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Strontium and Actinide Separations from High Level Nuclear Waste Solutions Using Monosodium Titanate 1. Simulant Testing

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Abstract: High-level nuclear waste produced from fuel reprocessing operations at the Savannah River Site (SRS) requires pretreatment to remove ^{137}Cs, ^{90}Sr, and alpha-emitting radionuclides (i.e., actinides) prior to disposal. Separation processes planned at SRS include caustic side solvent extraction, for ^{137}Cs removal, and ion exchange/sorption of ^{90}Sr and alpha-emitting radionuclides with an inorganic material, monosodium titanate (MST). The predominant alpha-emitting radionuclides in the highly alkaline waste solutions include plutonium isotopes ^{238}Pu, ^{239}Pu, and ^{240}Pu. This paper provides a summary of data acquired to measure the performance of MST to remove strontium and actinides from simulated waste solutions. These tests evaluated the influence of ionic strength, temperature, solution composition, and the oxidation state of plutonium.

Keywords: Sorption, ion exchange, strontium, plutonium, neptunium, uranium

INTRODUCTION

Monosodium titanate (MST), $NaTi_2O_5 \cdot xH_2O$, first prepared by Lynch, et al. by a sol-gel method (1), is an amorphous white solid that exhibits high selectivity for many metallic ions in both acidic and alkaline waste solutions

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including those containing strontium and several actinides (2, 3). The Savannah River Site contractor selected MST for strontium removal in conjunction with cesium removal by precipitation as the tetraphenylborate salt for the in-tank precipitation (ITP) process (4). MST exhibited high strontium removal capacity at acceptable removal rates along with the added benefit of plutonium removal. SRNL developed a modified synthesis of MST that produced a material tailored for the ITP deployment in a high-level waste (HLW) tank (1.3 million gallon) equipped for the batch process.

Testing at SRNL during the 1980s and 1990s indicated that the MST successfully removed sufficient ^{90}Sr and alpha-emitting radionuclides to meet the requirements for disposing of the decontaminated waste solution in a low-level cement-based wasteform (5). Testing also indicated that the small quantity of MST required for ^{90}Sr and actinide removal did not adversely impact high-level waste glass chemistry and physical properties. Actinide removal characteristics of the MST became an increasingly important issue in the early 1990s as waste characterization data revealed an increasing need to remove alpha-emitting radionuclides from HLW supernates. Also of concern was the accumulation of fissile radionuclides onto the MST from a nuclear criticality safety basis (6). Accumulation of fissile isotopes onto the MST was found to be below levels that would pose a nuclear criticality safety concern (7). Thus, the use of MST proved acceptable for the ITP process.

The ITP facility operated for a brief time before shutting down permanently in 1998 due to operational and safety concerns unrelated to MST usage. SRS conducted an extensive evaluation process for alternate pretreatment processes to separate radioactive components from the high level nuclear waste solutions (8). The engineering evaluation and selection of the preferred treatment process included considerable research and development testing (9). This paper provides a summary of research data acquired on the performance of MST using simulated waste solutions for the engineering evaluation and selection process. A separate paper will provide a summary of testing results on the performance of MST using actual tank waste supernatant liquids. Tank waste solutions are much more complex chemical mixtures than the simulants used in these studies. Thus, minor and trace components such as transition and main group metal ions and lanthanides, may compete with strontium and actinides for sorption/ion exchange with the MST.

EXPERIMENTAL

Preparation of MST

All testing used samples of MST prepared on commercial scale by Optima Chemicals, Inc. (Douglas, GA). The MST is supplied as an aqueous slurry containing approximately 15 wt% MST and 0.10–0.15 M NaOH and 100–150 mg L^{-1} $NaNO_2$ added as corrosion inhibitors for storage in carbon steel tanks. The preparation of the MST follows a laboratory procedure developed by the Savannah River National Laboratory (SRNL), which is similar to Method 1 reported Lynch et al. (2) In Method 1, water is added a solution of titanium(IV) tetraisopropoxide and sodium methoxide in isopropanol. After precipitation of the MST solids is complete, the MST is isolated by filtration, washed with acetone and dried at 105°C.

Unlike the above method, the SRNL procedure first forms seed particles of MST and continues particle growth by simultaneous and controlled rate additions of a solution containing titanium(IV) tetraisopropoxide and sodium methoxide in isopropanol and a second solution comprised of water in isopropanol. After precipitation of the MST is complete, the slurry is heated to distill off the alcohol followed by the addition of water and corrosion inhibitors to provide an aqueous suspension containing approximately 15 wt% solids. Thus, the solids never contact acetone and are not dried at elevated temperatures in the SRNL synthesis method.

Preparation of Simulated High Level Nuclear Waste Solutions

We prepared all solutions using reagent grade chemicals and deionized distilled water. Table 1 provides a summary of the compositions for the simulated waste solutions used to evaluate the effects of ionic strength and temperature. After dissolving each of the salts, we added MST (Optima Chemical Company, Inc.) to the solution and mixed for a minimum of 48 hours to remove any strontium added as impurities from the reagent grade chemicals. The MST treatment was not applied to the simulated waste solution used to evaluate the influence of solution composition (see Table 4).

