

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/7735165>

# Metal Ion Sorption and Desorption on Zeolitized Tuffs from the Nevada Test Site

ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · FEBRUARY 2004

Impact Factor: 5.33 · DOI: 10.1021/es0343050 · Source: PubMed

---

CITATIONS

18

---

READS

37

2 AUTHORS, INCLUDING:



Wooyong Um

Pacific Northwest National Laboratory

91 PUBLICATIONS 798 CITATIONS

SEE PROFILE

# Metal Ion Sorption and Desorption on Zeolitized Tuffs from the Nevada Test Site

WOORYONG UM\* AND  
CHARALAMBOS PAPELIS

*Division of Hydrologic Sciences, Desert Research Institute,  
Las Vegas, Nevada, 89119*

Because of the hundreds of nuclear weapon tests conducted on the Nevada Test Site (NTS) during the Cold War, the migration of radionuclides and contaminants is a potential concern. The mobility of these compounds and our ability to remediate contaminated sites are controlled by sorption and desorption processes, which depend frequently on the nature of the contaminant, the mineralogy of the site, and the geochemical conditions. The sorption and desorption behavior of strontium (Sr) and lead (Pb), two metal cations with different chemistries, commonly found on nuclear test sites were studied. Strontium showed pH-independent and ionic-strength-dependent sorption, consistent with ion exchange processes at permanent charge sorption sites. The sorption uptake of Sr increased with decreasing ionic strength of background solution. Strontium desorption from the adsorbents was enhanced by increased background electrolyte concentration and was a function of background electrolyte composition. The fractional uptake of Pb was higher, compared to that of Sr, and was only pH dependent at the highest ionic strength used (1.0 M). This pH-dependent sorption behavior, consistent with formation of surface complexes at amphoteric surface hydroxyl sites or formation of surface precipitates, could explain the decreased Pb desorption, compared to that of Sr, especially at increased background electrolyte concentrations. Under conditions typical for the groundwater at the NTS ( $I = 0.003$  M,  $\text{pH} = 8.0$ ), both Pb and Sr are expected to bind strongly on tuffs with composition similar to the zeolitized tuffs used in this study. Any increase in the dissolved ion concentration of the groundwater, however, may result in, at least partial, release of Sr and enhanced Sr mobility.

## Introduction

The potential release of radionuclides and heavy metals from nuclear waste repositories or test sites may have severe environmental and human implications. Sorption and desorption, physicochemical interactions between adsorbent and adsorbates at mineral–water interfaces, are among the most important processes controlling the migration of toxic contaminants in the subsurface environment. An understanding, therefore, of the processes controlling the distribution of a contaminant of concern between the aqueous and solid phases is required to predict the transport of contaminants in nature.

Given the frequent occurrence of strontium (Sr) and lead (Pb) in nuclear waste repositories and nuclear weapon test sites, the sorption behavior of these contaminants onto clay minerals has been widely studied (1–5). Because of their high cation exchange capacity (CEC) and low permeability, clay minerals may be used as barriers to the migration of radionuclides and heavy metals. Zeolites have also been studied as possible adsorbents for the removal of radioactive wastes and heavy metals, because of their high CEC and molecular sieve structure (6–14).

According to previous studies, Sr sorption on smectite is controlled by cation exchange, and the sorption was reversible in the presence of a strong desorption reagent solution (1 N KCl) (5). Lead, however, shows a relatively stronger sorption affinity, compared to that of Sr, for kaolinite (2). These authors have attributed the strong Pb sorption affinity for the kaolinite surface to binding on either ion exchange sorption sites or surface hydroxyl sorption sites. Another possible immobilization mechanism of Pb is through the formation of a carbonate occlusion, as in calcareous clay sediments used in landfill liners (15). Finally, because of extensive hydrolysis, Pb sorption on iron and aluminum oxides is much stronger than Sr sorption on the same minerals (16).

Because of the interest in zeolites as exchangers for the removal of heavy metals and radionuclides, exchange isotherms for a variety of metal ions on several natural and synthetic zeolites have been obtained. Clinoptilolite, one of the most common zeolites, has been used in many ion exchange studies (11, 17–21). In addition, in several studies, selectivity series for a number of metal ions have been reported (10, 11, 17, 19). The ion exchange properties of these zeolites were found to be a function of solution composition (9, 10, 12), the specific form of the cation-exchanged zeolite (10, 18), temperature (14), and zeolite structure (Si/Al ratio) (21).

The desorption behavior of radionuclides and other contaminants is at least as important as their sorption behavior. The use of the ubiquitous equilibrium distribution coefficient ( $K_d$ ) to model ion partitioning at mineral–water interfaces also, by definition, assumes reversible sorption. This assumption is often valid in the case of organic chemicals, but it is not always justified in the case of inorganic chemicals where sorption may be at least partly irreversible. Sorption and desorption experiments with zinc, nickel, cobalt, strontium, and cesium on natural soils and clay minerals were conducted to estimate the reversibility of sorption and the mobility of metals of concern in an aqueous solution (5, 11, 22, 23). The reversibility of Pb sorption on clinoptilolite was examined as a function of other exchange cations present in the zeolite structure (20).

In considering the reversibility of sorption in the subsurface environment, it is important to determine if the geochemical conditions in the groundwater remain at steady state or change along the flow path due to mineral dissolution, precipitation, or redox reactions (24). If the geochemical conditions of the groundwater change, transport models that are based on condition-specific parameters, such as the linear isotherm equilibrium distribution coefficient ( $K_d$ ), may lead to significant errors whenever changes in solution conditions substantially affect the sorption behavior of the ions (24, 25).

The objective of this study was to investigate the sorption and desorption behavior of Sr and Pb on zeolitized tuffs from the Nevada Test Site (NTS). Strontium was chosen because it is one of the most commonly encountered radionuclides in nuclear test sites and radioactive waste material. Lead was chosen because it is also frequently found on the NTS,

\* Corresponding author phone: (509) 376-4627; fax: (509) 373-9675; e-mail: wooyong.um@pnl.gov. Current address: Pacific Northwest National Laboratory, Richland, Washington, 99352.

