CESIUM AND STRONTIUM SPECIFIC EXCHANGERS FOR NUCLEAR WASTE EFFLUENT REMEDIATION

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Final Report

Cesium and Strontium Specific Exchangers for Nuclear Waste Effluent Remediation

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Executive Summary

We have synthesized three families of tunnel type ion exchangers of composition $A_2Ti_2O_3SiO_4 \cdot nH_2O$, A=H, Na, K, Cs (CST type); $A_3HM(IV)_4O_4(SiO_4)_3 \cdot 4H_2O$ (pharmacosiderite type), A=Na, K, Cs, M(IV) = Ti, Ge and the trisilicates $A_2M(IV)Si_3O_9 \cdot H_2O$, A=Na, K, Cs; M=Ti, Zr, Sn, Pb. The crystal structures of these compounds as well as their protonated phases, coupled with ion exchange titrations, were determined and this information was used to develop an understanding of their ion exchange behavior. The ion exchange selectivities of these phases could be regulated by isomorphous replacement of the framework metals by larger or smaller radius metals.

In the realm of layered compounds, we prepared alumina, silica and zirconia pillared clays and sodium micas. The pillared clays yielded very high Kd values for Cs^+ and were very effective in removing Cs^+ from groundwaters. The sodium micas also had a high affinity for Cs^+ but an even greater attraction for Sr^{2+}. They also possess the property of trapping these ions permanently as the layers slowly decrease their interlayer distance as loading occurs. At a load of ~0.8 meq/g, the entrapment is complete.

Sodium nonatitanate, $Na_4Ti_9O_{20} \cdot nH_2O$, exhibited extremely high Kd values for Sr^{2+} in alkaline tank wastes and should be considered for removal of Sr^{2+} in such cases. For tank wastes containing complexing agents, we have found that adding Ca^{2+} to the solution releases the complexed Sr^{2+} which may then be removed with the CST exchanger.

In conclusion, we have prepared more than thirty different inorganic ion exchangers and regret that we were not able to work closely with those responsible for the remediation problems to target these exchangers for use in specific remediation projects.

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Introduction

During the past 50 years, nuclear defense activities have produced large quantities of nuclear waste that now require safe and permanent disposal. The general procedure to be implemented involves the removal of ^{137}Cs and ^{90}Sr from the waste solutions for disposal in permanently vitrified media. These ions are present in the waste solutions at concentrations of 10^{-3}-10^{-7} M admixed with many other species and at high salt concentrations. Therefore, highly selective sorbents or ion exchangers are required. Further, at the high radiation doses present in the solution, organic exchangers or sequestrants are likely to decompose over time. Inorganic ion exchangers are resistant to radiation damage and can exhibit remarkably high selectives.

A promising group of compounds are those with tunnel structures in which the tunnel space is fit to the size of the ion of interest. There are literally hundreds of inorganic compounds with tunnel structures or a combination of tunnels and cavities. However, for our purposes, the atoms constituting the framework must not be affected by either strong alkali or acid. Therefore, zeolites are unsuitable as are many compounds of amphoteric metals. Phosphates may be useable in acid solution but many of them hydrolyse in basic solution. For our purposes, we will choose certain compounds of titanium and zirconium as silicates and germanates for use in nuclear waste treatments. However, the principles we develop will be quite general and can be applied to situations other than nuclear waste systems. For use in mild acid, alkali or neutral solutions, a much wider range of elements may be suitable for construction of the framework and thus, many more compounds can be utilized.

Our most recent work has utilized pillared clays and sodium micas as inexpensive materials for Cs$^+$ sequestration.

Previous Relevant Work

A.   Sodium Silicotitanate

In previous reports, we have described mechanisms of ion exchange of the crystalline silicotitanate (CST) $Na_2Ti_2O_3SiO_4 \cdot 2H_2O$. We briefly summarize our results here. This compound has a tunnel structure built of Ti_4O_4 cubane units at corners bridged by silicate groups enclosing the tunnels(1) [Fig. 1]. There are two sites for the Na^+ ions, half are in the tunnels and the other half are held in openings in the framework that forms the tunnels. These framework sites are too small to accommodate Cs^+ (or K^+) so it is the sodium ions within the tunnels that are loosely held and readily displaced by Cs^+. The cesium ions form an eight coordinate complex (almost like a crown ether) with the framework silicate oxygens with the bond distances very close to the sum of the radii of Cs^+ plus oxide ion. Cesium ion is so large that it can only occupy half the tunnel sites, the remaining charge being neutralized by sodium ions trapped in the tunnels and hydrogen ion. Potassium ion can occupy the tunnel sites and can also displace some of the Na^+ in the framework walls by squeezing to a position within the tunnels near the site vacated by the sodium ions (2,3). More recently, we carried out a neutron diffraction study of the proton phase of CST and found that the protons are attached to the oxygens that form part of the Ti_4O_4 cubane units (4).