After removing the MST solids, we added the targeted amount of ^{85}Sr radiotracer (Perkin Elmer Life Sciences Cat. #NEZ082) and the actinides.

Table 1. Chemical composition of simulated waste solutions

	Concentration (M)		
Component	Solution #1	Solution #2	Solution #3
NaOH	1.78	1.07	1.33
$NaNO_3$	3.47	2.08	2.66
$NaNO_2$	0.178	0.107	0.134
$NaAl(OH)_4$	0.572	0.343	0.429
Na_2CO_3	0.0347	0.0208	0.0260
Na_2SO_4	0.694	0.416	0.521
Total Na	7.5	4.5	5.6
Ionic strength	8.2	4.9	6.1

Actinide sources included uranyl nitrate hexahydrate (Mallinckrodt Lot # 8640KDAL) and nitric acid solutions of plutonium(IV) (19.328 g L^{-1}) and neptunium(V) (67.1 g L^{-1}), which derive from plutonium and neptunium production operations at the Savannah River Site. After addition of the ^{85}Sr and actinides, we allowed the solutions to mix 1–3 weeks at ambient room temperature using a magnetic stirrer. After this equilibration time, we filtered the solutions through a 0.45-micron pore size nylon membrane filter to remove any residual solids.

Preparation of Pu(VI)

Plutonium oxidation state testing required the preparation of solutions containing single actinide components of Pu(IV) and Pu(VI). For tests with Pu(IV), we used the nitric acid stock solution of Pu(IV) as described above. For tests with Pu(VI) we oxidized Pu(IV) to Pu(VI) by treating 4.021 mL of a 0.965 g L^{-1} acidic solution of Pu (IV) with a stoichiometric amount (15.9 mL) of 0.001 M $KMnO_4$ (in 1 M HNO_3 acid) (10). The color of the solution provided an indicator of complete oxidation. The initial solution was colorless. Upon first addition of the purple-colored $KMnO_4$, the plutonium solution turned purple but soon thereafter turned colorless again. After addition of all required $KMnO_4$, the solution remained colored indicating complete oxidation.

Batch Ion Exchange/Adsorption Tests

Researchers added between 115 and 200 mL of the appropriate simulated waste solution into labeled polyethylene bottles and then randomly placed the bottles in a LabLine shaking waterbath (Cole-Parmer Catalog #E-01290-20) set to maintain a temperature of 25°C, 45°C, or 65°C. After incubating the solutions in the waterbath for one day, testing began with an initial sampling of each bottle followed by the addition of the appropriate quantity of MST to provide the desired MST concentration (typically 0.2 or 0.4 g L^{-1}). We operated the shaker at a speed of 175 rpm. Periodically we sampled each test bottle and analyzed the liquid phase for strontium and actinide content.

The sampling method consisted of removing the test bottle from the waterbath, briskly shaking manually for about 30 seconds to provide a homogeneous suspension, and pulling approximately 5–6 mL of the suspension into a disposable plastic syringe. We then inserted a 0.45 μm disk filter (nylon membrane) onto the syringe, collected about 5 mL of filtrate into a clean polyethylene sample bottle and pipetted 4 mL of the resulting filtrate into a glass vial containing 4 mL of 5 M nitric acid solution. Acidification of the sample reduces the potential for sorption of plutonium onto bottle walls and prepares the sample for radiochemical analyses. A white precipitate formed and gases evolved immediately upon mixing of the sample and the nitric acid. We then capped the glass sample vial, gently agitated it and then allowed it to stand at ambient laboratory temperature for a minimum of 2 hours. After several minutes the white precipitate dissolved in the nitric acid solution producing a clear colorless solution. We recapped the test bottle and returned it to the waterbath. The total time outside of the waterbath for sampling did not exceed three minutes.

The Analytical Development Section of SRNL performed all radiostrontium and actinide analyses. The ^{85}Sr activity was measured by gamma pulse height spectroscopy. We determined concentrations of ^{237}Np, ^{238}U, ^{239}Pu, and ^{240}Pu by inductively coupled plasma mass spectroscopy (ICP-MS) analysis. The $^{239/240}$Pu and ^{238}Pu activity determination relied on alpha spectroscopy after chemically separating the plutonium from neptunium and uranium.

RESULTS

Influence of Ionic Strength and Temperature

Initially we conducted tests at two different ionic strengths (Solution #1—$I = 8.2\,\mathrm{M}$, Solution #2—$I = 4.9\,\mathrm{M}$), where the ionic strength equals one half of the molar concentration multiplied by the square of the charge of the ionic species, to assess the effect of ionic strength on the performance of the MST to remove strontium, plutonium, neptunium, and uranium Eq (1).

$$I = \frac{1}{2}\sum_i c_i z_i^{\,2} \tag{1}$$

where c_i = concentration of ionic species i in units of mole/L, and z_i = charge of species i.