TABLE 1. Summary of Adsorbent Characterization

size fraction (mm)	specific surface area <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> )	average pore diameter <sup>a</sup> (nm)	cation exchange capacity (CEC) <sup>b</sup> (cmol kg <sup>-1</sup> )
<0.25	12.27	13.63	143
0.25–0.5	9.38	14.29	
0.5–1.18	9.92	13.49	130
1.18–2.8	8.17	13.84	

<sup>a</sup> Specific surface area and average pore diameter were measured by the BET-N<sub>2</sub> method (27). <sup>b</sup> Cation exchange capacity (CEC) was measured using exchangeable NH<sub>4</sub><sup>+</sup> at soil pH (28).

originating from the shielding of nuclear devices. On the basis of significant differences in the aqueous chemistry of the two elements, it was assumed that their sorption and desorption behavior would also be significantly different.

## Materials and Methods

**Materials.** Zeolitized tuffs used in this study were collected from an outcrop on the Rainier Mesa at the NTS with longitude 116° 9' 51" W and latitude 37° 11' 58" N (NAD 27). The physicochemical characteristics of the adsorbents are shown in Table 1. The surface morphology of zeolitized tuffs was investigated by scanning electron microscopy (SEM) and elemental composition was determined using an energy-dispersive X-ray (EDX) attachment (26). An electron micrograph of the zeolitized tuff rock sample, before size reduction, showed anhedral masses of zeolites and a clinoptilolite crystal of typical coffin-shape habit with major elements silicon (Si) and aluminum (Al). Zeolitized tuffs were crushed in the laboratory, and the particle-size distribution was determined using a Micromeritics Sedigraph 5100. The crushed tuff particles smaller than 0.25 mm had a median diameter, based on a distribution by mass, of 11.84  $\mu$ m.

The mineralogy of the adsorbents was determined by X-ray diffraction (XRD) using Cu K $\alpha_1$  radiation ( $\lambda = 0.15405$  nm). An XRD spectrum of a tuff sample is shown in Figure 1. The average semiquantitative estimate of the mineralogical composition of the tuff, based on duplicate samples, was 50% clinoptilolite and 50% feldspars (mostly albite and anorthite, the Na and Ca end members of plagioclase feldspars, respectively), with minor concentrations of quartz and traces of iron oxides. The specific surface area and the pore-size distribution of different size fractions were estimated using a Micromeritics ASAP 2010 surface area analyzer and the BET-nitrogen method (27). The specific surface area increased with decreasing particle size. The CEC of the adsorbents was determined at the measured pH of the solid suspension (8.2) with an ammonia acetate electrode according to the procedure of Busenburg and Clemency (28). The measurement of CEC was conducted in duplicate and the results were averaged.

**Macroscopic Sorption and Desorption Studies.** All experiments were conducted at ambient temperature (20–22 °C) using reagent-grade chemicals and NANOpure water (reagent-grade water with at least 18 M $\Omega$  cm<sup>-1</sup> resistivity). Zeolitized tuffs were washed with 0.1 N hydrochloric acid to remove the easily soluble metal ions and organic coatings. The solid was then rinsed as required with NANOpure water until the concentration of the metal ion of interest (Sr and Pb) in the leachate was less than 10<sup>-7</sup> M, which was less than 10% of the lowest metal concentration used in these experiments (see below). The concentration of Pb was negligible in all samples and no rinsing would have been required if it had been the only metal of concern. The concentration of Sr, however, was occasionally higher. This is not surprising given that Sr is the 15th most abundant element on the earth's crust (384 ppm), whereas Pb is the

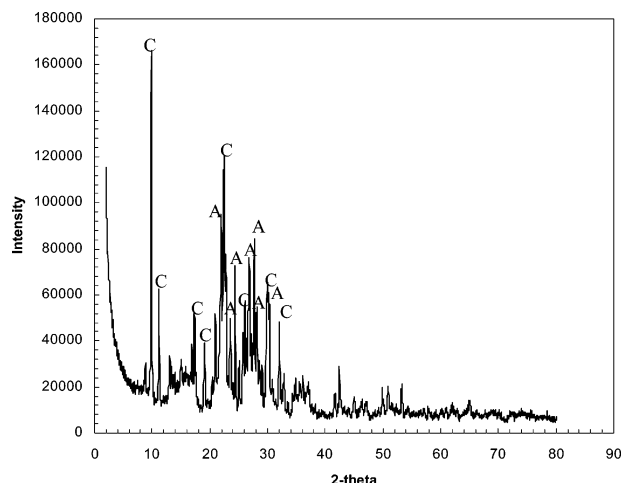


FIGURE 1. X-ray diffraction (XRD) spectrum of a zeolitized tuff sample. The peaks labeled C correspond to the mineral clinoptilolite and the peaks labeled A correspond to the mineral albite.

36th most abundant element (13 ppm) (29). Although rinsing the adsorbent may alter the sorptive properties of the soil (at least with respect to Sr sorption), the presence of naturally occurring Sr would render interpretation of sorption results very difficult. Interpretation of desorption results would be even more questionable, given that the origin of the measured Sr concentration could not have been determined.

Batch sorption experiments were conducted in 12-mL polypropylene centrifuge test tubes by mixing ground zeolitized tuffs with the metal ions of interest. The size fraction smaller than 0.25 mm was used for all batch sorption and desorption experiments. Sodium nitrate (NaNO<sub>3</sub>) was used to adjust the ionic strength of the background solution. Nitric acid (HNO<sub>3</sub>) and sodium hydroxide (NaOH) were used to adjust the solution pH between 3 and 9. Aqueous metal solutions of Sr and Pb were prepared from strontium nitrate (Sr(NO<sub>3</sub>)<sub>2</sub>(s)) and lead nitrate (Pb(NO<sub>3</sub>)<sub>2</sub>(s)), respectively.

