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Assessment of a Sodium Nonatitanate and Pharmacosiderite-Type Ion Exchangers for Strontium and Cesium Removal from DOE Waste Simulants

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Several inorganic ion exchangers were tested for ^{89}Sr and ^{137}Cs removal from simulated DOE aqueous defense wastes (NCAW and 101SY-Cs5) and a Hanford groundwater solution (N-springs). The materials used in this scoping study consisted of the three-dimensional tunnel-structured pharmacosiderites [$M_3H(AO)_4(BO_4)_3 \cdot 4-6H_2O$ (M = H, K; A = Ti, Ge; B = Si, Ge)]; the layered sodium nonatitanate, $Na_4Ti_9O_{20} \cdot xH_2O$; and two commercially available exchangers, AW-500 and clinoptilolite. ^{89}Sr and ^{137}Cs distribution coefficient (K_d) measurements showed that all of the synthetic exchangers removed at least 97% of the ^{89}Sr from the N-springs groundwater simulant in a single static equilibration. This simulant also contained parts per million levels of Ca^{2+}, Mg^{2+}, K^+, and Na^+. Similarly, many of the same materials also efficiently removed ^{137}Cs (>98%) from the same solution, except for sodium titanate, which exhibited the lowest K_d of 1210 mL/g for Cs^+. These preliminary K_d values provide an indication that these exchangers may act as dual Cs^+ and Sr^{2+} sorbers for groundwater remediation applications. The different phases were also tested as potential exchangers for ^{137}Cs and ^{89}Sr in different nuclear waste simulants. While the materials showed little preference for ^{137}Cs in highly basic solutions containing large concentrations of $NaNO_3$, a potassium titanosilicate and the sodium titanate yielded ^{89}Sr K_d values of 20 180 mL/g (DF = 91) and 235 120 mL/g (DF = 1177), respectively.

Introduction

A series of titanosilicate, germanium-substituted titanosilicate pharmacosiderites, and titanate inorganic ion exchangers were developed by the Department of Chemistry at Texas A&M University in conjunction with AlliedSignal and the Pacific Northwest National Laboratory (PNNL) for the selective removal of strontium or cesium from different contaminated aqueous defense wastes and groundwater.

Over the past 50 years, the Hanford nuclear plant located in Washington State accumulated over 65% of our nation's high-level radioactive waste (HLW) resulting from chemical extraction processes for the production of nuclear weapons-grade ^{239}Pu. Consequently, the radioactive HLW is presently stored in 177 steel tanks, whose estimated volume is approximately 65 million gal. Although the elemental compositions for each tank are ambiguous, previous studies reveal that all of the tanks contain triphasic systems consisting of metal hydroxide sludges, alkaline supernates, and salt cakes (*1*). Much of the radioactivity in the supernate arises from ppm to ppb levels of ^{90}Sr and ^{137}Cs isotopes, while the actinides tend to be concentrated in the hydroxide sludges.

In order to dispose of this waste in an economical and safe manner, the Department of Energy proposed a method for converting the HLW into a low-level radioactive waste (LLW) that is safe for underground burial while at the same time minimizing the volume of HLW for ultimate disposal. Of equal concern is the removal of ^{90}Sr and ^{137}Cs from groundwater, rivers, lakes, and streams. Detectable levels of ^{90}Sr have already been reported in the nearby Columbia River as a result of tank leakage into the surrounding soil (*1*).

Our approach is to use highly selective inorganic ion exchangers as novel separation methodologies for removing ^{90}Sr and ^{137}Cs from tank wastes and groundwater (*2*−*5*). We chose inorganic materials because of their high chemical, thermal, and radiation stabilities as compared to conventional organic ion exchange resins. Furthermore, inorganic ion exchangers typically have high capacities and selectivities for a wide variety of monovalent and divalent metal cations (*6*−*13*). Another important property is the ability to structurally modify the compounds by altering the synthetic conditions by which the materials are prepared. Another example of structural manipulation resides in the pharmacosiderite materials. It is possible to substitute different metal atoms into the framework structures, which in turn increases or decreases the effective cavity diameters (*3*). Therefore, structural modification causes a corresponding change in selectivity toward different metal cations. In a sense, we can design materials and "fine tune" their properties for different remediation applications.

Specifically, the pharmacosiderite exchangers in this study contain linked framework metal octahedra and tetrahedra that create three-dimensional zeolite-like tunnel structures with the general formula, $M_3H(AO)_4(BO_4)_3 \cdot 4-6H_2O$ (M = H, K, Na; A = Ti, Ge; B = Si, Ge) (*2*, *15*−*21*). It is important to note that the pharmacosiderite exchangers are not structurally related to the crystalline silicotitanate currently marketed by UOP as IONSIV IE-910 and IE-911 (*14*). The charge-neutralizing, exchangeable cations (M) reside close to the face-centers where they bind to eight oxygens from the silicate or germanate tetrahedra (Figure 1). The potassium phases are generally selective for ppm−ppb levels of strontium and cesium in groundwater-type simulants that contain excess calcium (~30 ppm) and moderate levels of magnesium, potassium, and sodium (*21*). This compound also efficiently removes strontium from certain defense waste simulants but not with the same effectiveness as the sodium titanate. The sodium nonatitanate, on the other hand, is a layered material with an ideal empirical formula of $Na_4Ti_9O_{20} \cdot xH_2O$ (*9*). The hypothesized structure consists of TiO_6 octahedral chains linked into layers with exchangeable sodium cations located between the layers. This material is typically of low crystallinity, thus its crystal structure has never been accurately determined.