B.   Pharmacosiderites

A second type of tunnel structure ion exchanger, similar to CST, is based on the mineral pharmacosiderite $KFe_4(OH)_4(AsO_4)_3 \cdot 4H_2O$. We are concerned with the titanium analog $K_3H(TiO)_4(SiO_4)_3 \cdot 4H_2O$. We prepared it based on the method of Chapman and Roe (5) and solved its structure "ab initio" from X-ray powder data (6). The structure is composed of Ti_4O_4 cubane-like units at the corners of a cubic unit cell bonded to each other through silicate bridges. This arrangement creates tunnels similar to those in the CST titanosilicate but there are three such intersecting tunnels at right angles to each other. The K^+ ions sit in the cube face centers.

The difference between this structure and the CST is that the latter is tetragonal. The *a*- and *b*-axes of CST are about the same size as the *a*-axis dimension of the titanium-pharmacosiderite. However, the *c*-axis is ~12Å compared to ~7.8Å in the pharmacosiderite and the cubane groupings in CST are connected by oxo-groups, not silicate groups. This use of oxo-connectivity brings the cubane groups closer together in the *c*- direction than in the *a*- and *b*-directions. As a result, only Na^+ can fit into the framework sites. To put it another way, the channels running parallel to the *a*- and *b*- unit cell directions in the CST are smaller than the tunnel running parallel to the *c*- axis whereas the channels or tunnels are all identical in pharmacosiderite.

This feature has interesting consequences. With K^+ in each face center, there is no room for a fourth K^+ in the center of the unit cell, so the fourth cation is H^+.

In the case of the Cs^+, the repulsion of the cations is such that the Cs^+ is disordered over the face-centered sites. That is, they are displaced about $\pm 0.5 \mathring{A}$ on either side of the faces. This weakens the coordination by the oxygen atoms so that the Ti-pharmacosiderite is not nearly as effective a Cs^+ sorbent as the CST. However, it does have a high affinity for Sr^{2+} because only half the sites need to be occupied and the cation-cation repulsion is less (7).

We were able to increase the affinity for Cs^+ by replacing silicate by the larger germanate as shown in **Figure 2** (8). The 100% germanium compound is the poorest exchanger for large ions because Ge^{4+} is considerably smaller than Ti^{4+}. Thus, in the germanium phase, the unit cell is smallest and the uptake of Cs^+ is negligible.

C. $\underline{K_2M(IV)(SiO_3) \cdot H_2O \ M(IV) = Ti, Zr, Sn, Pb}$

A third group of porous exchangers that we prepared have a complex tunnel or cavity system. We solved the structure from X-ray powder data for the Zr compound $K_2Zr(Si_3O_9) \cdot H_2O$ (9) and the Ti analog (10). The structure consists of infinite chains of condensed silicates that in turn are connected to each other by coordinating to the Zr (or Ti) atoms in such a way as to create two sets of tunnels. This is illustrated in **Figure 3** where it is observed that the structure contains relatively large 16 atom (8-rings in zeolite parlance) openings and smaller 12 atom (6-ring) openings creating tunnels parallel to the c-axis. These tunnels are connected to each other by 14 atom openings running roughly along the $a \ b$ diagonal. The Zr phase has a high affinity for Cs^+ ($Kd \cong 4000ml/g$) that is considerably diminished in the Ti compound (9,11). The titanium trisilicate is isostructural with the zirconium compound so that its openings to the cavities are somewhat smaller than those of the zirconium phase. As a result, very little Cs^+ is taken up, but the Kd value for cesium ion increases monotonically in the Ti-Zr trisilicate solid solution phases as the percent Zr increases. Although we prepared the Pb and Sn phases of the trisilicate, we were not able to investigate these phases or their solid solutions before the termination of the grant.

D.   <u>Pillared Clays</u>

Smectite or swelling clays are layered materials that consist of aluminum or magnesium-oxygen octahedra sandwiched between layers of silica-oxygen tetrahedra. Montmorillonite is a member of the smectite clay family in which the octahedral positions are occupied by aluminum ions and is termed a dioctahedral clay. Substitution of aluminum by divalent ions, usually magnesium, occurs in nature and results in a net negative charge on the clay lattice which is

counterbalanced by the presence of cations, usually Na^+ and Ca^{2+} between the clay layers. These cations are readily exchangeable and can be replaced by large polymeric cations such as the Al_{13} Keggin ion, $[Al_{13}O(OH)_{24}(H_2O)_{12}]^{7+}$ or cationic zirconium species based upon the tetrameric unit $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$. After calcination, the clay lamellae are permanently propped open by pillars of alumina or zirconia, leading to microporosity (12,13). A simplified schematic showing the pillaring of a clay by alumina is illustrated in **Fig. 4**. These materials have relatively high surface areas, uniformly sized pores, and no longer swell or disperse in aqueous media. A preliminary study of the ion-exchange properties of pillared clays was undertaken by Dyer and Gallardo (14) who showed that the ion-exchange behavior of pillared clays was largely associated with the pillar rather than the host clay, and that pillaring actually increased the ion-exchange capacity of the clays. However, no ion selectivity data were presented, and their results did not take into account that solubility of the pillar may occur at low or high pHs. Subsequently, we (15) showed that some alumina does dissolve in both acid and base, and if not taken into account yields misleading results in the ion-exchange titration data.