In a total volume of 10 mL, various metal concentrations (10<sup>-6</sup> to 10<sup>-4</sup> M) and solid concentrations (1, 3, and 10 g L<sup>-1</sup>) were used in the sorption and desorption experiments. The solid was weighed directly into individual centrifuge tubes. Sorption of metal ions on the polypropylene test tubes was also checked and was found to be negligible. Although the system was not CO<sub>2</sub>(g) free, the experimental protocol was designed to minimize the effects of CO<sub>2</sub>(g) presence. First, all experiments were conducted in test tubes closed to the atmosphere with minimal headspace. In addition, all stock solutions were acidified to minimize CO<sub>2</sub>(g) absorption. Thus, the samples were definitely undersaturated with respect to CO<sub>2</sub>(g), certainly under alkaline experimental conditions. Given the relatively low metal concentrations used in these experiments, which was further decreased by sorption on the mineral adsorbent, the precipitation of metal carbonate phases was unlikely.

In general, 8–10 test tubes were set up for sorption experiments under otherwise identical conditions, except for pH. A blank solution sample, without solid, was included in the set as a standard for the metal concentration. The samples were equilibrated by end-over-end rotation for 48 h. Previous kinetic studies showed that a 48-h equilibration period was sufficient (30). After equilibration, the samples were centrifuged at a relative centrifugal force of 9500 for 30 min to separate the solution from the solid. The final pH was measured and a 2-mL aliquot was removed from the supernatant. Metal concentrations were measured using graphite furnace atomic absorption spectrometry (GFAAS) (Perkin-Elmer 4110 ZL with Zeeman background correction). The fractional sorption uptake (expressed as a percentage of

the total metal concentration) was determined by the difference between the initial and the final metal concentration in the supernatant. All reported results are averages of duplicate measurements.

Sorption competition between Sr and Pb was evaluated by first determining the sorption uptake of each metal by zeolitized tuffs. Competition experiments were then conducted by adding both Sr and Pb but otherwise conducting the experiments as usual as a function of pH, ionic strength, and solid concentration. After a 48-h equilibration period, each metal concentration was measured by GFAAS, and the fractional sorption uptake of each metal was determined as usual.

Desorption experiments were conducted following the sorption experiments. After sorption steady state was reached, the test tubes were centrifuged and the supernatant (10 mL) was removed. The metal concentration in the supernatant was measured and the sorbed metal concentration on the solid was determined by difference. An equal volume (10 mL) of desorption solution, a solution without the metal of interest, was introduced into each test tube. The desorption solutions were of either the same or different composition, compared to the initial background electrolyte solution used during the sorption experiments, to test competition effects between background electrolyte ions and the metal ion of interest. Specifically, in addition to the NaNO<sub>3</sub> solutions used as a background electrolyte for the sorption experiments, Ca(NO<sub>3</sub>)<sub>2</sub> solutions were also used in the desorption experiments. The desorption for each metal ion was also tested by desorption experiments using the same background electrolyte solution. Individual test tubes were prepared, under the same conditions, including pH, for testing desorption as a function of time. The supernatant of individual test tubes was tested for metal concentration at different time intervals. Although the sampling frequency could be adjusted depending on previous results, typical sampling times included 12 h, and 1, 7, 14, 30, and 60 days.

## Results and Discussion

**Batch Sorption Experiments.** Although using powdered samples is convenient, it may present a number of problems when trying to use these data to predict sorption in the field because of the different surfaces exposed after size reduction. In addition, the fresh surfaces may have characteristics different from those of the undisturbed rock. Finally, even if the characteristics of the surfaces were not size dependent, the increased specific surface area of smaller particles would lead to increased metal ion sorption. Thus, retardation in the natural environment may be significantly less than what would have been predicted based on experiments with crushed rock samples. The combination of adsorbent characterization and types of experiments performed during this study were designed to address some of these issues. First, the adsorbent characterization was performed after the material was reduced in size, so that the observed sorption behavior could be at least correlated to the properties of the material. Second, as can be seen from Table 1, the high specific surface area of these samples was a rather weak function of particle size, suggesting that the majority of the surface area was internal and accessible, even in larger particles. Third, no organic or inorganic coatings were observed in the sample so that size reduction was not expected to result in creation of drastically different surfaces. Obviously, if iron or organic coatings were present in the original sample, crushing the rock would have resulted in the formation of sorbing surfaces with little mineralogical similarity to the original unaltered surfaces.

The sorption uptake of Sr and Pb by zeolitized tuffs under different ionic strength ( $I = 0.01, 0.1$ , and  $1.0$  M NaNO<sub>3</sub>) and pH conditions is shown in Figure 2. The error bars plotted

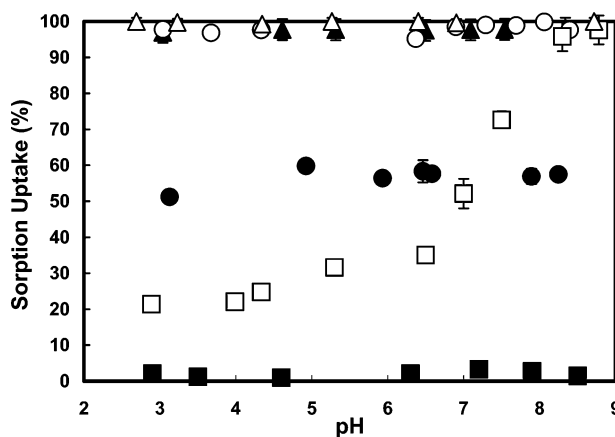


FIGURE 2. Sorption of Sr and Pb on 3.0 g/L zeolitized tuffs as a function of pH and ionic strength. Initial metal concentration:  $10^{-5}$  M. ( $\blacktriangle$ ) Sr,  $I = 0.01$  M NaNO<sub>3</sub>; ( $\bullet$ ) Sr,  $I = 0.1$  M NaNO<sub>3</sub>; ( $\blacksquare$ ) Sr,  $I = 1.0$  M NaNO<sub>3</sub>; ( $\triangle$ ) Pb,  $I = 0.01$  M NaNO<sub>3</sub>; ( $\circ$ ) Pb,  $I = 0.1$  M NaNO<sub>3</sub>; ( $\square$ ) Pb,  $I = 1.0$  M NaNO<sub>3</sub>. The error bars represent one standard deviation based on duplicate experiments.