In this paper, we report the syntheses and characterization of several pharmacosiderite materials and a semicrystalline sodium nonatitanate. The materials of interest were also evaluated by batch and column experiments for strontium and cesium removal from various defense waste simulants and a groundwater solution. All studies were performed

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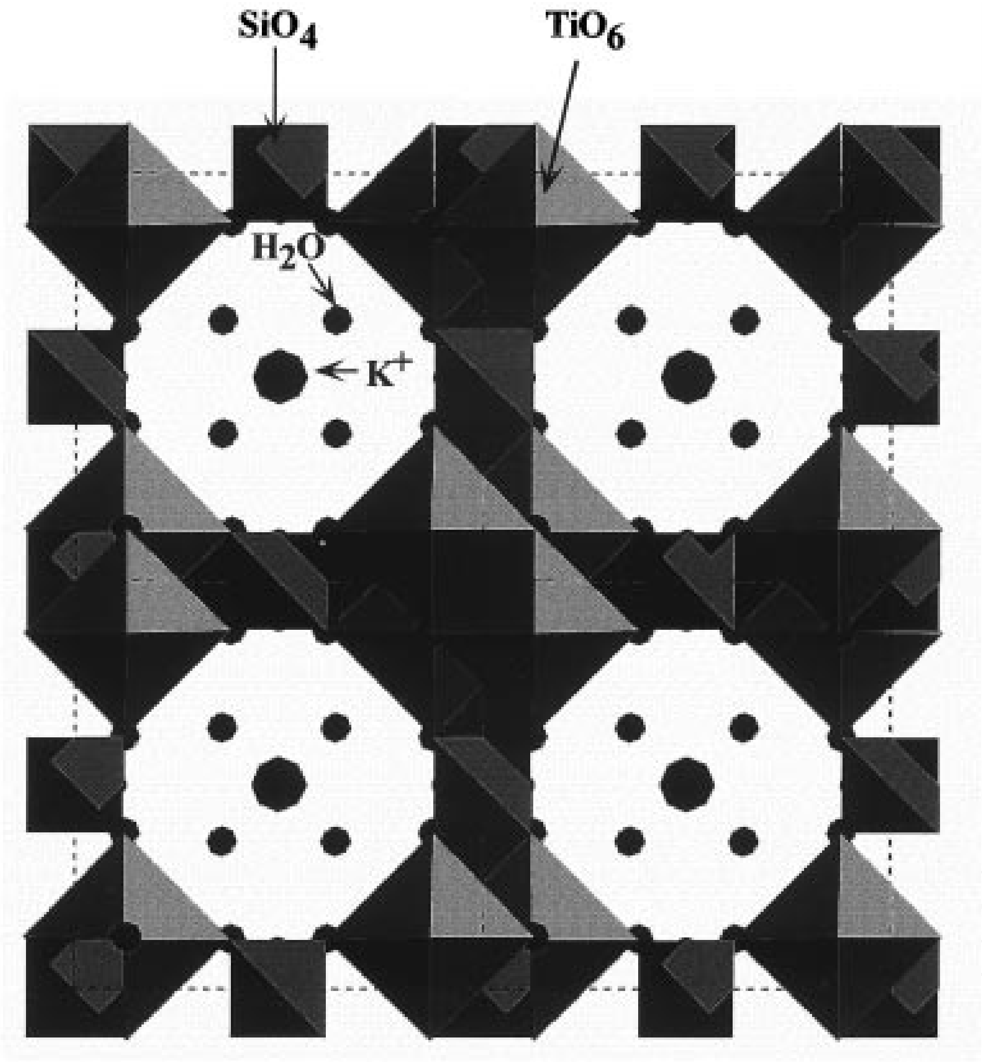

FIGURE 1. Polyhedral representation of the potassium titanosilicate pharmacosiderite. Clusters of TiO_6 octahedra are linked together by tetrahedral silicate groups. This arrangement of metal atoms creates a three-dimensional tunnel structure where the potassium ions and water molecules reside in the face centers.

radiochemically using the isotopes ^{89}Sr and ^{137}Cs. For comparison purposes, we additionally assessed "benchmark standard" strontium and cesium absorbers, AW-500 (pelletized chabazite) and a naturally-occurring clinoptilolite.

Experimental Section

Materials and Methods. All reagents were of analytical grade and used without further purification. AW-500, a pelletized natural zeolite, was purchased from Aldrich and has an ideal formula of $Ca_2Al_4Si_8O_{24}·13H_2O$, with a theoretical ion exchange capacity of 3.88 mequiv/g. A sample of natural clinoptilolite (batch 03160, retrieved from the Mud Hills deposit in the Mojahve Desert, CA) was provided by British Nuclear Fuels PLC and used without further conditioning. Clinoptilolite has an ideal formula of $Na_6Al_6Si_{30}O_{72}·24H_2O$ with a theoretical cation exchange capacity of 2.20 mequiv/g.