Experimental

Materials All chemicals used to prepare simulants were Fisher Analytical grade. ^{137}Cs was obtained from Amersham Life Science and had a specific activity of 2.5×10^4 Ci/g total Cs. ^{89}Sr was purchased from Isotope Products and had a specific activity of 69.3 mCi/g total Sr. Liquid scintillation counting was performed on a Wallac 1410 counter using Fisher Scientific Scintisafe Plus 50% scintillation cocktail.

Preparation of Ion Exchangers A sample of montmorillonite, SWy-1 (Crooks County, Wyoming) was obtained from Source Clays, University of Missouri, Columbia. This raw mixture was purified by wet sedimentation and converted to the sodium form. Approximately 3 g (dry weight) of purified SWy-1 was suspended in 200 ml of deionized water and heated to 100° C. 3-aminopropyltrimethoxy silane (10 g), $NH_2(CH_2)_3Si(OCH_3)_3$, was refluxed in 300 ml water for 20 h and added to the clay dispersion. This mixture was kept at 100°C for 24 h during which time an additional 100 ml of water was added. The solid product was recovered by centrifugation, washed and dried at 65° C. It was then heated to 500° C for 19 h. This sample is designated PS-II 55. The alumina-pillared clay was obtained from Laporte Absorbents and was prepared by exchanging the Al_{13} Keggin ion, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ into a Los Trancos montmorillonite followed by calcination at 550° C for 4 h. It is designated Al-PILC.

Zirconia Pillared Clay   The zirconia-pillared clay (Zr-PILC), was synthesized according to the method described by Dyer et al. (14).   The clay (33 g) was stirred for 24 hours at room temperature with 1000 mL of a 0.1 M $ZrOCl_2$ solution. The clay was then centrifuged and washed repeatedly with deionized water until the washings were free of chloride ions and did not cause a precipitate with silver nitrate solution. The product was then calcined at $300^{o}C$ for 24 hours and characterized using surface area analysis and X-ray powder diffraction.

Sodium Mica   A phlogopite mica of ideal formula $KAl_3Si_3AlO_{10}(OH)_2$ was treated with 2M NaCl at $180^{o}C$ to convert it to the sodium ion form.   A complete description of the preparation of sodium micas by hydrothermal treatment was provided previously (16).   The sample used in this study was obtained from AlliedSignal Corp., our industrial partner in the DOE sponsored projects.

Sodium Nonatitanate, $Na_4Ti_9O_{20} \cdot H_2O$ 8.4 g of a 50% NaOH solution was added dropwise to 7.7 g of titanium isopropoxide (Aldrich, 97%) in a Teflon round bottom flask with continuous stirring. The mix was then heated to $110^{o}C$ for 4 h and then transferred to a Teflon lined pressure vessel using 13 ml of deionized water in the process. The vessel was kept at $200^{o}C$ for 20 h and then quickly cooled under running tap water. The solid was filtered off and washed with 200 ml of ethanol and dried at $85^{o}C$ for two days.

K_d Determinations   The selectivities of the exchangers for ^{137}Cs and ^{89}Sr were investigated using simple batch studies.   Approximately 0.05 g of material was contacted with 10 mL of solution (giving a V:m ratio of 200) spiked with ^{137}Cs or ^{89}Sr, as appropriate, for 20 hours with constant rotary mixing.   The solution was then filtered through a Whatman No. 42 filter paper (which had previously been shown to be sufficient to exclude all of the clay fines from the supernate), and the activity in the aqueous phase measured using liquid scintillation counting. Distribution coefficients (K_ds) were then calculated according to:

$$K_d = [(C_i - C_f/C_f]V/m \qquad (1)$$

Where C_i = initial activity of solution

C_f = final activity of solution

V = volume of solution (mL)

m = mass of exchanger (g)

The radiotracers added resulted in a total cesium concentration in the N- Springs groundwater of approximately 2 ppb and a total strontium concentration of approximately 0.1 ppm in the NCAW. The contributions of the radiotracers to the total strontium in the groundwater (1.48 x 10^{-6} M) and the total cesium in the NCAW (5.0 x 10^{-4} M) were negligible. All Kd determinations were performed in duplicate with variations greater than 10% repeated until consistent results were obtained.