with each data point in Figure 2 and all subsequent figures represent one standard deviation of two replicates. Strontium showed ionic-strength-dependent sorption, irrespective of pH. At the lowest ionic strength,  $I = 0.01$  M, Sr was essentially quantitatively removed from solution (at least 95% sorption uptake) and the fractional uptake decreased with increasing ionic strength. The decrease in sorption with increasing ionic strength can be attributed to increased competition between Sr and sodium (Na) from the background electrolyte. Given the finite number of sorption sites, the increase of Na concentration by 2 orders of magnitude is likely to result in increasing exclusion of Sr from sorption sites.

Because the total Na concentration was 5 orders of magnitude higher than the total Sr concentration at the highest ionic strength (1.0 M), the orders-of-magnitude higher Na concentration compared to Sr can explain the exclusion of Sr from cation exchange sites, although the preference of clinoptilolite for Sr, compared to Na, is well-known (11). In addition, the observed preference of clinoptilolite for Sr, compared to Na, is expected on the basis of ion charge considerations (31). Given that the sorption mechanisms of Na and Sr, alkali and alkaline earth metals, respectively, are not expected to be dramatically different, it is not surprising that Sr sorption is increasingly suppressed by increasing Na concentration.

The results shown in Figure 2 are consistent with the above assumptions. Sorption of Sr decreased from approximately 95% to 55% to essentially zero for the three different ionic strengths used. In addition, the pH-independent sorption behavior, irrespective of ionic strength, is consistent with sorption at permanent charge, cation exchange sites of the zeolite minerals. Sorption by a cation exchange process is a plausible sorption mechanism, given the high CEC of the sorbent (Table 1) and the tendency of Sr to form outer-sphere complexes, regardless of substrate, as confirmed by many investigators (32, 33).

Lead sorption was significantly different. At the two lower ionic strengths used ( $I = 0.01$  and  $0.1$  M NaNO<sub>3</sub>) Pb was essentially quantitatively removed from solution, regardless of pH. The high affinity of Pb for clinoptilolite is well documented (10, 11, 17–19). The sorption behavior of Pb was qualitatively similar to the sorption behavior observed for Sr, although Pb sorption at the middle ionic strength (0.1 M) was substantially higher than that of Sr. These results would suggest that under these conditions, Pb, like Sr, sorbs by a cation exchange process, although the affinity of Pb for the tuff is higher than that of Sr. The quantitative differences



between Pb and Sr can probably be explained by the differences in hydrolysis of the two elements (34) and have been reported in previous studies of Pb and Sr sorption on clinoptilolite (10, 11). In both studies, Pb uptake exceeded Sr uptake, consistent with results in this study.

At the highest ionic strength ( $I = 1.0 \text{ M NaNO}_3$ ), however, Pb sorption became pH-dependent, increasing with increasing pH (Figure 2). This behavior would indicate that under these conditions, Pb is either sorbing on pH-dependent, surface hydroxyl sites, or that hydrolysis leads to the formation of surface polynuclear complexes or precipitates. The existence of hydrolyzable aluminol and silanol sites at the edges or corners of zeolite channels or on the surfaces of feldspar minerals is documented. Lead interaction with such sites would become increasingly important with increasing pH, leading to the observed behavior.

The difference in sorption behavior between Pb and Sr at the highest ionic strength can be attributed to the different affinities of the two elements for surface hydroxyl sites. The formation of Pb inner-sphere complexes on amphoteric sites of oxides has been documented (35, 36). Strontium, however, has never been shown to form inner-sphere, coordination complexes on any hydrated mineral surface. The different sorption mechanism of Pb binding on surface hydroxyl sites, compared to that of Sr, could be used to explain the observed difference in sorption behavior. In the case of Sr, given that it binds exclusively as an outer-sphere complex (weak and ionic strength dependent binding), sorption by cation exchange is the predominant binding mechanism. Given the abundance of cation exchange sites compared to pH-dependent sites on these tuffs and the highly acidic character of the pH-dependent sites of quartz and feldspars, sorption of Sr is expected to be controlled by cation exchange. When the Na concentration is high enough to suppress Sr binding by cation exchange, it would also be high enough to suppress sorption on pH-dependent sites. On the other hand, under the same high ionic strength conditions when Pb is excluded from cation exchange sites, formation of inner-sphere complexes, polynuclear complexes, or surface precipitates is still possible. Under these conditions, the sorption of Pb is expected to show strong pH dependence. In fact, Pb sorption under even higher ionic strength (2.0 M, not shown here) was essentially indistinguishable from the results at 1.0 M ionic strength.

Macroscopic experiments alone, however, cannot be used to differentiate between inner- and outer-sphere complex formation. Spectroscopic techniques, such as X-ray absorption spectroscopy (XAS), can be used to distinguish between the two different sorption mechanisms. Results of XAS analysis indeed suggest that Sr formed mononuclear outer-sphere complexes, whereas Pb formed polynuclear inner-sphere complexes at the zeolite–water interface at high pH (37). At low pH (3–5), cation sorption on the fully protonated surface hydroxyl sites should not be significant, while limited sorption on cation exchange sites could explain the observed behavior. Compared to Sr, Pb uptake by cation exchange sites was higher, at any ionic strength, and that may explain the limited sorption of Pb at the highest ionic strength, whereas no appreciable sorption of Sr was observed.