^{89}Sr (269 mCi/g total Sr) and ^{137}Cs (2.5×10^4 mCi/g total Cs) were purchased from Isotope Products Laboratory and Amersham Life Science, respectively. X-ray powder diffraction data (no internal standard) were gathered on a Scintag PAD-V or Rigaku (RU200) rotating anode diffractometer with Ni-filtered CuKα radiation. Structural analysis by X-ray powder diffraction for some of the pharmacosiderite compounds was reported previously(*2*, *3*). Thermogravimetric measurements were performed on a DuPont thermal analysis unit, Model 951, under N_2 atmosphere at a heating rate of 10 °C/min. Radioactive tracer activities were measured using a Wallac 1410 liquid scintillation counter (LSC). Germanium, titanium, silicon, and potassium analyses for the Ge-substituted pharmacosiderite materials were performed by Galbraith Laboratories (Knoxville, TN). Silicon and titanium analyses for the potassium titanosilicate pharmacosiderite was accomplished in-house using a Specta Span VI direct-current plasma (DCP) emission spectrometer.

Preparation of the Sodium Nonatitanate, $Na_4Ti_9O_{20}·xH_2O$ (NaTi). A semicrystallline sodium titanate was prepared by adding 77.5 g of titanium isopropoxide (97%, Aldrich) to a Teflon round-bottom flask. Under constant stirring, 84.35 g of a 50 wt % NaOH was added to the flask, resulting in a white gelatinous precipitate. The precipitate was subsequently stirred for 1 h, heated at approximately 108 °C for another 3 h, and then transferred to a Teflon-lined stainless steel hydrothermal vessel using 128 mL of distilled deionized (dd) water. The reaction mixture was heated at 200 °C for 21 h. after which the product (NaTi) was vacuum filtered through a 0.2-μm membrane, washed with 2 L of absolute ethanol, and dried at 60 °C for 48 h (final mass: 33.1 g). The TGA curve showed 18.1% weight loss up to 700 °C, which corresponds to interstitial water and surface hydroxyl molecules.

Preparation of the Ge-Substituted Pharmacosiderites, $HK_3(TiO)_4(GeO_4)_3·4H_2O$ (KTiGe) and $HK_3(TiO)_{3.5}(GeO)_{0.5}$-

$(SiO_4)_{0.5}(GeO_4)_{2.5}\cdot4H_2O$ (KTiSiGe). The partially Ge-substituted pharmacosiderite was prepared by mixing 1.831 g of titanium isopropoxide (97%, Aldrich), 0.375 g of fumed silica (99.7%, Sigma), and 10 mL of distilled deionized (dd) water to form a white gel. The gel was stirred overnight after which it was centrifuged, the supernatant was discarded, and an additional 3 mL of dd water was added. A separate cesium germanate solution was prepared by combining 0.673 g of GeO_2 (99.999%, STREM) with 23.54 g of CsOH (50 wt %, Aldrich). The cesium germanate solution was then mixed with the gel, and the final mixture was heated in a 100 -mL Teflon-lined steel vessel at 200 °C for 48 h. The final product (CsTiSiGe) was filtered, washed with dd water, and dried at 60 °C (final mass: 1.51 g). Analytical data: Observed: Ge, 19.37%; Ti, 14.53%; Si, 1.89%; H_2O loss up to 800 °C, 4.42%. Calculated: Ge, 19.33%; Ti, 14.87%; Si, 1.25%; H_2O, 6.39%.

Complete Ge-substitution for Si was accomplished by entirely replacing GeO_2 for fumed silica in the above synthetic preparation. 1.770 g of titanium isopropoxide was mixed with 6.6 mL of dd water to form a white gel. A separate cesium germanate solution was made with 1.884 g of GeO_2 and 38.3 g of CsOH. The two different mixtures were combined and stirred to homogenize thoroughly. The gel was then reacted in a 100-mL Teflon-lined steel vessel at 200 °C for 48 h. The product (CsTiGe) was filtered, washed with dd water, and dried at 60 °C (final mass: 1.13 g). Analytical data: Observed: Ge, 20.18%; Ti, 15.41%; H_2O up to 800 °C, 6.93%. Calculated: Ge, 19.16%; Ti, 16.84%; H_2O, 6.33%.

Because highly crystalline, pure potassium Ge-substituted phases could not be prepared directly by using KOH in the syntheses, the cesium compounds synthesized as described above were ion exchanged with KCl to give their respective potassium phases. Typically, each compound was heated between 60 and 80 °C in 2 M KCl for 8 h. Each ion exchange reaction was repeated for a total of three times to ensure complete K^+. Each product was filtered, washed with dd water, and dried at 60 °C. Elemental analysis (Galbraith Laboratories) revealed that most of the K^+ exchanged for Cs^+. For example, the observed %K for KTiSiGe was 11.95% (calculated 13.8%). X-ray structural analyses by Rietveld methods coupled with analytical data established empirical formulas of $HK_3(TiO)_{3.5}(GeO)_{0.5}(SiO_4)_{0.5}(GeO_4)_{2.5}\cdot4H_2O$ for KTiSiGe and $HK_3(TiO)_4(GeO_4)_3\cdot4H_2O$ for KTiGe (3).