Figure 1 provides a plot of strontium concentration versus time upon addition of 0.2 g $\mathrm{L^{-1}}$ MST with the three different ionic strength solutions, I = 4.9 M, 6.1 M, and 9.2 M, maintained at 25°C. The strontium concentration decreased rapidly with time in all three ionic strength solutions. Similar curves are observed with the other sorbates, plutonium, neptunium, and uranium. The general shape of the curves is consistent with typical sorption reactions involving a solid sorbent and liquid sorbate. Sorption proceeds rapidly when the sorbate concentration and the fraction of available sites on the sorbents are high. Sorption decreases as the sorbate concentrations decrease and the concentration of sorbate on the sorbent increases.

Table 2 provides the batch distribution constants (K_d) for each of the four sorbates at the different ionic strengths upon contact of the simulated waste solutions with 0.2 g $\mathrm{L^{-1}}$ of MST for 168 hours at three different temperatures,

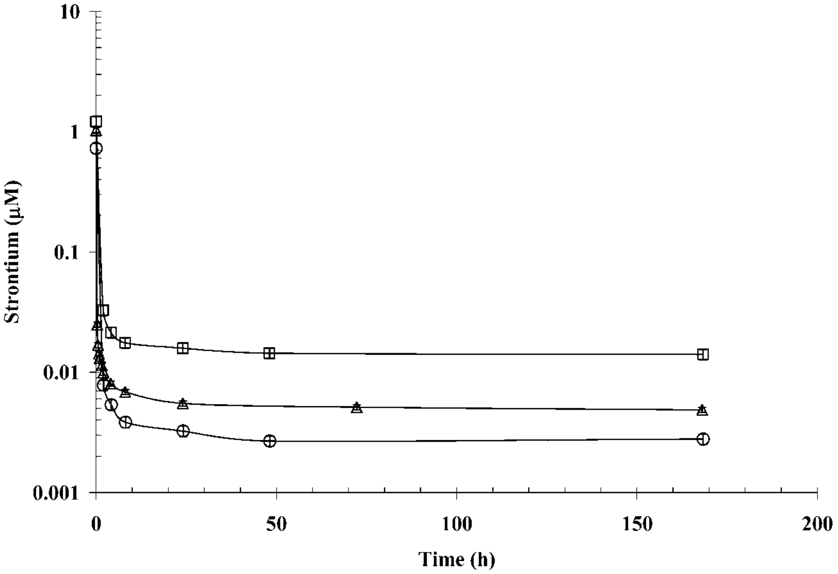

Figure 1. Strontium concentration (μM) versus time (h) at 25°C and 0.2 g L^{-1} MST (Ionic strength of solutions: ○ = 4.9 M, △ = 6.1 M, and □ = 8.2 M).

Table 2. Sorbate batch distribution constants (K_d) measured at different ionic strengths and temperatures

	Distribution constant (mL g^{-1})		
Ionic strength (M)	25°C	45°C	65°C
Strontium			
4.9	1.58E+05	1.37E+05	7.82E+04
8.2	2.54E+04	2.50E+04	2.59E+04
Plutonium			
4.9	3.64E+04	4.38E+04	1.02E+04
8.2	1.14E+03	4.05E+03	9.26E+03
Neptunium			
4.9	7.62E+04	>3.98E+05	>4.92E+05
8.2	1.20E+04	1.64E+04	1.24E+04
Uranium			
4.9	5.96E+03	7.99E+03	7.84E+03
8.2	1.97E+03	3.40E+03	3.75E+03

25°C, 45°C, and 65°C. The batch distribution constants, K_d (mL g^{-1}) were calculated from the experimental data using Eq. (2),

$$K_d\,(\text{mL g}^{-1}) = \frac{V[(S_o/S_f) - 1]}{m^*} \tag{2}$$

where, V is the volume of treated salt solution (mL), m is the mass of MST (g), S_o is the initial sorbate concentration and S_f is the final sorbate concentration. For all four sorbates we observed that the K_d values decreased with increasing ionic strength. For strontium, K_d values decreased with increasing temperature at the lower ionic strength (4.9 M) and remained unchanged across the range of temperatures at the higher ionic strength (8.2 M).

For the actinides, the general trend is a small increase in the K_d with temperature. We observed a sharp decline in the plutonium K_d at 65°C in the low ionic strength solution. This trend appears inconsistent with that of plutonium at the higher ionic strength and the other actinides at either ionic strength. For neptunium and uranium, we observed either no change (within experimental error) or increases in the K_d value with increasing temperature. Thus, the low K_d value for plutonium at 65°C appears to be the result of experimental error.

Figure 2 provides plots of sorbate concentration versus time for a single solution (I = 6.1 M) contacted at 25°C with either 0.2 or 0.4 g L^{-1} MST.