**Sorption Competition.** To investigate the sorption competition between the two metals for limited sorption sites, sorption experiments were conducted in which  $10^{-5} \text{ M}$  Sr and Pb were added simultaneously (Figure 3). As expected, based on the previous results with individual metals, Pb sorbed stronger compared to Sr under all conditions. At low ionic strength ( $I = 0.01 \text{ M NaNO}_3$ ) and at the higher solid concentration ( $3 \text{ g L}^{-1}$ ), Sr and Pb sorption was indistinguishable from the results obtained with individual metals (more than 95% sorption uptake). Apparently, under these conditions of ionic strength and solid and metal concentra-

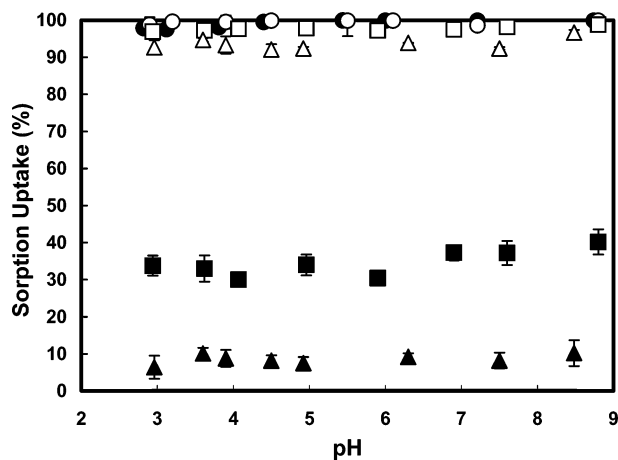


FIGURE 3. Sorption competition between Sr and Pb under different ionic strengths and solid concentrations. Initial metal concentration:  $10^{-5} \text{ M}$ . (●) Sr,  $I = 0.01 \text{ M NaNO}_3$  and solid =  $3.0 \text{ g/L}$ ; (■) Sr,  $I = 0.1 \text{ M NaNO}_3$  and solid =  $3.0 \text{ g/L}$ ; (▲) Sr,  $I = 0.1 \text{ M NaNO}_3$  and solid =  $1.0 \text{ g/L}$ ; (○) Pb,  $I = 0.01 \text{ M NaNO}_3$  and solid =  $3.0 \text{ g/L}$ ; (□) Pb,  $I = 0.1 \text{ M NaNO}_3$  and solid =  $3.0 \text{ g/L}$ ; (△) Pb,  $I = 0.1 \text{ M NaNO}_3$  and solid =  $1.0 \text{ g/L}$ .

tion, sufficient sites were available to accommodate both metals. As the ionic strength increased, however, from 0.01 to  $0.1 \text{ M NaNO}_3$ , and while using the same solid concentration ( $3 \text{ g L}^{-1}$ ), competition for a limited number of sorption sites became evident. Although Pb sorption did not appear to decrease compared to the previous results, Sr sorption was reduced from approximately 55 to 35% fractional uptake in the presence of Pb. The effects of competition with Na ions could be observed at this ionic strength, even in the single metal experiments, but the additional presence of the stronger binding Pb ion reduced Sr sorption even further. These results clearly demonstrate that Pb ions have a much higher sorption affinity for zeolitized tuffs compared to Sr ions. The difference in the affinity of the two metals for cation exchange sites becomes more evident as the number of sites decreases. As the solid concentration decreased from 3 to  $1 \text{ g L}^{-1}$  with  $0.1 \text{ M NaNO}_3$ , because of the more limited number of available sorption sites, Sr sorption was essentially suppressed, while Pb uptake did not decrease substantially.

**Batch Desorption Experiments.** Desorption experiments were conducted to test Sr and Pb sorption behavior under different geochemical conditions. It should be noted that in a strict thermodynamic sense testing for the reversibility of sorption reactions requires the derivation of complete sorption and desorption isotherms. During this process, the solution concentration is changed as little as possible and the system is allowed to reach equilibrium before an additional change is imposed. Obviously, this would be a very time-consuming process, especially if the sorption or desorption reactions are slow. Instead, both sorption and desorption were performed as single steps in this study. Therefore, although these experiments may not demonstrate the reversibility of sorption in a true thermodynamic sense, they nevertheless provide at least a measure of reversibility and effects of competition between the initially sorbed metal ions of interest and major background electrolyte cations.

Kinetic sorption uptake and desorption release of Sr ions are plotted in Figure 4. Kinetic sorption data for the same particles as those used in this study were obtained from previous kinetic experiments (30). According to that study, equilibrium was reached within 2 days for both Sr and Pb (30). Following sorption at the lower ionic strength ( $I = 0.01 \text{ M NaNO}_3$ ), the supernatant was replaced by a solution of the same ionic strength but without Sr.

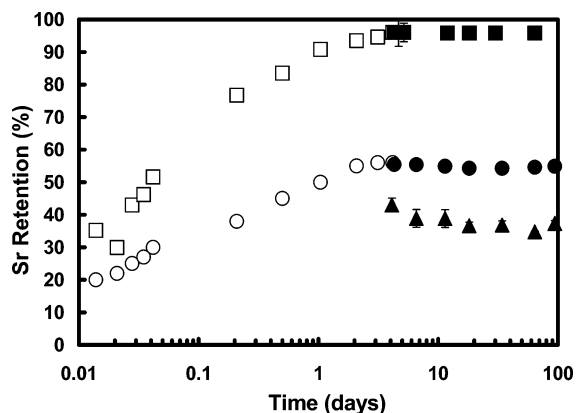


FIGURE 4. Sr sorption/desorption as a function of time. Initial metal concentration:  $10^{-4}$  M. ( $\square$ ) Sr sorption under  $I = 0.01$  M  $\text{NaNO}_3$ , pH = 7.2; ( $\blacksquare$ ) Sr desorption by  $I = 0.01$  M  $\text{NaNO}_3$ , pH = 7.2; ( $\circ$ ) Sr sorption under  $I = 0.1$  M  $\text{NaNO}_3$ , pH = 6.8; ( $\bullet$ ) Sr desorption by NANOpure water; ( $\blacktriangle$ ) Sr desorption by  $I = 0.1$  M  $\text{NaNO}_3$ , pH = 6.8.