Preparation of Potassium Titanosilicate $HK_3(TiO)_4(SiO_4)_3\cdot4H_2O$ by a Gel and Solution Method. A potassium titanosilicate was prepared as previously described (*2*) via a gel method, except that the reagents were scaled up for a 1-L hydrothermal vessel. The final gel composition for SiO_2:TiO_2:K_2O was 1:0.5:1.3. The gelatinous precipitate was treated hydrothermally in a 1-L Teflon-lined steel vessel at 200 °C for 2 days, yielding 20.03 g of product (sample designated as KTSgel). Previous X-ray refinement showed an ideal formula of $K_3HTi_4O_4(SiO_4)_3\cdot4H_2O$ (calculated: 9.99% H_2O, 11.69% Si, 26.56% Ti, 16.3% K; observed: 12.6% H_2O, 12.4% Si, 21.8% Ti, 18.8% K); however, our analytical data for this larger-scale batch yielded a composition of 10.7% H_2O, 12.4% Si, 20.5% Ti, and 16.2% K. Analytical data provided from Galbraith yielded a composition close to that reported above: Ti 22.02% and Si 13.57%. The TGA spectrum showed 10.7% water loss up to 500 °C, which corresponds to 4.3 mol of H_2O.

The same compound was synthesized using a homogenous titanium and silicon solution. A total of 20 g SiO_2 gel (Aldrich, Grade 923) was combined with 80 mL of 10 M KOH and 140 mL of dd H_2O. In a separate beaker, 62 mL of titanium isopropoxide, 40 mL of 30% H_2O_2, 200 mL of dd H_2O, and 60 mL of 10 M KOH were all added at once under vigorous stirring. The two separate solutions were combined, stirred to homogenize, placed in a 1-L Teflon-lined hydrothermal vessel, and reacted at 190 °C for 4 days. The product (KTSsol) was filtered, washed with absolute ethanol, and dried at 60 °C (final mass: 38.9 g). TGA data revealed 13.7% weight loss up to 500 °C.

TABLE 1. Simulant Profiles for N-Springs, NCAW, and 101SY-Cs5

	concentration (M)		
species	N-Springs	NCAW	101SY-Cs5
Al	0	0.43	0.42
Ba	1.12E-07	0	0
Ca	7.27E-07	0	4.20E-03
Cs (inactive)	0	5.00E-04	4.19E-05
Fe	0	0	1.96E-04
K	0	0.12	0.034
Mg	2.16E-04	0	0
Mo	0	0	4.20E-04
Na	2.61E-04	4.99	5.1
Ni	0	0	2.50E-04
Rb	0	5.00E-05	4.20E-06
Sr (inactive)	1.48E-06	0	2.90E-07
Zn	0	0	5.00E-04
carbonate	1.25E-04	0.23	0.038
chloride	4.51E-05	0	0
fluoride	1.05E-05	0.09	0.092
hydroxide	n/a	3.4	3.78
hydroxide (free)	1.66E-03	1.68	2.11
nitrate	1.94E-04	1.67	1.29
nitrite	0	0.43	1.09
sulfate	2.16E-04	0.15	4.75E-03
phosphate	0	0.025	0.02
citric acid	0	0	5.00E-03
tetrasodium EDTA	0	0	5.00E-03
N-(2-hydroxyethyl)EDTA	0	0	3.75E-3
iminodiacetic acid	0	0	0.031
nitriloacetate	0	0	2.50E-04
sodium gluconate	0	0	0.013
theoretical pH	11.2	14.5	14.4

^{89}Sr and ^{137}Cs Batch Exchange Studies. Two defense waste simulants, NCAW (neutralized current acid waste) and 101SY-Cs5, and one groundwater simulant, Hanford 100 area N-Springs, were prepared according to the recipes provided to us by PNNL. NCAW represents Hanford tank waste 102-A2 diluted to 5 M Na^+, which is thought to be the highest Cs^+ concentration in all of the tanks, and 101SY-Cs5 exemplifies a typical complexant-bearing waste also diluted to 5 M Na^+. Table 1 lists the approximate concentrations (mol/L) for all the species in the simulants. Each simulant was spiked with an appropriate initial concentration of ^{89}Sr or ^{137}Cs that yielded an equilibrium concentration (after contact with the solid) that could be measured with statistical accuracy on the LSC. Distribution coefficients (K_d) were determined by the batch method. Between 25 and 50 mg of each sample was weighed into a PTFE vial, and the various spiked simulants were added to the vial to give volume:mass ratios of 200:1 or 1000:1. Equilibration time was 24 h or less at ambient temperature with constant rotary mixing. Samples were filtered using Whatman No. 42 or No. 1 filter paper. Aliquots of the filtered samples were combined with scintillation cocktail, and their ^{89}Sr or ^{137}Cs activities (counts/min) were measured using LSC. K_d values were calculated according to

$$K_d = \frac{C_o - C_{eq}}{C_{eq}} \frac{V}{m} \tag{1}$$

where C_o is the initial activity of ^{89}Sr or ^{137}Cs in solution, C_{eq} is the equilibrium activity, V is total volume, and m represents the mass of exchanger. A distribution coefficient represents the concentration of cation exchanged onto the solid versus the concentration left in solution. Throughout this investigation, the units of K_d are milliliters per gram. For each sample, decontamination factors (DF) were also calculated in a similar manner by dividing the initial activity by the equilibrium activity.