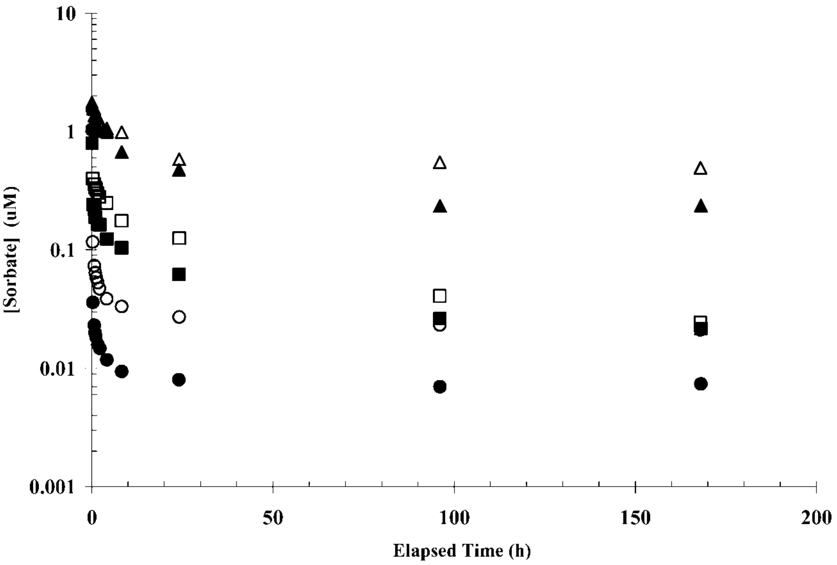

Figure 2. Sorbate concentration (μM) versus time (h) at 25°C and 0.2 g L^{-1} and 0.4 g L^{-1}. MST (I = 6.1 M): O = Sr–0.2 g L^{-1} MST, ● = Sr–0.4 g L^{-1} MST □ = Pu–0.2 g L^{-1} MST, ■ = Pu–0.4 g L^{-1} MST, △ = Np–0.2 g L^{-1} MST and ▲ = Np–0.4 g L^{-1} MST.

Table 3. Typical strontium and actinide removal results upon contact of simulated waste solutions with 0.4 g L^{-1} MST

Sorbate	Initial conc. (μM)	DF	% Removed	Loading on MST (μmole g^{-1})
Sr	10	100	99	25
Pu	1	15	93	2.3
Np	2	5	80	4.0
U	40	2.5	60	60

The initial concentrations of strontium, plutonium, neptunium and uranium in this solution measured 1.0, 0.80, 1.7, and 39 μM, respectively. For each sorbate, the solution concentration decreased rapidly. Removal of strontium and neptunium proved higher with increased MST concentration. The quantity of plutonium removed was the same at either MST concentration.

Table 3 provides a summary of typical strontium and actinide removal results upon contact of a simulated waste solution having the chemical composition as reported for Solution #3 in Table 1 ($I = 6.1$ M) with 0.4 g L^{-1} MST. For this solution composition, the extent of removal followed the order Sr > Pu > Np > U. On a mass loading basis, the loading onto MST followed the order U > Sr > Np > Pu. The much higher loading for uranium results from the much higher mass concentration of uranium (4–40 times higher) compared to the other sorbates.

Influence of Solution Composition

Solution composition testing featured a statistically designed test matrix based on mixture experimental design problems (11) and consisted of 11 experimental trials, as listed in Table 4. The first six trials examined whether a linear relationship exists between MST adsorption ability and the concentrations of $NaNO_3$, NaOH, $NaNO_2$, $NaAl(OH)_4$, Na_2CO_3, and Na_2SO_4. Trials #7 and #8 of the experimental series served as replicates of the centroid composition. Initial sorbate concentrations in each were in close agreement (See Table 2). Trial #9 is the center point composition with added trace salts. Trace salts included sodium oxalate (0.008 M), sodium phosphate (0.010 M), sodium fluoride (0.032 M), sodium chloride (0.025 M), sodium silicate (0.0040 M), sodium molybdate (0.0020 M), potassium nitrate (0.015 M), and cesium nitrate (0.00014 M). Trial #10 features the same centroid composition as Trials #7 and #8, but without the addition of MST. Trial #11 serves as a comparison to previous testing (see reference 12) and provides the same composition as that provided in Table 1 for Solution #3.

Trial #10 served as a control with no added MST. This trial served as a means to correct for removal of sorbates by sorption onto the bottle walls or

Table 4. Chemical and sorbate concentrations in simulants used to evaluate influence of solution composition

	Component concentration									
Trial	$NaNO_3$ (M)	NaOH (M)	$NaNO_2$ (M)	$NaAl(OH)_4$ (M)	Na_2CO_3 (M)	Na_2SO_4 (M)	Sr ($\mu g\,L^{-1}$)	Pu ($\mu g\,L^{-1}$)	Np ($\mu g\,L^{-1}$)	U ($\mu g\,L^{-1}$)
1	1.000	3.000	0.500	0.100	0.020	0.490	621	231	241	7,050
2	1.000	3.000	0.100	0.100	0.200	0.443	656	102	244	8,080
3	3.000	1.070	0.100	0.100	0.020	0.600	302	42.8	242	5,960
4	3.000	1.630	0.500	0.100	0.200	0.100	541	140	249	7,120
5	1.730	1.000	0.500	0.500	0.200	0.600	537	121	249	4,490
6	2.170	3.000	0.100	0.500	0.020	0.100	828	119	190	5,490
7	1.959	2.122	0.292	0.299	0.106	0.379	617	208	218	6,620
8	1.959	2.122	0.292	0.299	0.106	0.379	649	203	220	6,980
9	1.907	2.066	0.284	0.291	0.104	0.369	742	242	307	10,400
10	1.959	2.122	0.292	0.299	0.106	0.379	628	203	225	6,950
11	2.600	1.330	0.134	0.429	0.026	0.521	568	65.7	215	4,320

