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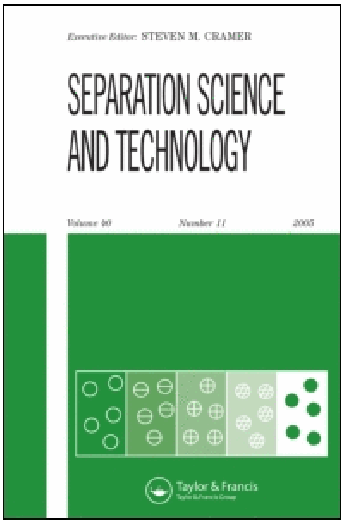

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The Removal of Strontium from Simulated Hanford Tank Wastes Containing Complexants

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ABSTRACT

Two inorganic ion-exchange materials, a sodium nonatitanate and a sodium titanosilicate, were evaluated for the removal of strontium from two simulated Hanford tank wastes, both of which contained substantial amounts of complexing agents. In simulant 101-SY, both exchangers gave distribution coefficients (K_ds) $<$ 220 mL/g at a volume-to-mass ratio of 200. However, in a second simulant, 107-AN, the titanosilicate gave a K_d of 2240 mL/g while the nonatitanate gave a similar K_d to the value obtained in the 101-SY simulant. The reason for the difference in behavior was determined to be the concentration of calcium in the waste simulants. A high calcium concentration (as found in 107-AN) resulted in strontium, previously chelated by EDTA and other complexants, being released into solution and absorbed by the titanosilicate. Consequently, by adding sufficient calcium to 101-SY simulant to saturate the EDTA present, it proved possible to improve the strontium K_ds for the titanosilicate from 215 mL/g to in excess of 8000 mL/g. The titanate exhibited a high selectivity for calcium in comparison to the titanosilicate, and thus the high concentrations of calcium in the waste simulants competed with the strontium ions for the available ion-exchange sites and resulted in low Sr K_ds. As expected, K_ds for the titanate showed little improvement, and the addition of calcium only resulted in a modest increase from 185 to 395 mL/g. Waste generation is minimal, so the addition of calcium to the tank wastes to facilitate the removal of strontium by ion exchange is an economical approach to the remediation of complexant-bearing Hanford tank wastes.

Key Words. Nuclear waste; Ion exchange; Strontium; Hanford; Complexants

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INTRODUCTION

Over the last 50 years, large amounts of aqueous high level radioactive wastes (HLW) have been produced at the Hanford nuclear site in Washington State as a result of chemical extraction processes designed to extract ^{239}Pu from irradiated uranium fuel (1–3). At present the HLW is stored in 177 steel-lined tanks and has an estimated volume of approximately 65 million gallons. The composition of the waste varies considerably from tank to tank; however, previous studies have shown that all of the tanks are believed to contain three distinct phases (4). These phases consist of salt cake at the top of the tank, an alkaline supernate, and a metal hydroxide sludge at the bottom. ^{90}Sr predominantly occurs in the hydroxide sludges but is also found entrained within the salt cake and in the alkaline supernate. The amount of ^{90}Sr present in the supernate in the majority of the tanks is very low and, following Department of Energy (DOE) requirements, it does not require removal for the waste to meet the criteria for low level waste (LLW) classification (5). However, the presence of large amounts of complexants and their radiolytic degradation products has ensured that the level of ^{90}Sr in some of these complexant-bearing supernates is considerably higher, and this is likely to require treatment to reduce the amount of strontium present.

We have evaluated two synthetic inorganic ion exchangers which have previously been shown to exhibit good stability in alkaline media and a high strontium selectivity (6–8), and attempted to identify the major factors limiting their performance in tank waste simulants containing complexants.

EXPERIMENTAL

Materials

All chemicals were of reagent grade and were used without further purification. ^{89}Sr (69.3 mCi/g total Sr) was purchased from Isotope Products Laboratory, California. ^{89}Sr activities were measured by a Wallac 1410 liquid scintillation counter and Fisher Scientific Scintisafe Plus 50% scintillation cocktail using a ratio of 1 mL of sample to 9 mL of scintillation cocktail.

