfate (Na_2SO_4) and 7.735 x 10^{-4} M ($CaSO_4$). The ionic strength of the solution was 6.861 x 10^{-3} M.

4. Tracer solutions

Plutonium-239 tracer solution. The ^{239}Pu(V) stock solution contained 7.65 x10^{-4} mole (M) of Pu with 99.7% of Pu(V), and consists of 93.9% of ^{239}Pu. A ^{239}Pu(V) experimental solution was prepared by diluted 1.6 ml of ^{239}Pu(V) stock solution with 998.4 ml of nanopure deionized water resulting in a solution containing 1.143 x 10^{-7} M of Pu. The activity of the work solution was determined using a liquid scintillation analyzer. The α activity of ^{239}Pu(V) was 277,870 Bq kg^{-1}. The pH value of the work solution is 6.03.

Strontium-85 tracer solution. The ^{85}Sr stock solution contained 1.0 mCi of Sr in 0.1 M HCl, and consists of 99.98% of ^{85}Sr (half life $t_{1/2}$ = 64.8 d). The ^{85}Sr activity of 1.0 mCi was measured in January 14, 1998 when ^{85}Sr stock was shipped to our Lab. A ^{85}Sr experimental solution was prepared by diluted 0.15 ml of ^{85}Sr stock solution with 999.85 ml of nanopure deionized water resulting in a solution containing 0.165 mCi L^{-1} of ^{85}Sr. The activity of the experimental solution was determined using a gamma spectroscopy. The result was corrected by a fact of 0.28 (the efficiency of the gamma spectroscopy) and also by decay factor related to January 14, 1998, referred to as t = 0. The γ activity of the ^{85}Sr work solution was 632,555 counts per minute per milliliter (CPM ml^{-1}). The pH value of the work solution is 5.91

5. Sorption procedure

Sorption experiments were performed in duplicate at room temperature. One gram of rock powder sample, 20 mλ of each water (e.g., 4076, 4100, DI-4076, or DI-4100) and 3 mλ of ^{239}Pu(V) or ^{85}Sr work solution were placed in a pre-weighed Oak Ridge centrifuge tube (50-m), and were agitated on an orbital shaker at 150 rpm for 5 days. At the same time, blank samples were also set up using 20 mλ of each water without any rock samples and 3 mλ of ^{239}Pu(V) or ^{85}Sr experimental solution. At the end of sorption period, the samples and blanks were centrifuged at 38,300 g for 30 minutes. The supernatant was filtered through a 0.2-μm nylon filter membrane using a syringe. The adsorbed values of ^{239}Pu(V) or ^{85}Sr onto rock samples were corrected with results from blank samples.

The α activities of the supernates collected from Pu sorption experiments were determined using liquid scintillation analyzer. The γ activities of the supernates collected from Sr sorption experiments were measured as follows: one milliliter of the supernate collected from each rock sample was placed in a counting tube and counted for 20 minutes by gamma spectroscopy. The results were then converted to counts per minute per milliliter (CPM ml^{-1}) and corrected by a factor of 0.28 (the efficiency of the gamma spectroscopy), followed by decay correction related to the initial time, January 14, '98, referred to as t = 0.

The sorption distribution coefficient (Kd_S, ml g^{-1}) of Pu or Sr on each rock sample is calculated using the following equation:

$$Kd_S = [(C_oV_o - C_i)/M]/C_I \qquad [1]$$

where C_o is the initial adsorptive concentration of ^{239}Pu(V) or ^{85}Sr per milliliter solution, V_0 is the adsorptive solution volume (ml) in contact with rock samples, C_i is the total radioactivity of ^{239}Pu(V) or ^{85}Sr remaining in the solution after sorption (CPM), C_I is the radioactivity remained in unit solution (CPM ml^{-1}), and M (g) is the mass of rock sample used in the sorption process.