Results

The physical characteristics of the Los Trancos and SWy-1 clays and the PILCs prepared from them are shown in Table 2. X-ray powder diffraction showed that the Los Trancos clay was relatively pure with the only obvious impurity being a minor amount of quartz. Earlier work (13) had shown that this clay has a cation exchange capacity of approximately 1 meq/g. The major exchangeable cation is Ca^{2+} together with minor amounts of Na^+ and K^+. Both the alumina and zirconia pillared clays were microporous but the silica pillared clay (SWy-1 PILC) contained substantial (~44%) mesopores. The initial d-spacing in the X-ray powder patterns (**Table 2**) correspond to the interlayer

Table 2
Physical Characteristics of the Los Trancos and SWy-1 Clays and the Zr-PILC and the Al-PILC and Si-PILC

Clay	Pillar	Calcination Temperature (°C)	Surface Area (m²/g)	Micro-porosity (%)	d-Spac-ing (Å)
Los Trancos	None	65	73.7	45	15.1
Al-PILC	Alumina	550	264	82	18.3
Zr-PILC	Zirconia	300	171	84	Not seen
SWy-1	None	—	41.8	38.8	9.65
SWy-1-Si	Silica	500	170	56	17.6

Spacings of the clays and their pillared products The low interlayer spacing of 9.65 Å for the SWy-1 clay shows that it was not swollen, whereas the layer spacing and surface area for the Los Trancos clay indicates that it is in the swollen condition. The increased spacings obtained for the heat-treated Al-PILC and SWy-1-Si sample, as well as the porosity indicate that the clays have been successfully pillared instead of delaminated. The Zr-PILC did not yield a well-defined peak corresponding to the interlayer spacing after calcination. However, the increase in surface area and the high level of microporosity correlate well with the results reported by Dyer et al (14). Pore size measurements gave a mean micropore diameter of approximately 6.2 Å for the Al-PILC and 5.6 Å for the Zr-PILC.

The K_d values for removal of Cs^+ from the N-Springs simulant are shown in Table 3. Both the Al-PILC and the Zr-PILC gave excellent extractions of Cs^+ both at the V:m ratio of 200 and 1000. These results indicate a truly high selectivity of the PILC's since less selective materials usually show a decrease in Kd at high V:m ratios. This was shown to be the case for the commercially available sodium silicotitanate IE-911 which decreased from 900,000 ml/g to 88,6000 ml/g under similar conditions (13).

It is evident from the results in Table 4 that the pillared clays have very little affinity for Sr^{2+} and probably for alkaline earths in general. This lack is in contrast to the relatively high preference for alkali metals and suggests their use in separation of these two groups of metals. The best exchanger by far is the powdered pure form of the sodium titanium silicate (CST). We have previously described the synthesis, structure and ion exchange behavior of this compound (1-3). The sodium mica is interesting. We have found that as the sodium ion is replaced with larger ions the layers come together trapping the ions permanently. Therefore, this exchanger may be useful to entrap Cs^+ and Sr^{2+} radioisotopes in contaminated soils and keep them from migrating into the environment. The decrease in Kd for the sodium mica may indicate that this exchanger removes some K^+, Cs^+ and Ca^{2+} from the groundwater as well as Sr^{2+}. Consequently, for low ionic strength solutions such as the N-Springs groundwater, the exchange sites become filled by the more abundant competing ions and the Sr^{2+} uptake is reduced. Further works in column flow studies are necessary to determine whether this hypothesis is correct.

Kinetic Data The rate of uptake of Cs^{2+} and Sr^{2+} ion by selected exchangers is provided in Tables 5 and 6, respectively. The cesium ion data were obtained in 0.1 M $NaNO_3$ solution. The rate of cesium ion uptake by the pillared clays was found to be initially rapid followed by a

gradual increase in Cs^+ removal. By contrast, Cs uptake by the unpillared Los Trancos clay was variable with no trend with increased time observed.

Table 3.
Kd values and % removal of Cs^+ from the N-Springs simulant.

Sample	V:m = 200		V:m = 1000	
	Kd(ml/g)	% Cs^+ Removal	Kd(ml/g)	% Cs^+ Removal
Clinoptilolite	16,400	98.78	39,400	97.62
Na-Mica	11,400	98.26	3,300	77.65
Al-PILC	115,000	99.83	246,000	99.60
Zr-PILC	850,000	99.98	863,000	99.89
Si-PILC	23,000	99.14	—	—
PS-II 55	23,300	99.15	—	—
SWy-1	560	73.7	—	—
Los Trancos Clay	1880	90.34	1650	61.2

Table 4.
Kd values and % removal of Sr^{2+} from N-Springs simulant.

Sample	V:m = 200		V:m =1000	
	Kd (ml/g)	% Sr^{2+} Removal	Kd (ml/g)	% Sr^{2+} Removal
AW 500	30,600	99.35	26,700	96.41
Clinoptilolite	27,200	99.34	7,700	88.17
Na-Mica	240,000	99.92	14,200	93.93
Al-PILC	440	68.71	1050	51.5
Si-PILC	513	71.95	—	—
$Na_4Ti_9O_{20} \bullet 2H_2O$	25,300	99.21	322,000	99.69
IE-911	25,800	99.23	73,600	98.68
$Na_2Ti_2OSiO_4 \bullet 2H_2O$	326,000	99.94	863,000	99.89

Table 5.
Uptake of Cs^+ from 0.1 M $NaNO_3$ solution by selected
pillared clays as a function of time.