Samples of sodium titanosilicate, $Na_2Ti_2O_3SiO_4 \cdot 2H_2O$, (batch RC-5-23A) and sodium nonatitanate, $Na_4Ti_9O_{20} \cdot xH_2O$, (batch PS-II-35A) were prepared according to established methods described in previous papers (6, 7). The sodium titanosilicate was a highly crystalline material which had previously been shown using x-ray powder diffraction methods to possess a tunnel structure (9). The sodium nonatitanate was very poorly crystalline and the structure was unable to be determined using x-ray methods. However, it is believed to have a layered structure with sodium cations and water molecules intercalated between layers of TiO_6 octahedra (10–14).

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X-ray powder diffraction patterns of both materials were published in earlier works (6, 7).

Preparation of Simulants

Two waste simulants representative of tanks 107-AN and 101-SY were prepared according to information supplied by British Nuclear Fuels Inc. (BNFL) and Pacific Northwest National Laboratory (PNNL), respectively. The compositions of these two wastes are given in Tables 1 and 2. The 107-AN simulant was prepared by mixing the Solutions A and B detailed in Table 1. Solution A had a total volume of 800 mL of deionized water and Solution B had a total volume of 1100 mL. Sufficient of each component salt was added to each solution to give the stated final concentration in a total volume of 2 L, assuming no precipitation occurred. After adding Solution B to Solution A, the mixture was heated at 65°C for 4 hours, cooled, and allowed to stir overnight at room temperature. [Immediately on mixing, a white precipitate formed (predominantly calcium carbonate) which only partially dissolved after heating

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TABLE 1
Composition of 107-AN Simulant

Solution A	Final concentration (M) (after dilution to 2 liters)
$NaNO_3$	0.630
$Al(NO_3)_3$	0.300
$Ca(NO_3)_2$	0.200
$Fe(NO_3)_3$	2.50E-03
KNO_3	0.900
$La(NO_3)_3$	4.00E-04
$CsNO_3$	2.00E-04
Na_2EDTA[a]	1.87E-02
Na_3 citrate	3.83E-02
HEDTA[b]	2.23E-02
Na_2IDA[c]	0.112
Glycollic acid	0.706
Solution B	
NaOH	2.51
Na_2CO_3	0.330
$NaNO_2$	0.820

[a] NA_2EDTA: Ethylenediaminetetraacetic acid, disodium salt.

[b] HEDTA: *N*-(2-Hydroxyethyl)ethylenediaminetriacetic acid.

[c] Na_2IDA: Iminodiacetic acid, disodium salt.

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TABLE 2
The Composition of the Waste Simulant 101SY-Cs5

Species	Concentration (M)
$Ni(NO_3)_2$	2.49E-04
$Ca(NO_3)_2$	4.20E-03
$Zn(NO_3)_2$	5.00E-04
MoO_3	4.20E-04
$Fe(NO_3)_3$	1.96E-04
$CsNO_3$	4.19E-05
$RbNO_3$	4.20E-06
Na_4EDTA	5.00E-03
Na_3HEDTA	3.75E-03
Citric acid	5.00E-03
Na_3 nitrilotriacetate	2.50E-04
Iminodiacetic acid	3.05E-02
Sodium gluconate	1.25E-02
Na_2SO_4	4.75E-03
Na_2HPO_4	2.04E-02
NaOH	3.78
KF	3.38E-02
$Al(NO_3)_3$	4.15E-01
Na_2CO_3	3.75E-02
NaF	5.80E-02
$NaNO_2$	1.09

and stirring.] The total volume was made up to 2 L, and the solution was filtered through a 0.45-μm membrane and spiked with ^{89}Sr to give a total strontium concentration in solution of approximately 1.2 ppm or 1.37×10^{-5} M. The formation of a precipitate on mixing Solutions A and B means that the precise composition of the 107-AN simulant is not known, but it can be assumed that the solution is saturated with calcium.

Simulant 101-SY was prepared by dissolving the components listed in Table 2 (in the order in which they are listed) in approximately 600 mL of deionized water and then making up to 1 L with deionized water. PNNL recommended a total strontium concentration of 2.9×10^{-7} M in this simulant, but due to the relatively low specific activity of the ^{89}Sr supplied by Isotope Products, it was necessary to use a concentration of 1.37×10^{-5} M Sr to ensure sufficient residual activity after contact with the ion exchangers to allow accurate counting on the liquid scintillation counter (LSC).