N-Springs Column Study Using $HK_3(TiO)_4(SiO_4)_3 \cdot 4H_2O$. Because most of our inorganic exchangers are extremely fine powders, they typically have poor mechanical properties, which are unsuitable for column operations. Therefore, in order to conduct our column experiment, we first needed to pelletize the potassium titanosilicate (KTSgel) with an inorganic binder. This process was achieved by a proprietary method provided by AlliedSignal and will not be discussed further. The granular exchanger was sieved into 40−60 mesh (0.25−0.42 mm) particles and placed into a Bio-Rad plastic column (0.66 cm i.d, 5 cm length) resulting in a 1 mL bed volume. The column was connected to a peristaltic pump (Cole Parmer) using Tygon tubing, and distilled water was then pumped through the bottom of the column to allow for proper bed settling and packing. The column experiment was conducted using a 3-L reservoir of N-springs simulant spiked with negligible (0.025−0.03 ppm) ^{89}Sr concentrations (total [Sr] in the simulant was approximately 0.15 ppm). The column reservoir was kept full at all times by preparing additional spiked solutions and pouring these contents into the original supply without disrupting the pump or tubing. Initially, the column flow rate was 30 mL/h but turned progressively slower (~20 mL/h) as a result of bed packing. The final breakthrough for ^{89}Sr probably occurred slightly later than if the flow rate had remained constant at 30 mL/h. Eluent fractions were collected two times per day and were analyzed for ^{89}Sr activity using LSC. Percentage breakthrough (%BT) was calculated using

$$\%BT = \frac{C_o}{C_f} \times 100 \qquad (2)$$

Results and Discussion

XRD. Figure 2 shows the respective powder XRD patterns for the highly crystalline (a) KTiGe and (b) KTiSiGe and the semicrystalline (c) KTSsol, (d) KTSgel, and (e) NaTi compounds. Both XRD patterns look similar, but upon inspection, the peaks for KTiGe are shifted to lower 2θ because of the larger unit cell. We previously found that both (a) KTiGe and (b) KTiSiGe crystallize in the tetragonal space group, P$\bar{4}$62, with unit cell dimensions, $a = b = 11.215(1)$, $c = 7.9705(2)$ Å, and $a = b = 11.1571(2)$, $c = 7.9165(2)$ Å, respectively (*3*). An interesting aspect of the Ge-substituted compounds is their ability to undergo structural distortion depending on the nature of the charge-balancing cation as well as the degree of hydration (*15*, *20*, *22−25*). Because the Ge-substituted pharmacosiderite's unit cell dimensions increase with the larger charge-balancing cations, it is safe to assume that the channel diameters would slightly decrease for all the potassium phases used in this study. These innate structural characteristics may significantly hinder diffusion of larger cations into the tunnels, which in turn, alters selectivities toward different metals. As an example, preliminary results indicated that the selectivity for Cs^+ (10^{-3} M) in pure aqueous solutions increases with enlarging effective cavity dimensions (*26*). However, when we investigated Cs^+ distribution coefficients using complex, aqueous matrices, there was not a clear correlation between Cs^+ selectivity and structural parameters. In this case, there are additional thermodynamic parameters (i.e., ionic strength) and competitive exchange that assist in governing selectivity.

The potassium titanosilicates prepared by the soluble Ti method and the gel method are shown in Figure 2, panels c and d. Sample KTSgel (*d*) is identical to that reported in our previous paper (*21*) with unit cell dimensions of $a = b = c = 7.83 \pm 0.05$ Å, as calculated from the average of the (100), (200), and (300) reflections. KTSgel (*d*) is poorly crystalline as noted by its broadened and relatively low-intensity XRD peaks. KTSsol has even lower crystallinity than KTSgel, but as expected, Figure 2d reveals the cubic phar-