6. Desorption procedure

Plutonium-239-loaded rock samples and ^{85}Sr-loaded rock samples were obtained from sorption process. After the wet weights of the rock samples were obtained, the samples were extracted successively with ^{239}Pu-free, or ^{85}Sr- free water of 4076, 4100, DI-4076, or DI-4100 and were agitated on an orbital shaker at 150 rpm. Desorption of ^{239}Pu from rock samples was allowed to proceed from 10 days to 70 days. Desorption of ^{85}Sr from rock samples was proceeded for 15 days. Each sampling time, the extracts were separated applying the same centrifuge and filter procedures used in the sorption experiments. The activity of ^{239}Pu in the extracts was measured using liquid scintillation analyzer. The activity of ^{85}Sr in the extracts was measured using the same method applied in the sorption experiments. The results from ^{85}Sr desorption process were then converted to counts per minute per milliliter (CPM ml^{-1}) and corrected by a factor of 0.28 and by decay factor related to the initial time, t = 0.

RESULTS.

The rock samples were subject to x-ray diffraction analysis. The results are given in Table 1V.

Sample	Chlorite	Mica/ Illite	Quartz	Feldspar	Calcite	Dolomite/ Ankerite	Hematite	Magnetite	Total
#1	13 ± 1	1 ± 1	13 ± 1	63 ± 9	6 ± 1	3 ± 1	1 ± 1	1 ± 1	101 ± 9
#2	7 ± 1	3 ± 1	25 ± 2	38 ± 5	—	2 ± 1	1 ± 1	—	76 ± 6
#3	2 ± 1	3 ± 1	30 ± 2	58 ± 8	—	1 ± 1	Trc.	1 ± 1	95 ± 8
#4	7 ± 1	6 ± 2	16 ± 1	51 ± 7	—	Trc.	Trc.	—	80 ± 7
#5	Trc.	11 ± 3	24 ± 2	32 ± 4	18 ± 1	1 ± 1	11 ± 1	1 ± 1	98 ± 6
#6	9 ± 1	3 ± 1	29 ± 2	51 ± 7	2 ± 1	1 ± 1	Trc.	—	95 ± 8
#7	5 ± 1	3 ± 1	33 ± 2	39 ± 5	2 ± 1	—	Trc.	—	82 ± 6