These wastes are representative of complexant-bearing supernates found at the Hanford nuclear site, diluted to 5 M Na^+. Both simulants contain significant amounts of chelating agents such as EDTA and citric acid which will complex the strontium present, making removal by ion exchange far more dif-

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ficult than in the complexant-free tank wastes.

1) Effect of Complexants on Sr K_ds

Prior to evaluating the ion exchangers in the waste simulants, the effect of each of the complexants found in the waste simulants on strontium uptake by both the sodium titanate and the sodium titanosilicate was evaluated. A 0.01 M solution of each of the complexants was prepared in 1 M $NaNO_3$ and spiked with ^{89}Sr to give a total strontium concentration of approximately 1.2 ppm. The effect of the complexants on the percentage of the ^{89}Sr removed was then evaluated by comparing the results with the amount of ^{89}Sr removed from a solution of 1 M $NaNO_3$.

Ion exchanger (0.05 g) was placed in a scintillation vial, and 10 mL of solution was added. The mixture was then shaken for 24 hours using a rotary shaker, and then the aqueous phase was passed through a 0.02-μm syringe filter and counted using the LSC. The percentage of strontium removed was then calculated according to

$$\%^{89}\mathrm{Sr\ removed} = [(C_0 - C_f)/C_0]100 \tag{1}$$

where C_0 = initial activity of solution (cpm/mL)
C_f = final activity of solution (cpm/mL)

All percentages quoted are a mean of two or more separate determinations. Duplication of results was excellent, with repeat experiments generally being within 5% of each other.

Results for Part 1

The percentages of the strontium removed from the complexant solutions are given in Table 3. The behavior of the titanate and the titanosilicate differed markedly, with the titanate being least affected by the presence of complexants. The only complexant to significantly reduce the amount of strontium extracted by the titanate was EDTA, though HEDTA also caused a measurable reduction. By contrast, the extraction of strontium by the titanosilicate was impaired by nitrilotriacetate, EDTA, glycollic acid, and HEDTA, with EDTA having by far the greatest effect. The presence of 0.01 M EDTA in a solution of 1 M $NaNO_3$ reduced the amount of strontium removed from nearly 100% to less than 10%. Consequently, if the complexants are the major factor affecting the uptake of ^{89}Sr from complexant-bearing Hanford tank wastes, it would be expected that the titanate would perform far better than the titanosilicate.

2) Simulant Experiments

Ion exchanger (0.05 g) was accurately weighed into a scintillation vial to

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TABLE 3
The Removal of Sr from 0.01 M Complexant Solutions in 1 M $NaNO_3$ by Sodium Titanate and Sodium Titanosilicate

	% Strontium removed	
Complexant	Titanate	Titanosilicate
None	99.9	99.9
Na_3 citrate	99.9	99.8
Na_2 iminodiacetate	99.9	99.9
Na_3 nitrilotriacetate	99.8	96.7
Na_4 EDTA	86.2	8.96
Glycollic acid	99.9	69.4
Na_3HEDTA	98.3	49.5
Na gluconate	99.9	99.9

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give a V:m ratio of 200 and contacted with 10 mL of the waste simulant which had been spiked with ^{89}Sr to give a total strontium concentration of approximately 1.2 ppm. The vials were capped and placed on a rotary shaker for approximately 24 hours to ensure that equilibrium was reached. The mixtures were then filtered using Whatman No. 42 filter paper (which had previously been shown to be sufficient to retain any fines generated) and the residual activity in the solutions determined using the LSC. As a further precaution to remove any solids from the samples counted, each liquid sample was also filtered through a 0.2-μm syringe filter prior to counting. Distribution coefficients (K_ds) were then calculated using

$$K_d = [(C_0 - C_f)/C_f]V/m \tag{2}$$

where C_0 = initial activity of solution (cpm/mL)
C_f = final activity of solution (cpm/mL)
V = volume of solution (mL)
m = mass of exchanger (g)

All K_ds quoted are a mean of two or more separate determinations. Duplication of results in these experiments was also excellent with repeat K_d determinations generally being within 5% of each other.