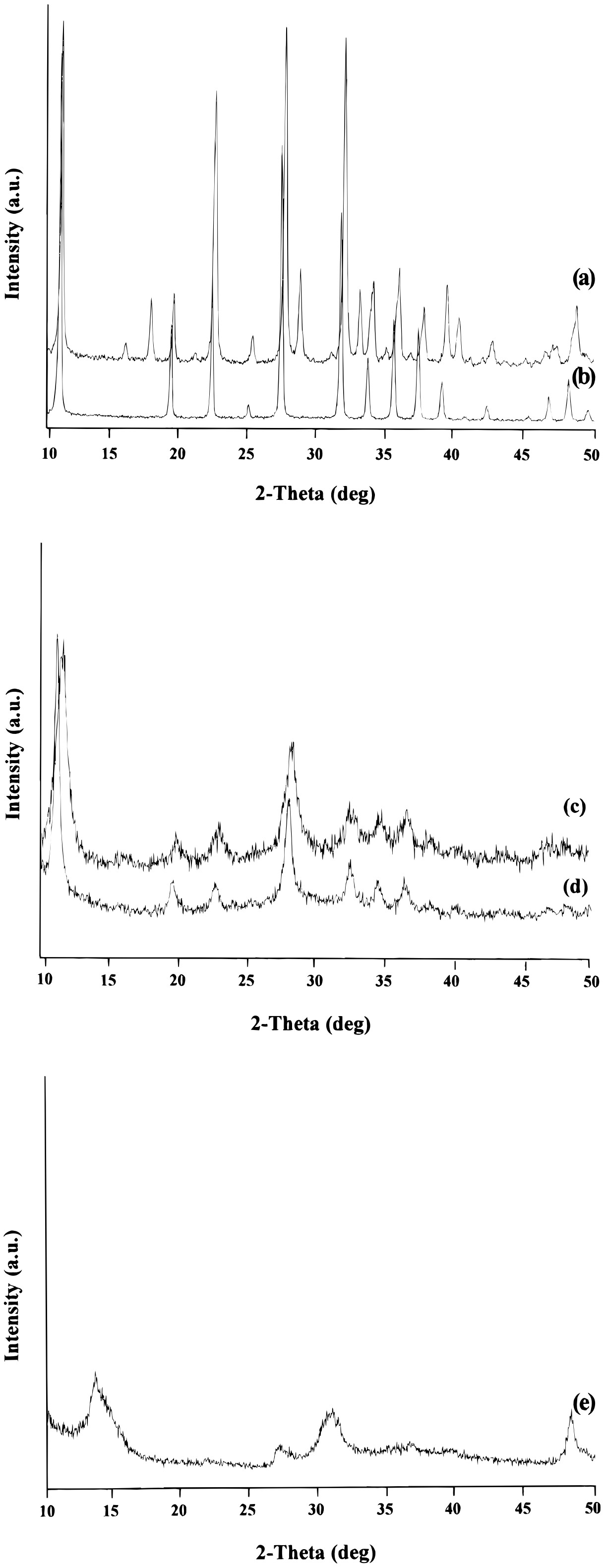

FIGURE 2. X-ray powder patterns shown for the highly crystalline (a) KTiGe and (b) KTiSiGe and the semicrystalline (c) KTSsol, (d) KTSgel, and (e) NaTi compounds.

TABLE 2. ^{89}Sr Distribution Coefficients (K_d) and Decontamination Factors (DF) for the N-Springs Simulant; $V{:}m = 200{:}1$

sample	K_d (mL/g)	DF
chabazite	30 645	153
clinoptilolite	27 190	152
KTiSiGe	25 280	129
KTSgel	5 090	25
KTSsol	57 610	319
NaTi	25 300	127

TABLE 3. ^{137}Cs Distribution Coefficients (K_d) and Decontamination Factors (DF) for N-Springs Simulant

sample	K_d (mL/g)		DF	
	$V{:}m =$ 200:1	$V{:}m =$ 1000:1	$V{:}m =$ 200:1	$V{:}m =$ 1000:1
chabazite	9 650	49 090	87	51
clinoptilolite	14 560	39 425	87	42
HTiSi	58 450	40 070	295	42
KTiGe	114 510	57 550	569	18
KTiSiGe	137 440	197 180	696	199
KTSgel	8 330	35 739	41	37
KTSsol	43 420	96 700	223	138
NaTi	1 210	4 920	7	6

TABLE 4. ^{89}Sr and ^{137}Cs Distribution Coefficients (K_d) with Decontamination Factors (DF) for the NCAW Simulant; $V{:}m = 200{:}1$

sample	^{89}Sr K_d (mL/g)	^{89}Sr DF	^{137}Cs K_d (mL/g)	^{137}Cs DF
chabazite	260	2.4	N/A	
clinoptilolite	N/A		7	1.0
HTiSi	44 820	223	23	1.1
KTiGe	1 570	9	19	1.1
KTiSiGe	120	2	13	1.0
KTSgel	9 100	37	52	1.3
KTSsol	20 180	91	20	1.1
NaTi	235 120	1177	13	1.0

macosiderite-type structure with $a = b = c = 7.71 \pm 0.01$ Å. The potassium titanosilicate pharmacosiderite has a slightly smaller effective pore diameter as compared with either the potassium titanogermanate or the Ge-substituted titanosilicate. Upon inspection, this observation seems intuitive because the typical Ge−O tetrahedral bond length is approximately 0.2 Å longer than Si−O. However, in some cases, enlarging the unit cell dimension is counterbalanced by an increase in the framework metal's larger radii, thus leading to no net gain in pore size.