As can be seen in Figure 4, essentially no Sr ions were released. When, however, the ionic strength was increased to 0.1 M, sorption was partly reversible, as can be seen in Figure 4, with approximately 30% of the total Sr desorbing, while desorption by NANOpure water was negligible.

Because these desorption experiments were conducted with a limited volume of desorbing solution under closed condition (single batch test), they could not reveal the whole mechanism of reversibility. However, on the basis of these results, the migration of Sr through zeolitized tuffs at ionic strengths of 0.01 M or lower would essentially be an irreversible process under these limited conditions (e.g., no significant concentration changes in subsequently incoming groundwater flow or recharge rate). Because the ionic strength of the groundwater collected in wells at the NTS is approximately 0.003 M, Sr desorption is expected to be minor, thereby substantially limiting Sr migration. As shown by the desorption experiments, however, Sr desorption may become at least partly measurable at increased ionic strength. If solution composition changes, Sr mobility can therefore increase. This reduced retardation may occur in the recharge areas of saltwater intrusion or carbonate aquifers with high dissolution rates. Because the brine water has a high concentration of Na and the dissolution of carbonate rocks increases Ca concentration, Sr mobility could increase substantially by Sr desorption. On the other hand, the increased Ca concentration may result in the formation of Sr carbonates, a process that might limit Sr mobility.

The overall result would be a function of aqueous Ca concentration and the rate of exchange between Ca and Sr on the zeolites. The results of Sr desorption by different desorption solutions are shown in Figure 5. Initially,  $10^{-5}$  M Sr was sorbed onto tuffs in a 0.01 M  $\text{NaNO}_3$  solution at pH 7.5. The fraction of Sr desorbed by the same solution ( $I = 0.01$  M  $\text{NaNO}_3$ ) was negligible, consistent with previous experiments (Figure 4). The fraction of Sr released increased with the increase of background electrolyte concentration. In addition, Sr release was enhanced by Ca compared to Na. The increased capacity of Ca to replace Sr, compared to Na, can be attributed to the similarity between Ca and Sr. Important considerations include the size of the hydrated ion and its charge. The divalent Sr has a hydrated radius closer to the radius of the divalent Ca, compared to the radius of the monovalent Na. The tendency of Sr to bind on Ca sorption sites in the channels of clinoptilolite was confirmed by XAS (37). Although Sr uptake by zeolitized tuffs, especially at low ionic strengths, was quantitative, the considerable release of Sr by another alkaline earth suggests formation of outer-sphere complexes at permanent charge sites.

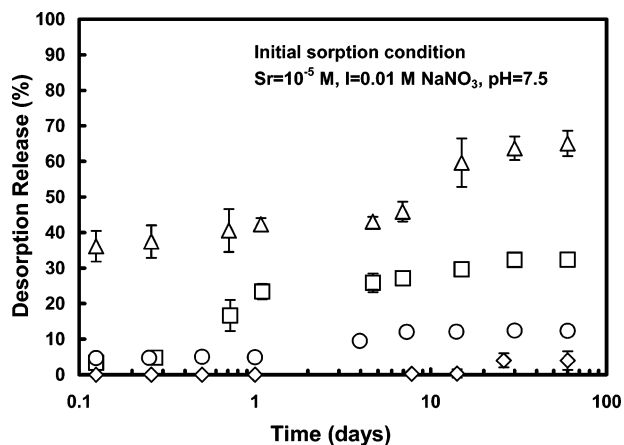


FIGURE 5. Sr desorption by different background solutions. ( $\Delta$ )  $I = 0.1$  M  $\text{Ca}(\text{NO}_3)_2$ ; ( $\square$ )  $I = 0.1$  M  $\text{NaNO}_3$ ; ( $\circ$ )  $I = 0.01$  M  $\text{Ca}(\text{NO}_3)_2$ ; ( $\diamond$ )  $I = 0.01$  M  $\text{NaNO}_3$ .

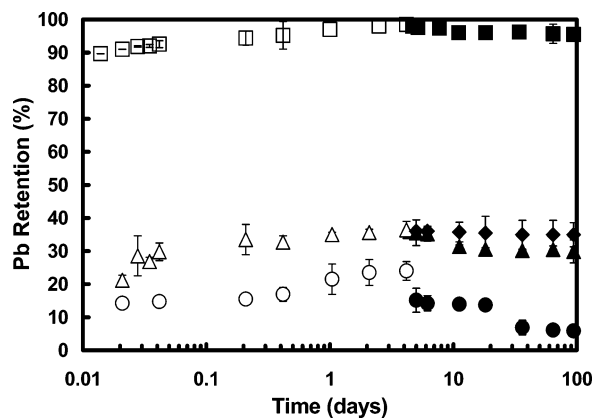


FIGURE 6. Pb sorption/desorption as a function of time. Initial metal concentration:  $10^{-5}$  M. ( $\square$ ) Pb sorption under  $I = 0.01$  M  $\text{NaNO}_3$ , pH = 7.0; ( $\blacksquare$ ) Pb desorption by  $I = 0.01$  M  $\text{NaNO}_3$ , pH = 7.0; ( $\Delta$ ) Pb sorption under  $I = 1.0$  M  $\text{NaNO}_3$ , pH = 6.8; ( $\blacktriangle$ ) Pb desorption by  $I = 1.0$  M  $\text{NaNO}_3$ , pH = 6.8; ( $\bullet$ ) Pb desorption by NANOpure water; ( $\circ$ ) Pb sorption under  $I = 1.0$  M  $\text{NaNO}_3$ , pH = 2.9; ( $\blacklozenge$ ) Pb desorption by  $I = 1.0$  M  $\text{NaNO}_3$ , pH = 2.9.