Results for Part 2

The Sr K_ds for the titanate and the titanosilicate in the tank waste simulants are given in Table 4. It can be clearly seen that in the 101-SY simulant, neither of the exchangers exhibited any appreciable affinity for strontium, with both K_ds being less than 220 mL/g. The K_d for the titanosilicate compares well with earlier work on the 101-SY simulant, but the performance of the titanate

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TABLE 4
K_ds and % Sr Removal from 101-SY Simulant at a *V:m* Ratio of 200

	101-SY		107-AN	
Ion exchanger	K_d (mL/g)	% Sr removed	K_d (mL/g)	% Sr removed
Na nonatitanate	192	49.0	185	48.1
Na titanosilicate	215	51.8	2240	91.8

is slightly less than the previously published K_d of 295 mL/g (6–8). This difference is due to minor variations in the performance of different batches of the sodium titanate. In the 107-AN simulant, the titanate again gave a low K_d but the titanosilicate gave a K_d of 2240 mL/g which is equivalent to the removal of 91.8% of the total strontium present. This is totally unexpected because the 101-SY simulant contains only approximately 0.005 M EDTA while the 107-AN simulant contains 0.0187 M EDTA. It has been shown that EDTA at a concentration of 0.01 M reduces the uptake of Sr by the titanosilicate from nearly 100% to less than 10% in 1 M $NaNO_3$, so it would be expected that the K_ds for the titanosilicate in 107-AN, which is 5 M in $NaNO_3$, would be very low indeed. Consequently, it cannot just be the concentrations of complexants which are affecting the strontium removal from the tank wastes.

Comparison of 107-AN and 101-SY Simulants

A comparison of the cations present in the two waste simulants indicated that the most likely cation responsible for the difference in the K_ds for the titanosilicate in 101-SY and 107-AN was calcium. This was present in the 101-SY at a concentration of 4.2×10^{-3} M while in the 107-AN the concentration was approximately 0.2 M. Ordinarily, the presence of calcium would be expected to reduce the K_ds for strontium because the Ca^{2+} ion competes with Sr^{2+} for the available ion-exchange sites. However, it was hypothesized that the higher concentration of calcium present in the 107-AN simulant may displace the Sr from Sr–EDTA complexes, thus freeing up strontium for removal by ion exchangers. This is supported by the $\log_{10}(\text{mol}^{-1}\cdot\text{dm}^3)$ of the stability coefficients (K_{stab}) for Sr–EDTA and Ca–EDTA complexes which are 8.6 and 10.7, respectively (15). Consequently, the addition of calcium to 101-SY simulant may therefore improve Sr K_ds. Fe^{3+} has a much higher stability coefficient (25.1) with EDTA than either Ca^{2+} or Sr^{2+} but is unlikely to be the cause of differences in the K_ds between the simulants because of the low concentrations of iron in both simulants. Attempts to add sufficient Fe^{3+} [as $Fe(NO_3)_3$ solution] to the simulants in order to complex the EDTA present resulted in

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the precipitation of iron hydroxide rather than chelation of the Fe^{3+} by the EDTA due to the high insolubility of Fe^{3+} in highly basic solutions. This precipitation resulted in the removal of up to 30% of the strontium from solution but did not free up the residual strontium for subsequent removal by the titanosilicate ion-exchanger. The addition of Fe^{3+} to waste streams to remove radionuclides from solution is well known and forms the basis of the Enhanced Actinide Removal Plant (EARP) at British Nuclear Fuels' Sellafield site in the United Kingdom. However, relatively large volumes of waste are generated, making precipitation using iron unsuitable for the treatment of Hanford wastes.

The sodium titanate is also selective for calcium, so excess calcium ions unchelated by EDTA may well affect the Sr K_ds. By contrast, the titanosilicate is much less selective for calcium, so the presence of excess calcium ions would not be expected to have too great a deleterious effect on the Sr K_ds. This difference in the selectivity of the two materials for calcium is well illustrated by comparing the Ca K_ds for the titanate and titanosilicate from a solution 10^{-3} M in $Ca(NO_3)_2$ and 1 M in $NaNO_3$. At a $V{:}m$ ratio of 200, the titanate gave a K_d of 7700 mL/g while the titanosilicate gave a K_d of only 450 mL/g (16). Consequently, in comparison to the titanosilicate, the titanate Sr K_ds will be very sensitive to the calcium concentration of the simulants.