A study of the XRD pattern (Figure 2e) revealed that the sodium titanate is a poorly crystalline material with the first d-spacing residing at approximately 10 Å, which corresponds to the interlayer distance between TiO_6 octahedra. Other broad peaks at 5.0 and 3.4 Å are clearly present, but there are insufficient reflections to deduce any crystallographic information. $Na_4Ti_9O_{20}\cdot xH_2O$ is the idealized formula of the nonatitanate, but in practice, some of the Na^+ ions will be replaced by $H^+(H_3O^+)$ ions during the washing procedure, so a more accurate formula would be $Na_{4-y}H_yTi_9O_{20}\cdot xH_2O$.

Ion Exchange Behavior. Tables 2−5 list all the experimental ^{89}Sr and ^{137}Cs K_d values obtained in this scoping study. As noted in Table 2, sample KTSsol produced the highest (57 610 mL/g) ^{89}Sr K_d in the N-Springs simulant, followed by chabazite, clinoptilolite, and the sodium titanate (NaTi). Surprisingly, the potassium titanosilicate pharmacosiderite (KTSgel) gave the lowest K_d of 5 090 mL/g. Although this value seems rather low in comparison with the others listed in Table 2, the K_d still corresponds to approximately 95−96% Sr^{2+} removal.

TABLE 5. ^{89}Sr Distribution Coefficients (K_d) and Decontamination Factors (DF) for the 101SY-Cs5 $V{:}m = 200{:}1$

sample	K_d (mL/g)	DF
HTiSi	164	1.8
KTSgel	31	1.2
KTiGe	0	0
NaTi	295	2.6

Our most recent results provided by PNNL showed that among many exchangers tested by batch methods, including potassium cobalt hexacyanoferrate (Selion CsTreat, 3M) and sodium titanate (NaTi, AlliedSignal; SrTreat, 3M), KTSsol removed the highest concentrations of Cs^+ and Sr^{2+} from actual K-Basin water (*27*). KTSsol even showed better Cs^+ decontamination factors than the leading Cs^+ exchanger, an engineered form of the crystalline silicotitanate (IONSIV IE-911, UOP). Like the sodium titanate, the potassium titanosilicate's selectivity for Sr^{2+} increases as a function of decreasing crystallinity. An explanation for this behavior may result from a dual adsorption and ion exchange mechanism. The semicrystalline exchanger most likely has a higher surface area than the highly crystalline analog, which contributes active surface sites for favorable adsorption, but simultaneously retains its tunnel structure for ion exchange purposes. We are in the process of systematically controlling the synthetic conditions to obtain optimum selectivity.

Sodium nonatitanate has been shown to be a selective inorganic ion exchange material for Sr^{2+} (or $Sr(OH)^+$) from alkaline media (*9*). On the other hand, as the pH decreases, its affinity for H^+ becomes apparent, and the observed K_d values drop dramatically below pH 7 (*9*, *27*). This is nicely illustrated in the alkaline NCAW study where a K_d greater than 200 000 (Table 4) was obtained, despite the presence of excess Na^+. In the less alkaline N-Springs simulant, a more modest K_d of 25 300 (Table 2) was observed. Although Ca^{2+} and Mg^{2+} are known intereferences for the selective Sr^{2+} absorption, our results indicate that the N-Springs K_d remains significantly high. Traditionally, the sodium nonatitanate has little affinity for Sr^{2+} at acidic pH; however, Nenoff and co-workers (*11*) recently revealed an antimony-substituted titanate, doped with different niobium, vanadium, bismuth, or zirconium oxides, which showed some selectivity for Sr^{2+} from acidic solutions.

The selectivity and chemical stability of sodium nonatitanate is dependent upon the degree of crystallinity. Consequently, by varying the time and temperature of reaction and the concentration of sodium hydroxide added, it is possible to produce a range of sodium titanate materials with different degrees of crystallinity and a range of Sr^{2+} selectivities. The material used in this study represents the optimum crystallinity to gain the maximum Sr^{2+} selectivity and was synthesized as part of an ongoing study on the relationship between synthetic conditions, crystallinity, and Sr^{2+} selectivity of the final product. The results of this study will be published at a later date. Sodium nonatitanate is also extremely stable in basic media, which is not surprising given its synthetic procedure, and makes it ideal for the treatment of Sr^{2+} from alkaline tank wastes such as NCAW. As is the case with most inorganic ion exchangers, the titanate exhibits good radiation and thermal stability, and as such, represents an ideal final waste form for ultimate disposal. Alternatively, the Sr^{2+} can be readily removed from the loaded titanate by simply washing with dilute mineral acid and sending the concentrated Sr^{2+} stream for direct incorporation into glass.