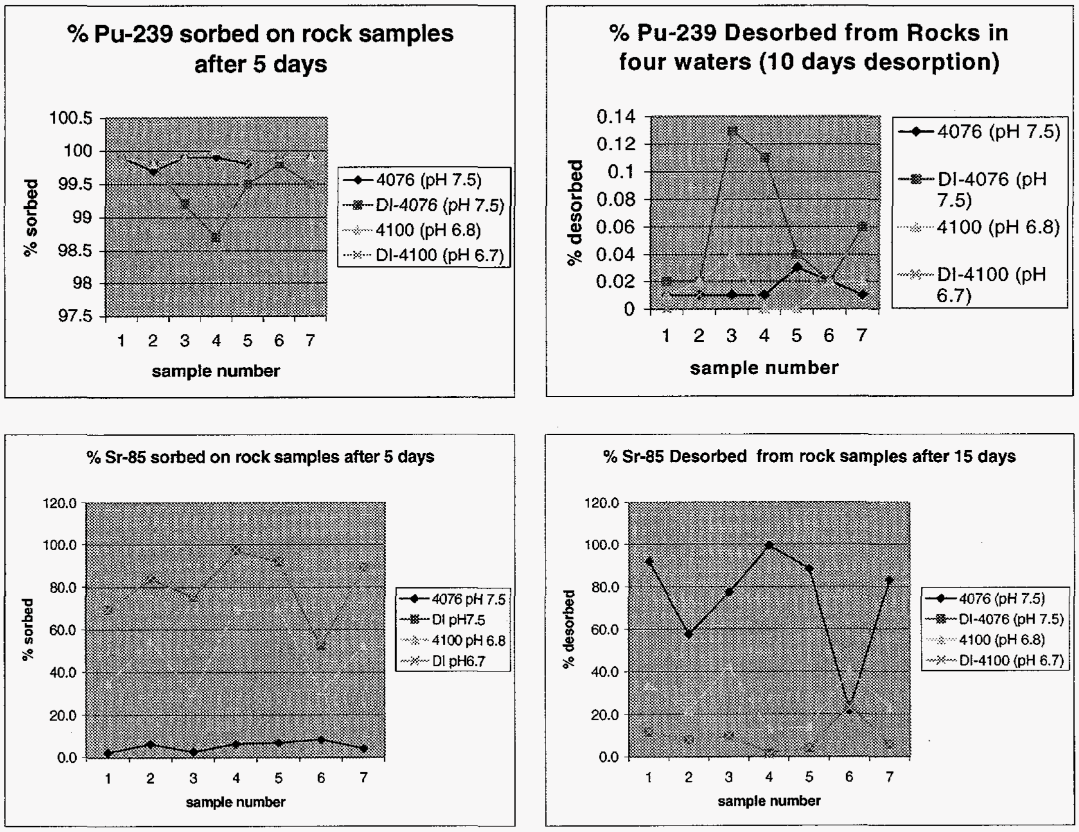
Table IV

Results of x-ray diffraction analyses.

Results are in weight percent. Errors are conservative 2-sigma values.

Trc. = Trace amount less than 0.5 weight percent. — = not detected.

Figure 3. Sorption and Desorption Data for ^{239}Pu(V) or ^{85}Sr



Discussion
Geology
Waters
Sorption data OS competitive ions Sr not sorbed onto illite

1. Chlorite	**2. Mica/ 3. Illite**	**4. Quartz**	**5. Feldspar**	**6. Calcite**	**7. Dolomite/ 8. Ankerite**	**9 Hematite**	**10. Magnetite**

Shows the arrangement of minerals which are common to many rock structures.
Primary minerals from igneous and metamorphic rocks formed at high temperatures:

Feldspars, quartz – most abundant

4. Quartz (SiO_2)
5. **Feldspar aluminum silicates $MAlSi_3O_8$ - greatest abundance (M= Na, K, Ca) tectosilicates**
2. **Mica- thin layered complex silicate – phyllosilicates clay minerals**
3. **Illite- hydrous mica**

Secondary minerals formed at low temperatures
layered silicates
and oxides

6. Calcite calcium carbonate Calcium –high exchange capacity
7. Dolomite magnesium calcium carbonate
8. Ankerite iron calcium carbonate

1. Chlorite –complex silicate mineral 2:1:1 layered silicate. Sheets of brucite magnesium hydroxide sheets between negativelt charged mica sheets. Reduces ion exchange capacity because effective CEC 100-400 mmoles (+)kg^{-1}

9. Hematite iron (III) oxide
10. Magnetite (ironII/III oxide)

Isomorphic substitutions in silicate structures Al (3+) for Si(4+) in tetrahedral structures
And Mg (2+), Fe (2+) and Fe (3+) for Al3+ results in charge imbalance

Micas, chlorite and feldspars are all complex silicates with arrangements of octahedral and tetrahedral silicates

Chlorites- non expanding silicates with low cation exchange capacities phyllosilicates

Adsorbed cations are held by layer silicates to balance the negative charge of the unit layerresulting from isomorphic substitution and from broken bonds on cruystakl edges. The magnitude of the exchange capacity of the crystal edge is a direct function of crystal size. When the layer charge is high , as in mica, bond energy great, adsorbed cations not exchangeable.

Particles too large to show clay properties (2 um)
Surface area and surface charge

Mica/ chlorite – layer charge of 1 , low cation exchange capacity. Affected bypH.
Factors affecting sorption:
Rock type
PH

Ionic strength
Competition between ions

All rock samples were from beneath the water table.
Th presence of the ions decreased the sorption of strontium, i.e. Sr at the lower concentration present could not compete for sorption sites.

The Sr is probably sorbed via ion exchange mechanisms as has been found in previous studies.

Clays have a negative surface charge which attract positive cations like Sr and Pu.

Most important factor is valence Pu occurs in environment as +5 (Clark reference) because such high OS competes successfully with any other potential cation as no other present as +5
Sr +2 so competes with Ca . high ionic strength means other cations present at high concentrations will also compete for exchange sites. Accounts for lower uptake in 4100 than in 4076. Ca and Sr similar (both divalent, dehydrated radii nm Ca^{2+} 0.099, Sr^{2+} 0.112)

Cation usually reversible, stoichiometric and reversible. But preferential sorption of polyvalent cations, like Pu .

In this study no organic component present because crushed rock used with no organics present as would be present in soils.

Acknowledgment
Many people have contributed to this study including Ines Triay, Ron Augustson, and Katy Griggs. Our thanks go out to all of them.

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