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3) Sr K_ds in Ca^{2+}/EDTA Solutions

In order to investigate the effect of a combination of Ca^{2+} and EDTA on the Sr K_ds for both the sodium titanate and the sodium titanosilicate, a series of experiments were undertaken where the relative concentrations of Ca^{2+} and Na^+ were kept constant and the concentration of EDTA was increased. Three solutions were prepared as shown in Table 5 and spiked with ^{89}Sr to give a total strontium concentration of approximately 1.2 ppm. Ion exchanger (0.05 g) was placed in a scintillation vial and 10 mL of solution added. The mixtures were placed on a rotary shaker for 24 hours to ensure equilibrium was reached and then filtered through a 0.2-μm membrane. The residual ac-

TABLE 5
Sr K_ds for the Titanate and the Titanosilicate in the Presence of Ca^{2+} and EDTA

$[NaNO_3]$ (M)	$[Ca(NO_3)_2]$ (M)	$[Na_4EDTA]$ (M)	Titanate K_d (mL/g)	Titanosilicate K_d (mL/g)
1.0	0.10	0	23	37
1.0	0.10	0.01	26	44
1.0	0.10	0.10	230	6560

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tivities were measured using the LSC, and the K_ds were calculated according to Eq. (2).

Results for Part 3

The K_ds for both the titanate and the titanosilicate are given in Table 5. In the presence of no EDTA or 0.01 M EDTA, the calcium competes effectively with the Sr for the available ion-exchange sites on both materials and the observed K_ds are very low (<50 mL/g) for both exchangers. In the presence of 0.1 M EDTA, which should be more than sufficient to complex the 0.1 M Ca^{2+}, the K_d for the titanate is still low, 230 mL/g, but the K_d for the titanosilicate has improved to 6560 mL/g. This can be directly attributed to the high selectivity of the titanate toward calcium (even in the presence of an excess of EDTA) when compared to the titanosilicate. This causes calcium to be absorbed by the titanate in preference to strontium, resulting in low K_ds. By contrast, the titanosilicate has a much lower selectivity for calcium, and when sufficient EDTA is added to chelate the majority of the Ca^{2+} ions present, the Sr^{2+} ions are made available for ion exchange and hence the K_ds for strontium increase. This explains the difference between the K_ds for the titanosilicate in 101-SY (Ca unsaturated) and 107-AN (Ca saturated) simulants.

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4) Addition of $Ca(NO_3)_2$ to 101-SY Simulant

The concentration of calcium in 101-SY simulant was increased by the addition of solid calcium nitrate. Solid was added rather than a solution to reduce any dilution effects which might have occurred. The effect of increasing the calcium concentration in 101-SY simulant was investigated by three experiments.

To 100 mL of 101-SY simulant, 0.331 and 0.662 g of $Ca(NO_3)_2{\cdot}4H_2O$ were added and the mixtures shaken for 3 days to allow equilibrium to be obtained. If all of the added calcium nitrate dissolved, this would lead to total calcium concentrations of 1.82×10^{-2} M and 3.22×10^{-2} M, respectively, which should be sufficient to saturate the 5×10^{-3} moles of EDTA present. The solutions were then filtered to remove any undissolved calcium salts and spiked with ^{89}Sr to give a total strontium concentration of 1.2 ppm. These solutions were labeled A and B, respectively, and were filtered again prior to use to ensure no further precipitation occurred after the addition of ^{89}Sr.

Solution C was prepared by spiking 100 mL of 101-SY simulant with ^{89}Sr to give a total concentration of 1.2 ppm. $Ca(NO_3)_2{\cdot}4H_2O$ (0.331 g) was added and the mixture shaken for 3 days. The solution was then filtered to remove any precipitates before being used for ion-exchange experiments. Solutions A, B, and C initially had approximately the same activity, indicating that no strontium was lost from solution through precipitation.