Table 3 presents the ^{137}Cs K_d values for the N-Springs simulant. As the data in Table 3 indicate, we synthesized several materials that are highly selective (K_d > 40 000 mL/g) for Cs^+ in groundwater solution. Two impressive K_d values should be noted. The first was obtained for the potassium titanogermanate (KTiGe) with a K_d of 114 510 mL/g at a V:m = 200:1 ratio. Secondly, the partially Ge-substituted potassium titanosilicate (KTiSiGe) produced an even higher K_d of 137 440 mL/g, V:m = 200:1. In addition, sample KTSsol performed remarkably well for Cs^+ removal (K_d = 43 420 mL/g) from the groundwater simulant. Another interesting result was that for compound HTiSi, which is the protonated (acid) form of the titanosilicate ($H_4(TiO)_4(SiO_4)_3 \cdot 8H_2O$) and yielded a Cs^+ K_d of 58 450 mL/g. This is not unexpected because a preliminary experiment showed that the protonated titanosilicate was selective for Cs^+ at low pH (*2*). The Cs^+ K_d values for KTiGe and HTiSi decrease with a higher V:m loading because the selective exchange sites become saturated with competing cations in solution. Not surprisingly, clinoptilolite and chabazite produced low Cs^+ K_d values for N-Springs because high Ca^{2+} concentrations decrease Sr^{2+} and Cs^+ selectivity.

The K_d results for ^{89}Sr and ^{137}Cs removal from the NCAW and 101SY-Cs5 waste simulants are displayed in Tables 4 and 5. None of our synthetic materials were efficient at removing ^{137}Cs from NCAW and ^{89}Sr from 101SY-Cs5 simulants, the highest K_d values being 52 mL/g for KTSgel and 295 mL/g for NaTi, respectively. Not even the "benchmark" Sr^{2+} standard, chabazite, was able to exchange Sr^{2+} with any degree of effectiveness, K_d = 260 mL/g. Chabazite is a zeolite, which like clinoptilolite, exhibits a high selectivity for Cs^+ and Sr^{2+} over Na^+ and, consequently, has found uses within the nuclear industry. It appears from our studies, however, that this commercially available material might fail as a Cs^+ selective exchanger for the highly alkaline tank wastes.

Initial ^{89}Sr K_d values for the NCAW simulant reveal encouraging results. As discussed previously, the titanate (NaTi) performed exceedingly well at removing Sr^{2+} from high concentrations (~5 M) of Na^+ and alkaline pH, yet in groundwater solutions that contain excess Ca^{2+}, the Sr^{2+} K_d values drop off precipitously for this compound. Currently, there are few explanations for why the sodium titanate has a high affinity for Sr^{2+} over Na^+ but not for Ca^{2+}. Previous literature by Lehto et al. revealed that the nonatitanate clearly contains two different exchange sites, but how these sites affect selectivity toward metal cations continues to remain ambiguous (*28*). Regardless, these preliminary results for the batch Sr^{2+} NCAW study indicate that the sodium nonatitanate is an excellent candidate for certain defense tank waste simulants, but not so much for groundwater remediation applications. Despite the high K_d, column experiments are needed in order to assess Sr^{2+} capacities for NCAW or any other defense waste simulants that we deem appropriate.

N-Springs Column Study. Figure 3 exhibits the ^{89}Sr breakthrough data that was generated for the bound potassium titanosilicate using the N-springs groundwater simulant. Up until 14 790 bed volumes, more than 99% Sr^{2+} is retained by the exchanger, which corresponds to an uptake of 2.2 mg (0.11 mequiv/g exchanger) total Sr^{2+}. After this point, the concentration of ^{89}Sr in the effluent begins to slowly rise because the exchange sites progressively saturate with Sr^{2+}, Ca^{2+}, and Na^+ ions. At 20% breakthrough, the column retained an additional 1.47 mg of Sr^{2+}, totaling 3.67 mg (0.18 mequiv/g exchanger). Extrapolating the breakthrough curve to 100% gives the total Sr^{2+} loading around 0.3 mequiv/g.

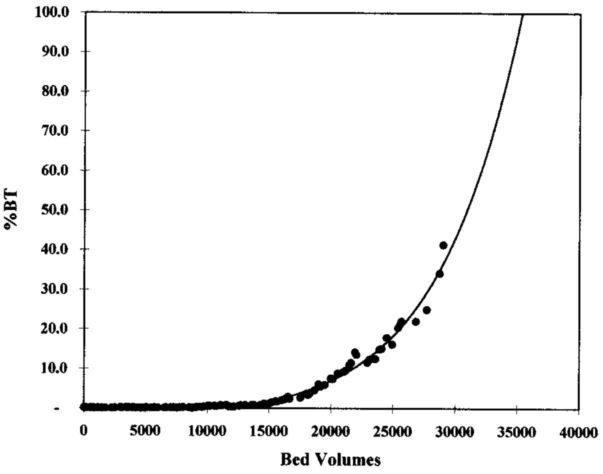

FIGURE 3. ^{89}Sr breakthrough column curve for the bound potassium titanosilicate exchanger using N-springs simulant. Flow rate = 20−30 bed vol/h; 1 mL bed vol.

We also performed a comparative batch K_d study in order to estimate the binder's contribution to the total Sr^{2+} uptake, and it does selectively absorb Sr^{2+} as evidenced by a K_d of several thousand. For high K_d exchangers like KTSsol, the binder will contribute slightly to the overall column capacity but will become significant when both the pure binder and exchanger have similar K_d values. Figure 2 also reveals that the binder does not significantly alter dynamic mass transfer characteristics. Even at such high flow rates, the Sr^{2+} uptake kinetics are extremely fast, as noted by the almost complete Sr^{2+} absorption from 0 to 8500 column volumes.

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