	% Cs removal at							
Sample	5 min	10 min	20 min	30 min	1 h	2h	5h	24h
Clay[a]	75.81	76.75	77.24	77.96	77.97	76.01	74.89	82.09
Zr-PILC	96.02	97.06	97.91	98.18	98.38	99.09	99.30	99.57
Al-PILC	90.00	92.66	94.68	94.89	96.23	97.14	97.81	97.87

[a]Los Trancos

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Table 6.
Uptake of Sr^{2+} from N-Springs simulant by
selected exchangers as a function of time.

Exchanger	**Percent Strontium Removal**					
	5min	**10 min**	**20 min**	**30 min**	**60 min**	**24 h**
AW 500	96.56	97.69	98.23	98.44	98.84	99+
$Na_4Ti_9O_{20} \bullet 2H_2O$	99.95	99.95	99.95	99.95	99.95	99.90
Al-PILC	29.5	30.8	41.6	42.7	48.4	51.5

Table 7. K_ds and % Cs Removal from the TAN Groundwater Simulant

Sample	**V:m = 200**		**V:m = 1000**	
	K_d(mL/g)	% Cs Removed	K_d(mL/g)	% Cs Removed
AW500	3.68×10^4	99.46	4.37×10^4	97.82
IE-96	5.32×10^4	99.63	5.86×10^4	98.32
Clinoptilolite	1.63×10^4	98.79	2.04×10^4	95.27
Los Trancos Clay	1.58×10^3	88.91	9.94×10^2	50.47
Zr-PILC	5.45×10^4	99.64	3.88×10^4	97.44
Al-PILC	1.87×10^4	98.94	2.54×10^4	96.18

From the data in **Table 6** it is evident that the uptake of Sr^{2+} by the sodium nonatitanate is very rapid being complete in 5 min. The uptake by the zeolite, AW 500 is also rapid but followed by a slow approach to equilibrium. This type of behavior also characterizes the Al-PILC but at a much slower rate of uptake.

TAN Groundwater The equilibrium uptake of Cs^+ from TAN groundwater is presented in Table 7. All of the exchangers exhibited high uptakes except the Los Trancos clay. There was a slight decrease in the percent uptake at the higher V:m ratio and this is probably due to the high content of Na^+ and K^+ in the TAN groundwater. The effect of electrolyte concentration on uptake of Cs^+ by the Al and Zr PILCS had been reported earlier (12). Potassium ion was the most effective followed by Na^+ in reducing the exchange of Cs^+ however, even in 1M Na^+ $Kd \cong 10,000$ml/g. As already shown, the pillared clays do not readily take up alkaline earths and hence only a slight reduction in Kd values for Cs^+ were observed even in 0.1 M supporting alkaline earth electrolyte solutions.

NCAW The Cs^+ uptake of the pillared clays in the NCAW simulant were extremely low (17) due to the high level of Na^+ and K^+ in the simulant. The results for removal of Sr^{2+} are given in Table 8. Sodium titanate and the sodium titanium silicate gave excellent results. For the latter

compound the Kd value decreased by 16% but the sodium titanate exhibited a much larger decrease. Nevertheless, this exchanger was able to remove Sr^{2+} from 1000 bed volumes before breakthrough and nearly 4000 bed volumes to 50% BT (18). The Kd values for the two PILCs were unexpectedly high. However, it is quite likely that the high pH for the NCAW solution dissolved some silica that in turn precipitated strontium silicate. In alkaline solutions not only are clays unstable but the alumina pillars are also soluble (15). Long exposure to strong alkali solutions would then result in destruction of the PILCs.

Table 8.
Kd values and percent uptake of Sr^{2+} from NCAW simulant.

Exchanger	V:m = 200		V:m = 1000	
	Kd(ml/g)	**% Sr^{2+} Removed**	**Kd(ml/g)**	**% Sr^{2+} Removed**
AW 500	260	56.5	—	—
Clinoptilolite	48	19.3	—	—
Swy-1	274	57.8	—	—
Si-PILC	6620	97.1	—	—
Al-PILC	3300	94.3	—	—
$Na_4Ti_9O_{20} \bullet 2H_2O$	235,000	99.92	39,600	97.52
$Na_2Ti_2O_3SiO_4 \bullet 2H_2O$	269,500	99.93	226,000	99.56

In our final research effort, we discovered that addition of Ca^{2+} to tank wastes, (Tank 107-AN) released the Sr^{2+} held in solution by complexants in the tank. The strontium could then be efficiently removed by use of the exchanger $Na_2Ti_2O_3SiO_4$ (18).

Conclusions

Our laboratory has prepared dozens of inorganic ion exchangers ranging from amorphous beads to fine crystals. Some can be used in acid solutions and others in neutral and basic solutions. The fine powders can be fashioned into spheres or cylinders with or without inorganic binders. In the present report we have shown that pillared clays exhibit interesting ion exchange behavior. They can be prepared on a large scale inexpensively and may be ideal for removal of Cs^+ from certain waste systems. Many other layered exchangers and those with tunnel or cavity structures have been prepared and show high selectivities for specific ions under different solution conditions. The point is that the exchangers can be prepared to fit the needs of the different solutions and conditions that are encountered in the overall nuclear waste remediation program.

