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PLUTONIUM AND URANIUM ADSORPTION ON MONOSODIUM TITANATE (U)

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SUMMARY AND RECOMMENDATIONS

The adsorption of plutonium and uranium onto monosodium titanate (MST) in alkaline salt solution has been measured experimentally. Changes in the particle size distribution of the MST do not significantly affect the loadings of actinides. The maximum loading of plutonium-239 is determined to be 0.68 wt% at a concentration of 0.79 mg/L of plutonium. This loading is below the infinitely safe value of 0.80 wt%. The maximum loading of uranium-235 onto MST is determined to be 1.4 wt% at a concentration of 20.3 ± 2.0 mg/L of uranium. This is slightly higher than the infinitely safe limit of 1.2 wt% calculated using the rule of fractions and the plutonium-239 infinitely-safe limit.

Experimental data indicated there is competition between plutonium and uranium for sites on the MST, and that the loading will favor the higher concentration species. Since the solubility of uranium is 10-100 times higher than of plutonium, uranium will be loaded to its maximum limit, but plutonium will be below its maximum limit. To ensure that the concentration of fissile materials cannot exceed nuclear safety limits, it is recommended that plutonium and uranium solubility tests be conducted with solutions which bound the compositions of waste which will be treated in ITP process.

INTRODUCTION

Monosodium titanate strongly adsorbs divalent ions such as strontium in alkaline salt solutions and will be used in the In-Tank Precipitation (ITP) process to remove radio-strontium species from salt solution. Certain actinides have also been reported to be adsorbed by MST.¹ The capacity of MST for plutonium and uranium has not been determined under conditions which will occur during ITP. Low concentrations of fissile materials, such as plutonium-239 and uranium-235, are present in the alkaline salt solution which will be treated in the ITP process. The capacity of the MST to adsorb plutonium and uranium was measured in order to determine if the accumulation of a critical mass of fissile material is possible during the ITP process.

During the ITP process, breaking of the MST particles may occur as a result of high shear forces encountered in the slurry pumps and in the sintered metal filters. A decrease in the particle size may increase the adsorption capacity of the MST by increasing the number of sites available for adsorption. Therefore, experiments were also conducted to determine if changes in the particle size affect the adsorption properties of the MST.

EXPERIMENTAL

Adsorption Tests

All adsorption experiments were conducted using synthetic salt solutions having the composition given in Table I. The salt solutions were prepared using deionized, distilled water and reagent grade chemicals. All but one of the experiments were conducted with a single MST slurry prepared by AFF, Inc, which has a strontium DF value of 65 at a MST concentration of 0.5 g/L. The concentration of MST in this slurry was determined gravimetrically to be 4.6 wt%. A single loading test experiment was conducted to isolate and analyze the MST solids for fissile content. The MST slurry used in this experiment was prepared by Boulder Scientific (Lot # BSC-265-0005), and has a strontium DF of 240 at a MST concentration of 0.5 g/L.

Strontium-85 in the chemical form of strontium chloride supplied by New England Nuclear (NEZ-082, Lot #90M20K7) was used as the radiotracer for determining the adsorption properties of the MST for strontium. Sufficient strontium-85 was added to the salt solution to provide an initial strontium concentration of between 1.4×10^{-7} and 2.0×10^{-7} mole/L.

Table I. Composition of Synthetic Salt Solution

<u>Species</u>	<u>Concentration (mole/L)</u>
NaOH	2.0
NaNO ₃	1.5
NaNO ₂	0.60
NaAl(OH) ₄	0.30
Na ₂ SO ₄	0.14
Na ₂ CO ₃	0.16
Total Na	5.0

Plutonium-doped salt solutions were prepared by adding a solution of weapons-grade plutonium (approximately 93% Pu-239) in nitric acid to the synthetic salt solution and stirring for a minimum of three days. The solution was then filtered through a 0.20 μm nitrocellulose filter and stored in a clean polyethylene bottle. The target concentration of plutonium in the salt solution was 4.0×10^{-6} mole/L.

Uranium-doped salt solutions were prepared from uranium oxide (U₃O₈) which was dissolved in 8 M nitric acid and then added to the salt solution. Two sources of uranium were used; enriched uranium-235 (90.2 atom %, NBS Standard Reference Material U-900) and depleted uranium-238. After addition of the uranium solution, the uranium-doped salt solutions were stirred for 3-5 days, and then filtered through a 0.20 μm nitrocellulose filter. The uranium concentration in the solutions was approximately 6-7 mg/L.