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TABLE 6
The Effect of $Ca(NO_3)_2$ Addition to ^{89}Sr K_ds from 101-SY Simulant

Solution	$Ca(NO_3)_2$ added per 100 mL/g	Titanate K_d (mL/g)	Titanosilicate K_d (mL/g)
A	0.331	314	2660
B	0.662	384	8120
C	0.331	395	4560

Exchanger (0.05 g) was contacted with 10 mL of solution for 24 hours, filtered through a 0.2-μm membrane, and the liquid analyzed for activity using the LSC. All experiments were performed in duplicate.

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Results for Part 4

The Sr K_ds obtained after the addition of calcium nitrate to the 101-SY simulant are given in Table 6. It can be seen that the addition of calcium to the 101-SY has only a very marginal effect on the K_ds observed for the sodium titanate, with values only increasing from an initial value of 192 to 395 mL/g. By contrast, the K_ds for the titanosilicate markedly improved. Without any addition of calcium to the simulant, the Sr K_d was only 215 mL/g, but the addition of 0.662 g of $Ca(NO_3)_2 \cdot 4H_2O$ per 100 mL increased that K_d by more than an order of magnitude to 8120 mL/g. Addition of Ca^{2+} to the simulant already spiked with ^{89}Sr, which would be closer to a real-life scenario than spiking a simulant after the addition of extra calcium, also improved the K_d to 4560 mL/g.

DISCUSSION

The two exchangers recommended for use in the removal of strontium from tank wastes are of two different types. Sodium nonatitanate is layered with an interlayer spacing of about 10 Å. This spacing is variable dependent on the water content (13). This compound is poorly crystalline, with only a handful of reflections in the powder pattern. Hydrothermal treatment in a strong base (8–9 M) at ~200°C yields a more crystalline product but with a much reduced affinity for strontium and may signal a phase change. Thus, the structure of the nonatitanate is unknown. However, it has a high affinity for strontium in mildly alkaline to strongly alkaline solutions (10–12, 14). It has been shown (10) that in the 2–6 pH range, the strontium exchanges as Sr^{2+} and above pH 12 as $Sr(OH)^+$. In between these pH values there is an equilibrium between the two strontium species. The nonatitanate also exhibits a reasonable affinity

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for the other alkaline earth metal ions with the sequences

$$Ba^{2+} > Sr^{2+} > Ca^{+} > Mg^{+} \qquad \text{pH } 6$$

$$Sr > Ca > Ba > Mg \qquad \text{pH } 12$$

No charge is assigned to the second sequence of alkaline earth ions because of the +2, +1 equilibrium. The affinity for alkali metal ions is much less than for the alkaline earths (12).

With the background presented above, we may now explain what happens in the presence of complexants. We shall use EDTA as the model for all the complexing agents because it is the one having the greatest effect on the behavior of strontium and calcium. EDTA forms a one-for-one complex with cations in general:

$$Sr^{2+} + Na_4Y \rightleftharpoons Na_2Sr^{2+}Y^{2-} + 2Na^{+} \tag{3}$$

$$Na_2Sr^{2+}Y^{2-} \rightleftharpoons 2Na^{+} + [SrY]^{2-} \tag{4}$$

where Y represents the tetrabasic EDTA anion. In 1 M $NaNO_3$ these equilibria are shifted to the left and a portion of the Sr^{2+} is in solution at neutral pH (Part 1).

The ion-exchange reaction with the nonatitanate is represented by

$$Na_4Ti_9O_{20} + Sr^{2+} \rightleftharpoons Na_2SrTi_9O_{20} + 2Na^{+} \tag{5}$$

This reaction is in competition with the EDTA complexing reaction, and because of the high affinity of the nonatitanate for Sr^{2+}, a large proportion of the total Sr^{2+} is exchanged in the absence of calcium ions.