Time-dependent sorption and desorption experiments with Pb are shown in Figure 6. At the lower ionic strength ( $I = 0.01$  M  $\text{NaNO}_3$ ), sorbed Pb was not desorbed by a solution of the same ionic strength as the initial sorption solution. Only at the highest ionic strength used ( $I = 1.0$  M  $\text{NaNO}_3$ ) were Pb ions released by the desorption solution, because of the highly increased concentration of background electrolyte.

The fraction of Pb desorbed from the adsorbents increased at low pH, suggesting increasingly stronger Pb binding with increasing pH at this high ionic strength. These results are consistent with the Pb sorption paradigm presented above. At the highest ionic strength ( $I = 1.0$  M  $\text{NaNO}_3$ ) and at low pH, Pb is presumably binding at permanent charge sites as an outer-sphere complex, but as pH increases, sorption on amphoteric surface hydroxyl sites and possibly formation of polynuclear complexes and surface precipitates also increases. Formation of inner-sphere complexes under these conditions could explain the increased stability of Pb sorption.

Lead desorption was also investigated as a function of background electrolyte solution composition. As shown in Figure 7, Pb ions sorbed at 0.01 M ionic strength and at least neutral pH were not easily released from the adsorbents, even if the concentration of the desorption solution increased. Desorption by 0.01 M  $\text{NaNO}_3$  was negligible and was not plotted in Figure 7 to avoid clutter. Lead sorption at high

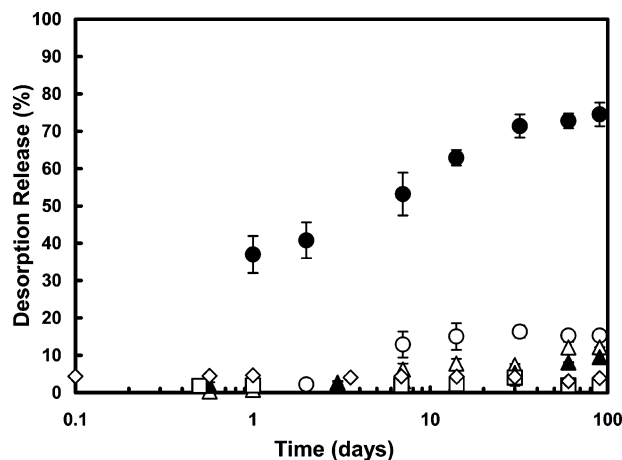


FIGURE 7. Pb desorption by different background electrolyte solutions. (●) Pb desorption by  $I = 1.0\text{M NaNO}_3$  (initial Pb sorption under  $I = 1.0\text{M NaNO}_3$ , pH = 2.6); (○) Pb desorption by  $I = 1.0\text{M NaNO}_3$  (initial Pb sorption under  $I = 1.0\text{M NaNO}_3$ , pH = 6.8); (Δ) Pb desorption by  $I = 0.01\text{M Ca(NO}_3)_2$  (initial Pb sorption under  $I = 0.01\text{M NaNO}_3$ , pH = 3.5); (▲) Pb desorption by  $I = 0.01\text{M Ca(NO}_3)_2$  (initial Pb sorption under  $I = 0.01\text{M NaNO}_3$ , pH = 3.5); (□) Pb desorption by  $I = 0.01\text{M NaNO}_3$  (initial Pb sorption under  $I = 0.01\text{M NaNO}_3$ , pH = 7.5); (◇) Pb desorption by  $I = 0.01\text{M Ca(NO}_3)_2$  (initial Pb sorption under  $I = 0.01\text{M NaNO}_3$ , pH = 7.5). The error bars represent one standard deviation based on duplicate experiments.

ionic strength was partly desorbed by a background solution of higher concentration ( $I = 1.0\text{M NaNO}_3$ ), and the degree of desorption at low pH was much higher than at high pH. The presence of Ca in solution at low pH increased Pb desorption slightly compared to Na. At high pH, however, even at high Ca concentration ( $I = 0.01\text{M Ca(NO}_3)_2$ ), Pb desorption did not increase, which was different from the Sr results. Irreversibility of Pb sorption in a Pb–Na cation exchange system has been reported (20). In addition, Carriere et al. (38) reported that the release of Pb(II) from a fine sandy loam using calcium chloride ( $\text{CaCl}_2$ ) was less than the release obtained using EDTA or hydrochloric acid (HCl). These results indicate that Pb sorption and desorption on zeolitized tuffs was highly dependent on pH, and Pb sorbed at pH around neutral or higher was not easily released from the adsorbent, irrespective of the type (Na or Ca) and the concentration of the background electrolyte. Using XAS, Um and Papelis (37) distinguished between two different Pb sorption mechanisms at low and higher pH and at the highest ionic strength. At low pH, Pb reacted with permanent charge sites forming outer-sphere complexes or with surface hydroxyl sites forming corner-sharing monodentate inner-sphere surface complexes, a weaker sorption mechanism compared to edge-sharing bidentate inner-sphere surface complex formation at neutral pH or above.

On the basis of the batch sorption and desorption experiments performed in this study, zeolitized tuffs appear to be excellent sorbents for important radionuclides, such as Sr, and other divalent metal cations. Given the high degree of sorption capacity and limited desorption, migration of these contaminants is expected to be very limited, given the geochemical conditions at the NTS, namely low ionic strength and neutral to slightly alkaline pH. The potential migration for some of these ions, however, may be increased significantly if higher concentrations of background electrolyte ions result in the release of the more weakly binding cations. Increased concentration resulting from the dissolution of carbonate rocks may enhance the mobility of Sr in the groundwater. Lead sorption on zeolitized tuffs is significantly stronger than that of Sr. Because Pb reacts with zeolitized tuffs at the NTS strongly and presumably forms inner-sphere

bidentate complexes or surface precipitates at the pH of the NTS groundwater, sorbed Pb would not be easily desorbed, even at higher ionic strength conditions.