Adsorption experiments were conducted by placing a weighed amount of the MST slurry in a clean polyethylene bottle or an Erlenmeyer flask equipped with a magnetic stirring bar. The synthetic salt solution containing the desired radiotracer(s) was added by pipet to provide the desired MST concentration (0.05-0.90 g MST/L solution). The polyethylene bottle was tightly stoppered and shaken on an orbital shaker for 48 hours. Experiments conducted in Erlenmeyer flasks were stoppered and mixed for 48 hours with a magnetic stirrer. Bottles and flasks with no MST added were also prepared in order to correct for the adsorption of plutonium and uranium on bottle, flask, and filter surfaces. After shaking or stirring, the mixture was filtered through a 0.20 μm nitrocellulose filter, and the filtrate placed in a clean polyethylene bottle.

In an alternative experiment, approximately one liter of a salt solution containing 20.3 ± 2.0 mg/L of uranium was placed into each of two 1-liter polyethylene bottles equipped with magnetic stirring bars. Both solutions were mixed for several days and then sampled to determine the amount of uranium, if any, which had deposited on the interior bottle surfaces. Weighed amounts of the MST slurry (BSC-265-0005) were added and the bottle contents stirred for a minimum of three days. The bottles were then resampled to determine the uranium concentration in solution. MST additions were continued until concentrations of 0.137 g/L and 0.492 g/L of MST were reached. The mixtures were filtered through 0.45 μ m nitrocellulose filters. The MST solids were washed with small portions of deionized, distilled water, dried to constant weight, dissolved in a mixture of sulfuric, hydrochloric and hydrofluoric acids, and analyzed for uranium and titanium content. The wash waters were collected, weighed, and analyzed for uranium content. The total amount of uranium in the wash waters was less than 3% of that found on the MST solids.

Radiotracer activities were determined by counting techniques developed by ADS. Strontium-85 activity was determined by gamma counting of the filtrate. Plutonium activity was determined by liquid scintillation counting after separating the plutonium by an ion-exchange purification procedure. Enriched uranium activity was determined by gamma counting. Depleted uranium concentrations were determined by ICP-MS.

Particle Size Tests

The particle size distribution of the MST was altered by two different techniques; (1) physical separation by a combination of flotation and settling, and (2) treatment in a high shear blender. The particle size distribution of the samples was measured using a Microtrac instrument. Sample preparation consisted of placing 1-2 drops of each sample into the sample recirculator of the analyzer.

In the physical separation experiment, the slurry was placed in a vertical glass tube in which water was rising at a slow rate. The rate was adjusted such that the majority of the particles tended to sink. The cloudy effluent stream was collected in an Erlenmeyer flask. After settling overnight, the particles which were still suspended in the flask were filtered using a 0.2 micron cellulose nitrate disposable filter. All of the settled solids were recombined to form the "large particle" fraction. The solids in the filter were designated the "small particle" fraction.

In the blender experiment, the "as-received" MST slurry was diluted with an equal volume of water and treated at the highest speed for up to 120 minutes. Samples of the slurry were taken after 15, 30, 60 and 120 minutes of treatment. Immediately after stopping the blender a thermistor probe was inserted into the slurry and the temperature measured.

RESULTS

Competition Experiments

Decontamination factors for strontium, plutonium and uranium from each of the synthetic salt solutions tested are given in Table II. Each experiment was conducted in duplicate or triplicate. The standard deviations of each set of experiments are also reported in Table II.

The decontamination factor is defined as the ratio of the initial activity of the solution to that at equilibrium upon addition of MST. (see equation 1). An estimate of the error for the DF

$$DF = [M]_0 / [M] \quad (1)$$

where, $[M]_0$ is the initial solution concentration of adsorbing species, M , and $[M]$ is the concentration of adsorbing species, M , at equilibrium.

Graphs of the decontamination factor as a function of the MST concentration are presented in Figure 1 for the plutonium experiments and in Figure 2 for the uranium experiments. The error bars in the graphs are the standard deviations reported in Table II.

The DF increases with an increase in the MST concentration. The strontium DF's are not significantly changed in the presence of plutonium. MST removes 90-98% of the plutonium when added to a salt solution at initial levels close to the solubility limit for plutonium. In contrast to plutonium, the MST removes only 9-33% of the uranium. The presence of uranium appears to decrease the adsorption of plutonium as evidenced by the higher DF's observed in the experiments with only plutonium present and/or plutonium and strontium present as compared to that with uranium, plutonium and strontium present.