Sodium titanosilicate has a framework structure built up of Ti_4O_4 clusters bridged by silicate groups (9). The TiO clusters have a cubane-like structure and are placed at the corners of a square. They are connected to each other in the *a* and *b* (*x* and *y*) directions by silicate groups forming an infinite two-dimensional lattice. These layers are then connected to similar ones in the *c* (*Z*) direction by oxo groups. This framework creates tunnels running parallel to the *c*-axis direction, and the space between layers in the framework takes the form of a void or cavity in all four sides of the framework. As a result, there are two types of ion-exchange sites. Those within the tunnel can accommodate Cs^{+}, forming an eight-coordinate Cs—O polyhedron. The voids in the framework are occupied by Na^{+} in a six-coordinate Na—O octahedral complex. In both cases the bond distances are close to the sum of their ionic radii. This accounts for the extraordinarily high affinity for Cs^{+} in the tunnel sites and a high affinity for Na^{+} in the framework sites. In the sodium titanosilicate, half the sodiums are in the framework and half are loosely held in the tunnels and easily displaced. Thus, in high sodium ion media we expect the strontium would displace the sodium in the tunnels. Since Sr^{2+} is much smaller than

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Cs^+ and holds its hydration shell more strongly, the K_d values for Sr^{2+} in neutral and acid solutions are quite low. The K_d values increase significantly in highly alkaline solution, probably because of the strong binding of $Sr(OH)^+$ to the framework. We have not yet determined these sites but are attempting to do so from x-ray diffraction studies.

Consider now what may happen in the presence of 0.1 M EDTA and 1 M $NaNO_3$ (Part 1). In this solution the sodium titanosilicate has almost no preference for the free Sr^{2+} and therefore takes up very little, the bulk of the Sr^{2+} being complexed by EDTA (Table 3). Likewise, the titanosilicate has a very low affinity for Ca^{2+} in acid or base solution but EDTA prefers Ca^{2+} to Sr^{2+}. In the simulant 107-AN, 0.2 M in Ca^{2+}, most of the complexants are in the Ca form since, for EDTA (as an example), the formation constants, K, for EDTA are 8.63 for the Sr–EDTA complex and 10.7–10.96 for the Ca–EDTA complex (17). Thus, most of the strontium is present in solution and is taken up in the tunnels of the titanosilicate. The high concentration of Ca^{2+} or $Ca(OH)^+$ in this simulant must leave sufficient calcium uncomplexed to compete for sites with strontium on the sodium titanate. As a result, only half as much Sr is taken up by the nonatitanate. Since no calcium is present in simulant 101-SY, the titanosilicate and sodium nonatitanate take up similar quantities of Sr.

Finally, addition of calcium nitrate to the 101-SY simulant frees up the Sr from the complexants, allowing the titanosilicate to take up the bulk of the Sr (~97%). In contrast, excess Ca must also be present which does not affect the titanosilicate but competes with Sr for sites on the titanate. Remember the strontium is present in 10^{-5} M concentration so the ratio of excess Ca to total Sr is very high. Proper adjustment of the added calcium is required to optimize the process.

CONCLUSIONS

This work has shown that both calcium and complexant concentrations in tank waste simulants have an effect on the ability of ion-exchange materials to remove strontium. Although sodium titanate has been shown to be able to remove strontium in the presence of complexants more effectively than sodium titanosilicate, the presence of large quantities of calcium ions strongly hinders the ability of the titanate to remove strontium from solution. By contrast, the titanosilicate is much less affected by high calcium concentrations, thus allowing calcium to be added to the waste simulants to free up complexed strontium which can then be removed by ion exchange.

The amount of calcium required to release the strontium for ion exchange is very low. An addition of 0.662 g of $Ca(NO_3)_2{\cdot}4H_2O$ per 100 mL of simulant equates to the production of a maximum of 0.157 g of waste (calculated as calcium oxide, CaO) per 100 mL, assuming that none of the calcium nitrate dissolves. If we add to that the 0.5 g of exchanger added per 100 mL, the total

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maximum waste (as oxides) amounts to only 0.657 g per 100 mL or 6.57 g per liter. Since a considerable amount of the added calcium nitrate actually dissolves into the simulant, the actual amount of waste generated will be considerably less, and the use of the exchanger in a column rather than in a batch process would reduce the amount of waste still further. Furthermore, Sr^{2+} is readily removed from the titanosilicate in acid solution, so the exchanger may be recycled.

In conclusion, an effective means of removing strontium from Hanford tank waste simulants containing complexants using an ion-exchange method, without the generation of undue amounts of solid waste, has been demonstrated.

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