Analytical statistics for Trials 7, 8 and 10: (a) average—631, 205, 221, and 6,850 $\mu g\,L^{-1}$; (b) standard deviation—16.3, 2.89, 3.61, and 200 $\mu g\,L^{-1}$; and (c) RSD—2.58%, 1.41%, 1.63%, and 2.92% Sr, Pu, Np and U, respectively.

filter membranes and precipitation. The results indicated no significant removal of sorbates in the control sample throughout the duration of the experiments. For this reason, the testing results did not require correction for sorption by mechanisms other than that with MST.

Additional input to the development of these trials included two constraints. First, we required that the ionic strength would remain constant for each trial solution at 6.13 M (i.e., ionic strength for 5.6 M Na^+ simulated waste solution of composition provided in Table 1—Solution #3). The second constraint required that the concentration of $NaNO_3$ in the salt solutions equaled at least three times that of the $NaAl(OH)_4$ concentration. This requirement originates from the simulant preparation method. The solution preparation generates $NaAl(OH)_4$ from the reaction of $Al(NO_3)_3$ and four equivalents of NaOH releasing three equivalents of nitrate per equivalent of aluminum.

Researchers targeted strontium, plutonium, neptunium and uranium concentrations in the simulated waste solutions at 100, 200, 400, and 10,000 $\mu g\,L^{-1}$, respectively. The actual concentrations differed from the targets and across the different solution compositions (see Table 4). The strontium concentrations exceeded the targeted values because we did not remove tramp strontium from the reagent chemicals prior to solution preparation. Neptunium concentrations measured lower than the targeted value due to the addition of a smaller aliquot of the stock neptunium solution. Plutonium and uranium concentrations varied considerably among the different solution compositions. We concluded that analytical errors were not responsible for the variance since the relative standard deviation of triplicate samples measured with the solution used in Trials #7, #8 and #10 (see Table 4) all measured below 3%. We attributed the wider range of plutonium and uranium values to the variance in solubility as a function of the solution composition.

Table 5 presents the DFs calculated from samples collected after 24-h and 168-h of contact with the MST. The DF values for the replicate trials (#7 and #8) showed good agreement except for the 24-h strontium result. The difference in the strontium sample analyses results at 24 h may reflect error associated with the handling of the sample prior to or during analysis. Reanalysis of the 24-h samples using the residues from the gamma and alpha counting aliquots confirmed the relatively high strontium concentration in Trial #8, which results in a low strontium DF value. Since good agreement resulted for the 7-day strontium values and all of the actinide values in both trials, we conclude that the 24-h result for Trial #8 cannot be discarded. Consequently, the statistical analysis includes the 24-h result for Trial #8.

Influence of Plutonium Oxidation State

These tests examined whether the oxidation state of plutonium significantly affected the extent and rate of removal using MST as the removal agent.

Table 5. Decontamination factors for strontium, plutonium, uranium, and neptunium measured upon contact of 0.4 g L^{-1} MST with solutions having varying salt compositions

	Decontamination factor (DF)							
Trial #	Sr 24-h	Sr 168-h	Pu 24-h	Pu 168-h	U 24-h	U 168-h	Np 24-h	Np 168-h
1	123	155	4.13	9.10	1.36	1.62	1.53	2.02
2	10.8	112	3.40	8.42	1.27	1.58	1.59	2.72
3	78.5	246	16.5	43.3	1.56	2.30	2.50	9.82
4	174	190	7.91	20.9	1.43	2.08	1.90	3.55
5	102	140	10.6	24.2	1.48	2.35	2.21	4.28
6	50.5	137	4.14	8.06	1.26	1.74	1.94	3.56
7	100	126	5.70	13.8	1.15	1.66	1.24	2.17
8	18.8	141	4.64	13.9	1.15	1.74	1.41	2.64
9	90.7	127	3.85	9.31	1.16	1.56	1.00	1.43
10	1.09	1.16	1.01	0.99	0.85	1.01	0.79	0.94
11	137	181	12.4	37.6	1.42	2.27	2.25	8.27

Note: Trial #10 represents a control test with no added MST.

The tests targeted Pu(IV) and Pu(VI) for comparison. We prepared individual salt solutions having the chemical composition of Solution #3 in Table 1 with each component and measured removal upon contact with 0.4 g L^{-1} of MST in triplicate. Results reported in Table 6 represent the average of the three tests.