We have shown, in two cases, that isomorphous substitution of a larger or smaller cation changes the selectivities of the exchanger. Thus, our concept that specific ions can be targeted for removal by proper control of the structure of the exchanger has a certain validity. Unfortunately, insufficient resources and time were allotted to this endeavor.

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FIGURE 1

Structure of NaH$_{0.75}$Cs$_{0.25}$Ti$_2$O$_3$SiO$_4$

Cs$^+$ fits perfectly into the center of the tunnel while Na$^+$ occupies sites in the framework cavities. Eight silicon oxygens coordinate the Cs$^+$ at distances equal to the sum of the ionic radii.
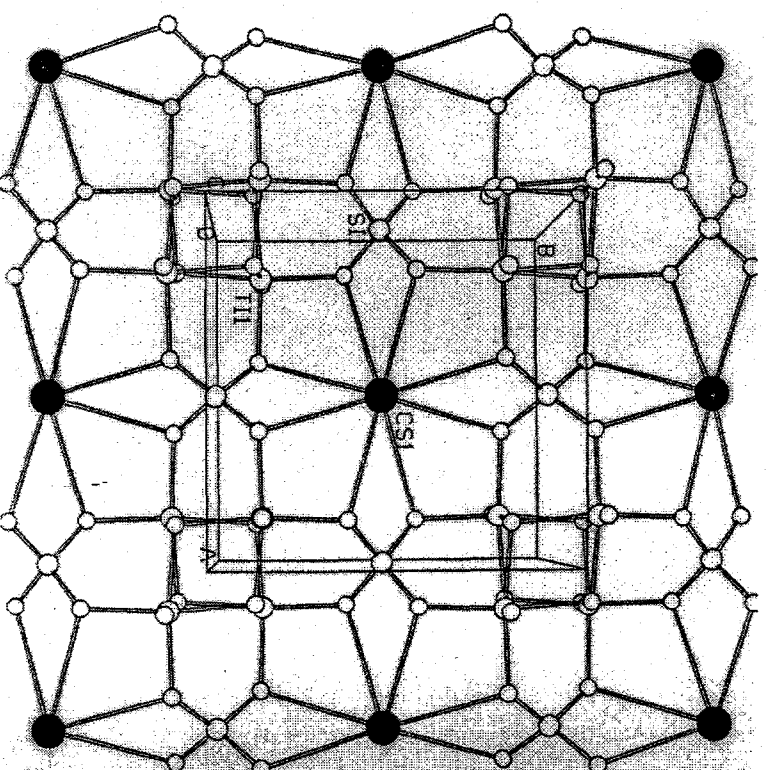
FIGURE 2

Correlation Between Cs Selectivity and Structural Parameters for
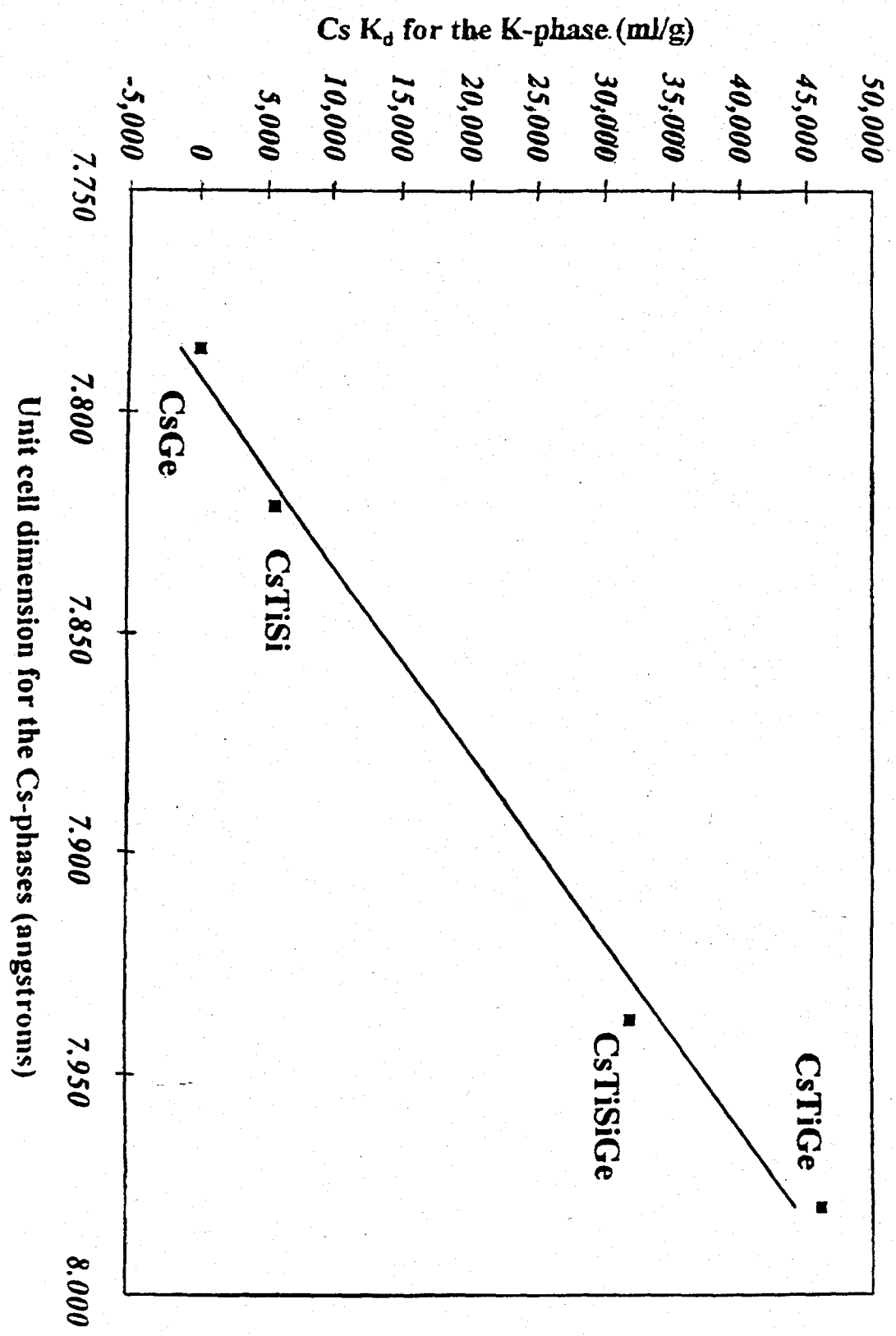the Various Pharmacosiderite Phases