## Acknowledgments

Financial support for this project was provided by the U.S. Department of Energy, National Nuclear Security Administration Nevada Operations Office, under Contract DE-AC08-00NV13609, and by the Desert Research Institute. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors.

## Literature Cited

- Rafferty, P.; Shiao, S.-Y.; Binz, C. M.; Meyer, R. E. *J. Inorg. Nucl. Chem.* **1981**, *43*, 797–805.
- Schindler, P. W.; Liechti, P.; Westall, J. C. *J. Neth. Agric. Sci.* **1987**, *35*, 219–230.
- Konishi, M.; Yamamoto, K.; Yanagi, T.; Okajima, Y. *J. Nucl. Sci. Technol.* **1988**, *25*, 929–933.
- Adeleye, A. S.; Clay, P. G.; Oladipo, M. O. A. *J. Mater. Sci.* **1994**, *29*, 954–958.
- Ohnuki, T.; Kozai, N. *Radiochim. Acta* **1994**, *66/67*, 331–325.
- Ames, L. L., Jr. *Am. Mineral.* **1960**, *45*, 689–700.
- Smyth, J. R.; Spaid, A. T.; Bish, D. L. *Am. Mineral.* **1990**, *75*, 522–528.
- Shanableh, A.; Kharabsheh, A. *J. Hazard. Mater.* **1996**, *45*, 207–217.
- Behrens, E. A.; Sylvester, P.; Clearfield, A. *Environ. Sci. Technol.* **1998**, *32*, 101–107.
- Blanchard, G.; Maunaye, M.; Martin, G. *Water Res.* **1984**, *18*, 1501–1507.
- Faghihian, H.; Marageh, M. G.; Kazemian, H. *Appl. Radiat. Isotopes* **1999**, *50*, 655–660.
- Grant, D. C.; Skriba, M. C.; Saha, A. K. *Environ. Prog.* **1987**, *6*, 104–109.
- Loizidou, M. D. In *Metals Speciation, Separation, and Recovery*; Patterson, J. W., Passino, R., Eds.; Lewis: Chelsea, MI, 1990; pp 417–435.
- Malliou, E.; Loizidou, M.; Spyrellis, N. *Sci. Total Environ.* **1994**, *149*, 139–144.
- Salim, I. A.; Miller, C. J.; Howard, J. L. *Soil Sci. Soc. Am. J.* **1996**, *60*, 107–114.
- Kinniburgh, D. G.; Jackson, M. L.; Syers, J. K. *Soil Sci. Soc. Am. J.* **1976**, *40*, 796–799.
- Inglezakis, V. J.; Loizidou, M. D.; Grigoropoulou, H. P. *Water Res.* **2002**, *36*, 2784–2792.
- Kesraoui Ouki, S.; Cheeseman, C.; Perry, R. *Environ. Sci. Technol.* **1993**, *27*, 1108–1116.
- Langella, A.; Pansini, M.; Cappelletti, P.; de Gennaro, B.; de Gennaro, M.; Colella, C. *Microporous Mesoporous Mater.* **2000**, *37*, 337–343.
- Loizidou, M.; Townsend, R. P. *Zeolites* **1987**, *7*, 153–159.
- Zhao, D.; Cleare, K.; Oliver, C.; Ingrad, C.; Cook, D.; Szostaketal, R. *Microporous Mesoporous Mater.* **1998**, *21*, 371–379.
- Bowman, R. S.; Essington, M. E.; O'Connor, G. A. *Soil Sci. Soc. Am. J.* **1981**, *45*, 1583–1595.
- Grutter, A.; Von Gunten, H. R.; Rossler, E.; Keil, R. *Radiochim. Acta* **1994**, *65*, 181–187.
- Reardon, E. J. *Ground Water* **1981**, *19*, 279–286.
- Bethke, C. M.; Brady, P. V. *Ground Water* **2000**, *38*, 435–443.
- Sloop, D. A. M.S. Thesis, Department of Geoscience, University of Nevada, Las Vegas, 1998.
- Brunauer, S.; Emmett, P.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309–319.
- Busenberg, E.; Clemency, C. V. *Clays Clay Miner.* **1973**, *21*, 213–217.
- Emsley, J. *The Elements*; Oxford University Press: Oxford, U.K., 1989.
- Bernot, P. A. M.S. Thesis, Department of Geoscience; University of Nevada, Las Vegas, 1999.
- Helferich, F. *Ion Exchange*; McGraw-Hill: New York, 1962.
- Stumm, W.; Morgan, J. J. *Aquatic Chemistry*, 3rd ed.; John Wiley & Sons: New York, 1996.
- Chen, C.-C.; Hayes, K. F. *Geochim. Cosmochim. Acta* **1999**, *63*, 3205–3215.

- (34) Baes, C. F., Jr.; Mesmer, R. E. *The Hydrolysis of Cations*; Robert E. Krieger Publ. Co.: Malabar, FL, 1986.
- (35) Chisholm-Brause, C. J.; Hayes, K. F.; Roe, A. L.; Brown, G. E., Jr.; Parks, G. A.; Leckie, J. O. *Geochim. Cosmochim. Acta* **1990**, *54*, 1897–1909.
- (36) Bargar, J. R.; Brown, G. E., Jr.; Parks, G. A. *Geochim. Cosmochim. Acta* **1997**, *61*, 2617–2637.
- (37) Um, W.; Papeis, C. *Am. Mineral.* **2003**, *88*, 2028–2039.
- (38) Carriere, P. P. E.; Reed, B. E.; Cline, S. R. *Sep. Sci. Technol.* **1995**, *30*, 3471–3487.

*Received for review April 4, 2003. Revised manuscript received October 20, 2003. Accepted November 1, 2003.*

ES0343050