Figure 3 compares the average plutonium concentration as a function of time for the salt solutions that contain only Pu(IV) or Pu(VI) as well as that previously reported with a salt solution containing four sorbates, Pu(IV), Np(V), U(VI) as uranyl and strontium (12). The initial plutonium

Table 6. Decontamination factors, batch distribution constants, and sorption/ion exchange rates for plutonium containing solutions

	Decontamination factor (DF)		Batch distribution constant $K_d \times 10^{-4}$ (mL g^{-1})		
Species	1 day	7 days	1 day	7 days	Rate constant (h^{-1})
Pu(IV)	14.8 (11.5)	18.5 (9.5)	3.46 (2.89)	4.36 (2.36)	0.0227
Pu(VI)	9.2 (0.53)	28.2 (1.2)	2.05 (0.12)	6.78 (0.23)	0.0176
Pu(IV)[a]	12.9 (0.99)	36.6 (0.16)	2.98 (0.23)	8.90 (0.039)	0.0250

Numbers in parenthesis are single standard deviation.

[a] From reference 12.

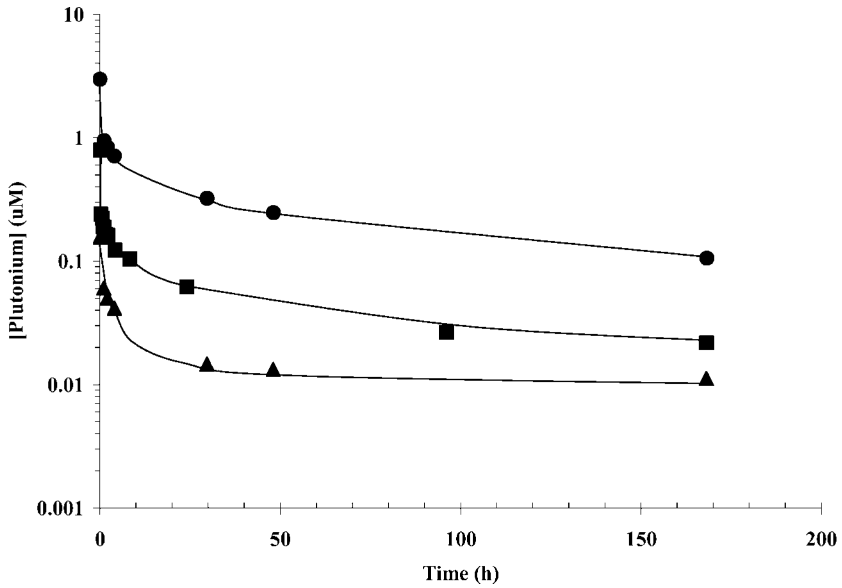

Figure 3. Plot of plutonium concentrations versus time upon contact of 0.4 g L^{-1} MST: ▲ Pu(IV) ; ● Pu(VI) ; ■ Pu(IV) reference 12.

concentration in the Pu(VI) tests measured 2.98 μM. Correspondingly, the starting plutonium concentration in the Pu(IV) tests measured 0.155 μM, nearly twenty times less than that of Pu(VI). In tests with multiple sorbates the initial soluble Pu concentration measured 0.795 μM.

Soluble plutonium concentrations for the tests with Pu(IV), Pu(VI) and Pu(IV) with multiple sorbates measured 0.0112, 0.106, and 0.0217 μM, respectively, after 168-h of contact with the MST. Inspection of Figure 3 indicates that only the test which initiated with Pu(IV) at 0.155 μM appeared to reach equilibrium. We base this finding on the very similar concentrations for the last three sampling times of 24-, 48- and 168-h. The other tests may be at equilibrium after 168-h, but the limited data between 96-h and 168-h does not allow confirmation that equilibrium had occurred within 168-h.

DISCUSSION

Savannah River Site high level waste supernatant liquids and dissolved saltcake are strongly alkaline concentrated salt solutions. Sodium serves as the major cation. The predominant anionic components include hydroxide, nitrate, nitrite, aluminate, carbonate and sulfate. Strontium and actinide concentrations in SRS high level waste supernates range from about 1 μg L^{-1}

to 25 mg L^{-1}. Typically, strontium and uranium concentrations range from 0.5–10 mg L^{-1} and are 1–2 orders of magnitude higher than plutonium and neptunium in SRS high level waste supernates. Neptunium concentrations are much lower than the reported solubility for Np(V) as discards of neptunium have generally been low compared to plutonium and uranium. The initial concentrations of strontium and actinides provided in Table 3 for use in the simulant studies reflect the typical concentrations that have been measured for strontium, plutonium and uranium, and the estimated maximum concentration for neptunium in SRS high level waste solutions.

As with previously reported findings (1–6), we observed that MST is a very effective sorbent/ion exchange material for the removal of strontium, plutonium, neptunium and uranium from strongly alkaline salt solutions (see Table 3). The removal of strontium and actinides ranges from about 60% to more than 99% for strontium and actinides even in presence of sodium concentrations that are 5 to 7 orders of magnitude higher than that of the strontium and actinides. This exceptional specificity makes MST an excellent material for the decontamination of radiostrontium and alpha-emitting actinides from the highly alkaline wastes presently stored at the SRS.