Cs K_d for the K-phase (ml/g)

Unit cell dimension for the Cs-phases (angstroms)

Figure 3. Polyhedral representation of $K_2ZrSi_3O_9$. There are two tunnels. The larger one is occupied by two K^+ (striped circles) and two water molecules (circles with centered dot) per unit cell while the smaller tunnel contains two K^+ per unit cell.
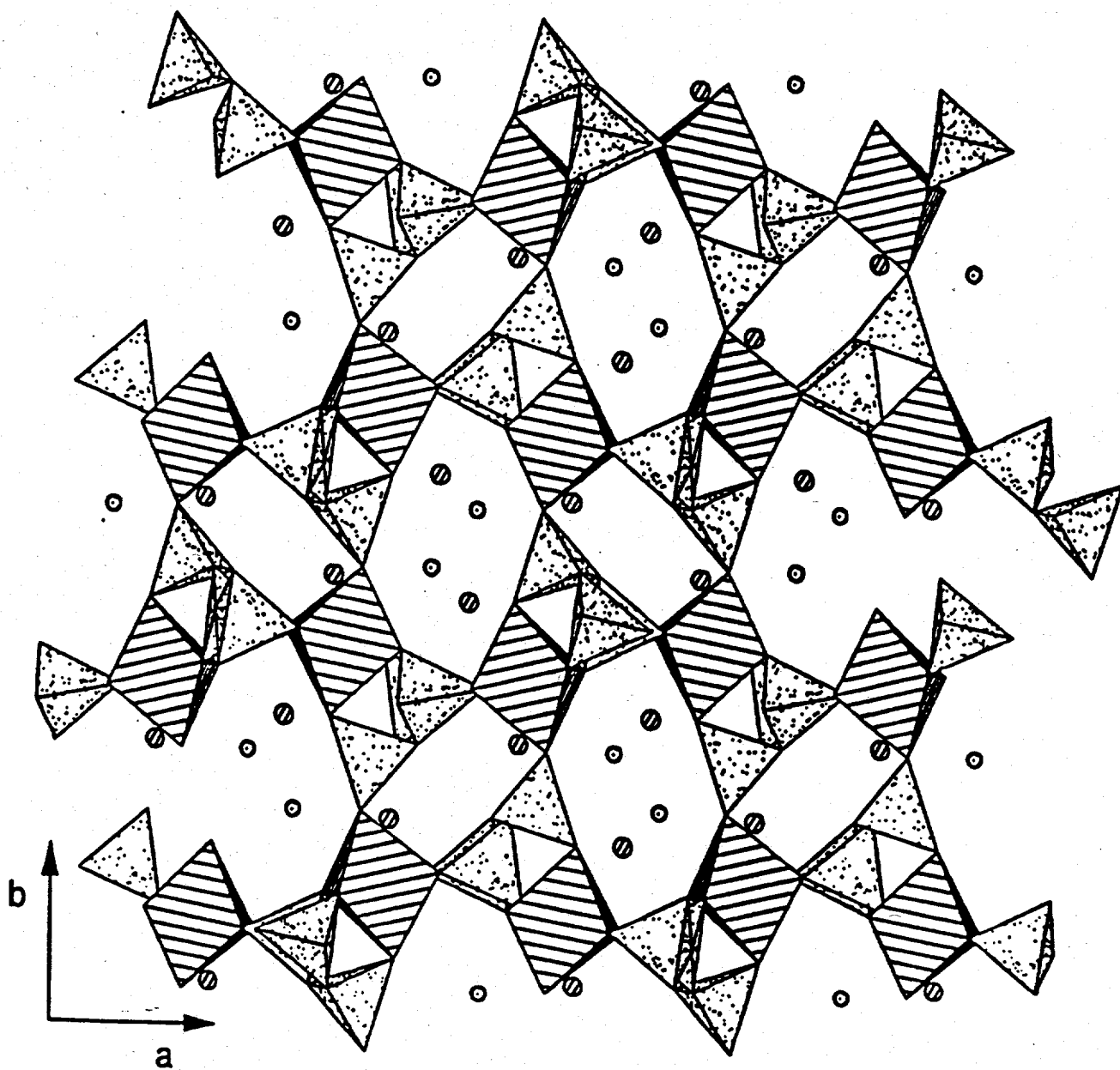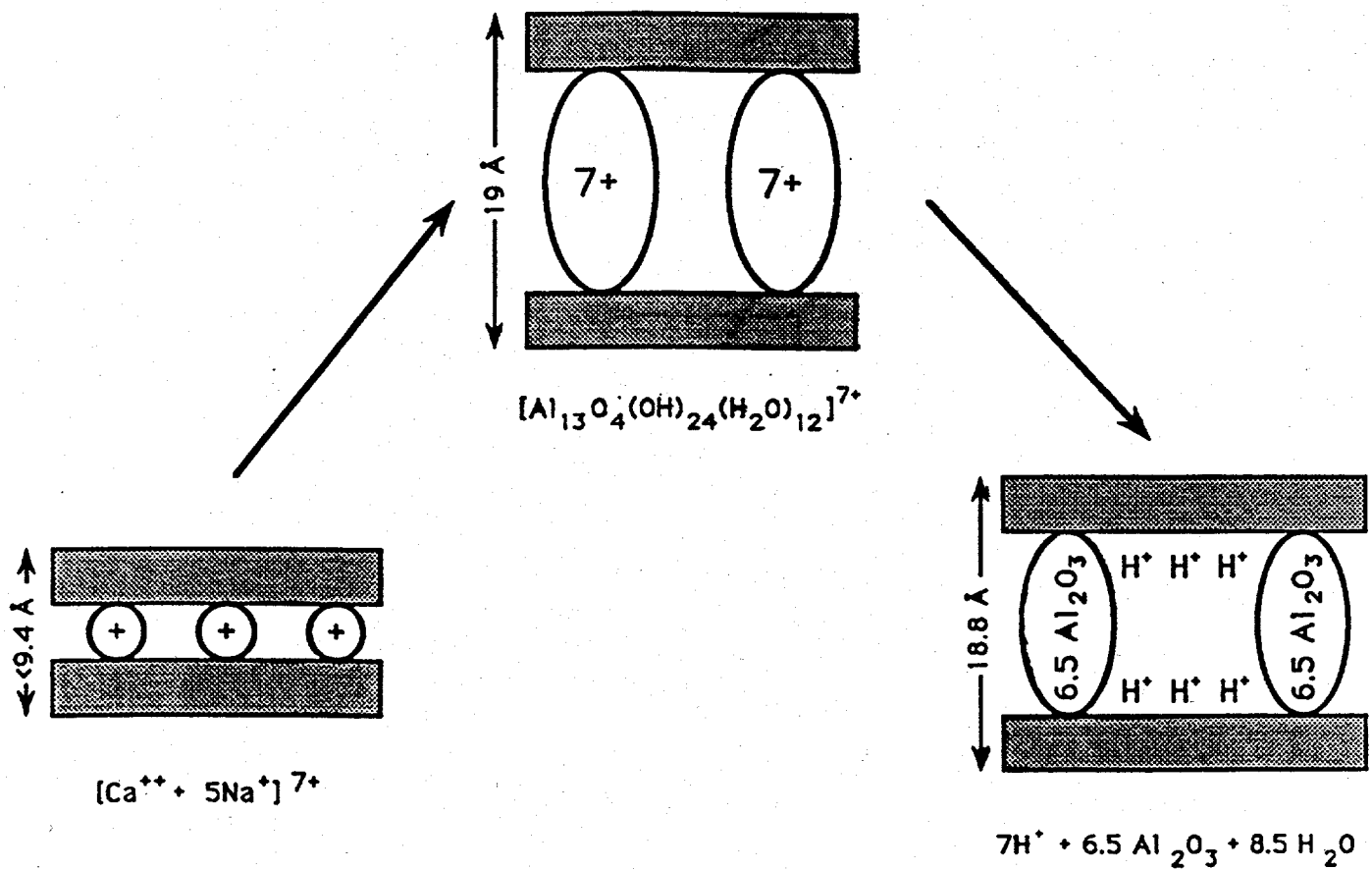
FIGURE 4

$$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$$

$$[Ca^{++} + 5Na^+]^{7+}$$

$$7H^+ + 6.5\ Al_2O_3 + 8.5\ H_2O$$

Cartoon representation (simplified) of the pillaring process.

Cesium and Strontium Specific Exchangers for Nuclear Waste Effluent Remediation

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