The theoretical ion exchange capacity of MST is 5000 micro-equivalents of Na exchange sites per gram (μeq g^{-1}) assuming an empirical formula of $NaTi_2O_5H$ (1). Given the loading values in Table 3 and assuming strontium loads as Sr^{2+}, plutonium as Pu^{4+}, neptunium as NpO_2^+ and U as UO_2^{2+}, the total loading of the four sorbates represents less than 3.7% of the theoretical capacity of the MST. Thus, at these conditions, the quantity of strontium and actinides exchanged with the MST appears well below the theoretical capacity of the material.

From Figure 2, decreasing the amount of MST added to the salt solution from 0.4 to 0.2 g L^{-1} decreased the extent and rate of strontium and neptunium removal. The extent of plutonium removal was unaffected by the quantity of MST added. However, the rate of plutonium removal was reduced at the lower MST concentration. These results suggest the effective capacity of the MST is well below the theoretical capacity in the highly alkaline salt solutions. The lower effective capacity is consistent with recently published results on the morphology and location of sorbed strontium on MST (13). High resolution transmission electron microscopy revealed the MST particles to contain a fibrous outer region and an amorphous glasslike inner core. Analysis of the strontium-sorbed MST located the strontium only in the outer fibrous region of the particle suggesting that the inner glasslike region is not readily accessible for sorption/ion exchange.

The finding of similar equilibrium concentrations for plutonium, but not for strontium and neptunium at the two different MST concentrations is consistent with other experimental results and modeling of sorption of strontium and actinides on MST (14). Adsorption isotherms for strontium, plutonium and neptunium indicate linear relationship between sorbate loading onto MST and equilibrium sorbate concentration. However, the adsorption isotherm for plutonium exhibits a much steeper slope compared to those for strontium and neptunium. Thus, for a change in the MST concentration of between 0.2 to 0.4 g L^{-1}, there is a sufficient change in the quantity of MST to produce a measurable change in the equilibrium concentrations of strontium and neptunium, but not for plutonium.

Influence of Ionic Strength and Temperature

Radiochemical separations from high level waste solutions must be capable of operating at high ionic strengths to minimize the amount of dilution water added to the waste. Current plans are to treat waste diluted to a sodium concentration of 5.6 M. To evaluate the influence of ionic strength on MST performance, we tested at sodium concentrations of 4.5 M and 7.5 M, which correspond to ionic strengths of 4.9 M and 8.2 M, respectively (see Table 1).

From Table 2, the K_d for each sorbate decreases upon an increase in ionic strength. This is the expected trend. At the higher ionic strength, the concentration of sodium ion is much higher making exchange of the sodium for strontium and actinides more difficult. This results in the lower value for the batch distribution constant. Plans are to operate waste pretreatment processes at or near 25°C. At this temperature the K_d values decrease for strontium, plutonium, neptunium and uranium by factors of 6.2, 32, 3.0, and 6.4, respectively upon an increase in the ionic strength from 4.9 M to 8.2 M.

At the lower ionic strength (4.9 M), we observed a decrease in the K_d for strontium upon an increase in the temperature. This result is consistent with the ion exchange/adsorption of strontium onto the MST being an exothermic reaction. For the actinides, we generally observed an increase in the K_d with temperature, which suggests that the exchange or sorption of the actinides onto the MST is an endothermic reaction.

Influence of Solution Composition

Previous studies have shown that the solubility of strontium and actinide elements in strongly alkaline salt solutions can vary over a wide range (15–17). In general, the solubility of the strontium and actinide elements in strongly alkaline salt solutions follows the order, Pu < Sr < U < Np. Independently, Delegard (16) and Hobbs (18) developed empirical prediction models for plutonium and uranium in alkaline salt solutions as a function of the anionic component concentrations. In general, the chemical potential for sorption of a species is proportional to the solution concentration. Thus, increased sorption would occur with increased sorbate concentration.

The composition of the waste solution may also influence the strontium and actinide species in solution, which could result in either increased or decreased sorption. Furthermore, the solution composition may also influence the surface site characteristics of the MST, which could result in decreased or increased sorption. Given these possible effects, we conducted tests to determine if the solution composition influenced sorbate removal characteristics of the MST.

Analysis of the data provided models for the decontamination factor of each sorbate at 24- and 168-h as a linear function of the six major anion concentrations. The predicted DF increased with increased nitrate concentrations for each sorbate. In general, the concentrations of the other anions exhibited a smaller affect or a decrease in the DF compared to the nitrate concentration. The influence of the minor salt components (e.g., oxalate, phosphate, fluoride, chloride, silicate, molybdate, potassium, and cesium) proved statistically insignificant.

We attribute the increased DF with increased nitrate concentration to the nature of the sorbate species. In general, nitrate forms much weaker complexes with metal ions than other components such as hydroxide and carbonate (19). For example, strontium and actinides are known to form hydroxide complexes that result in increased solubility with increased free hydroxide concentrations. Thus, as the salt solution composition changes from that which is low in nitrate and high in hydroxide to one that is high in nitrate and low in hydroxide, the degree of hydroxide complexation may be reduced. The reduced hydroxide-complexed strontium and actinides would favor ion exchange/sorption with the MST resulting in greater removal and a higher DF.

Note that even though the solution composition can have a measurable influence on the measured DF for a sorbate, the influence is relatively small in consideration of removal efficiencies required for the pretreatment of high level waste solutions at SRS. Based on the measured DFs for strontium and the actinides in this study (see Table 5), the treated waste solution would meet the current waste acceptance limits for waste disposal except for wastes containing bounding concentrations of plutonium and neptunium upon contact of the waste with $0.4\,g\,L^{-1}$ MST (20). For wastes with these high plutonium and neptunium concentrations, the waste would require treatment with increased quantities of MST to affect the necessary removal for the decontaminated waste to meet the waste disposal criteria for total alpha and ^{237}Np activities.

Influence of Plutonium Oxidation State

Plutonium exhibits multiple stable oxidation states in aqueous solutions. For example, alkaline solutions containing Pu(IV), Pu(V) and Pu(VI) can be prepared and are stable for long periods of time (21). In general the solubility of plutonium and neptunium increase as the oxidation state increases. The predominant oxidation state for plutonium in fresh HLW solutions is Pu(IV). However, conditions that occur during the evaporation, storage and retrieval of HLW solutions may result in the oxidation or reduction of the plutonium. For example, Delegard (16) and Karraker (22) reported evidence of Pu(V) and Pu(VI) oxidation states forming from Pu(IV) in simulated high level waste solutions at very high hydroxide concentrations. Thus, the oxidation state of the dissolved plutonium may not be limited to a single oxidation state such as Pu(IV).

The low concentrations of plutonium in alkaline salt solutions typical of high level nuclear wastes prevent the direct determination of plutonium species in solution by spectroscopic techniques at this time. Solubility data suggests that at the high hydroxide concentrations, typically greater than one molar in tank wastes, soluble plutonium is probably present as anionic hydroxide complexes. For example, Pu(IV) may be present as the dianionic complex, $Pu(OH)_6^{2-}$, Pu(V) as the trianionic, $[PuO_2(OH)_4]^{3-}$, and Pu(VI) as the dianionic complex, $PuO_2(OH)_4]^{2-}$ (23, 24). Given the possibility of plutonium in multiple oxidation states and differences in the reactivity of the different plutonium species, the oxidation state of the plutonium may have a pronounced influence on the sorption or ion exchange performance exhibited by the MST. Given these factors we carried out a series of tests to determine if two different oxidation states of plutonium, Pu(IV) and Pu(VI), exhibited a significant influence on removal by the MST.

Inspection of Fig. 3 indicates similar relative changes in the plutonium concentration with time for each test suggesting similar removal kinetics for both Pu(IV) and Pu(VI). Table 6 contains decontamination factors (DF) and distribution constants (K_d) from the average plutonium concentration data. The DF and K_d values derive from samples collected after 1 and 7 days of contact. DF and K_d data for the three data sets [Pu(IV), Pu(VI) and previous Pu(IV)] are within a factor of approximately two of each other. Given the similar results for the Pu(IV) and Pu(VI)-spiked solutions, we conclude that MST exhibits similar affinity for both plutonium oxidation states.

Removal rates for sorption or ion-exchange of sorbates and porous sorbents depend on three consecutive mass transport steps:

1. Bulk transport of the sorbate in the solution phase,
2. Transport of the sorbate through a hydrodynamic boundary layer or film, and
3. Transport of the sorbate within the pore volume of the sorbent to the active sorption or ion exchange site (25).

The latter step also includes the steps involved in sorption or exchange at the sorbent site (e.g., dehydration, exchange, etc.). Generally, the latter two steps are the major factors controlling rates of removal. Since these steps act in series, the slower of the two steps will be rate limiting. In the solutions with multiple sorbates, the removal kinetics may be further complicated by competition for sites among the sorbates (strontium, plutonium, neptunium, and uranium). Each sorbate could have a different rate limiting step or influence the transport of other sorbates during any of the above steps.

During the early stages of contact between the MST and alkaline solutions containing the sorbates removal kinetics may exhibit a first or second order dependence on the sorbate concentration. Over the total length of the experiment (168-h), the removal kinetics do not fit first or second order expressions in plutonium concentration. However, between 1 and 4-h, plutonium removal fits first order kinetics with respect to the concentration of plutonium.

We calculated removal rate constants from the linear fit of the average concentrations for the time interval of 1 to 4 h (see Table 6). Reaction rate constants are known to vary with oxidation state (26) and, thus, determination of the rate constants for the Pu(IV) and Pu(VI) spiked solutions may provide additional information concerning the stability and reactivity of Pu(IV) and Pu(VI) in alkaline solutions. The rate constants for the tests using the Pu(IV) spiked solutions ranged from 1.29 to 1.42 times greater than that for the solution spiked with Pu(VI). This suggests a slight increase in the removal rate for Pu(IV) compared to Pu(VI). However, given the experimental variance in rate constants calculated for each individual test, the ranges in rate constants, as defined by the measured value plus or minus two times the standard deviation (value $\pm 2\sigma$), overlap for all three test cases. Thus, with this limited data set, we cannot conclusively establish that Pu(IV) removal is faster than Pu(VI) between 1 and 4 h of contact with MST.

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