Table II. Strontium and Plutonium Decontamination Factors

<u>Solution Type</u>	<u>MST g/L</u>	<u>Sr</u>	<u>Average DF</u> <u>Pu</u>	<u>U</u>
Sr-doped	0.430	50.8 $\pm$ 0.55	-	-
	0.276	27.0 $\pm$ 0.26	-	-
	0.138	9.00 $\pm$ 0.36	-	-
Pu-doped	0.429	-	38.0 $\pm$ 0.07	-
	0.277	-	20.2 $\pm$ 1.6	-
	0.138	-	12.1 $\pm$ 1.7	-
U-doped	0.50	-	-	1.28 $\pm$ 0.15
	0.15	-	-	1.18 $\pm$ 0.03
	0.05	-	-	1.10 $\pm$ 0.14
Sr & Pu-doped	0.430	45.7 $\pm$ 2.5	47.2 $\pm$ 1.4	-
	0.276	24.4 $\pm$ 0.90	34.7 $\pm$ 1.2	-
	0.138	8.53 $\pm$ 0.23	19.8 $\pm$ 1.6	-
Sr, Pu & U-doped	0.900	-	-	1.23 $\pm$ 0.12
	0.721	-	-	1.34 $\pm$ 0.10
	0.450	-	-	1.18 $\pm$ 0.14
	0.430	57.1 $\pm$ 2.8	20.8 $\pm$ 0.36	-
	0.360	-	-	1.27 $\pm$ 0.05
	0.276	30.8 $\pm$ 0.57	15.0 $\pm$ 1.1	-
	0.138	10.7 $\pm$ 0.68	7.90 $\pm$ 0.10	-
	0.110	-	-	1.00 $\pm$ 0.10
	0.100	-	-	1.15

Figure 1. Plot of Plutonium Decontamination Factor Versus MST Concentration

Figure 2. Plot of Uranium Decontamination Factor Versus MST Concentration

Particle Size Experiments

The particle size of the MST slurry could be altered by physical separation or by mixing in a high speed blender. Particle size distribution data for the "as-received" material, the two fractions obtained by the physical separation technique and the slurry after various lengths of time at high speed in the blender are given in Table III. The physical separation experiment successfully removed the larger particles from the slurry producing a material which was composed of a much higher fraction of smaller particles.

Figure 3 shows the median value from the particle size distribution data plotted versus the blending time. After 120 minutes of treatment, the shearing of the MST particles appears to have nearly stopped as evidenced by the flattening of the curve. During the blender treatment, the temperature of the slurry increased. At the end of the second hour of treatment, the temperature of the slurry reached 57°C.

TABLE III. Particle Size Distribution Data for MST

MST Sample	Particle Size (μm)			Mean
	1%<	50%<	99%<	
"As-Received"	0.70	5.24	37.8	8.24
"large" particles	0.81	5.70	30.2	8.24
"small" particles	0.29	2.03	6.92	2.30
Blender 15 minutes	0.49	4.35	37.6	7.03
Blender 30 minutes	0.44	3.86	30.1	6.01
Blender 60 minutes	0.38	3.49	25.6	5.79
Blender 120 minutes	0.33	3.09	24.0	4.58

Figure 3. Effect of Blending Time on MST Particle Size Distribution

Uranium and strontium DF's were determined for the MST materials which were physically separated into a "large" particle fraction and a "small" particle fraction (see Table IV). Under similar solution conditions, the "large" and "small" particle fractions of the MST do not show significantly different DF's from the "as-received" material. Sr DF's were also determined for the MST slurry which was treated for 60 and 120 minutes in the blender. These results are also given in Table IV.

The strontium loading on the MST does not increase as a result of treatment in a high speed blender. Strontium loadings were actually decreased by the blender treatment. Although the particle size distribution of the MST indicates that the blender treatment broke the larger particles into smaller particles, the decrease in particle size does not increase the number of available adsorption sites since the loading does not increase (see Table V).

Table IV. Effect of Particle Size on Strontium and Uranium DF's

<u>MST Sample</u>	<u>g MST/L</u>	<u>Sr DF</u>	<u>U DF</u>
"Large" Particles	0.80	145.0 $\pm$ 6	
	0.50	77.0 $\pm$ 6	
	0.15		1.36 $\pm$ 0.06
	0.05	2.8 $\pm$ 0.1	
	0.80	133.0 $\pm$ 8	
"Small" Particles	0.50	64.0 $\pm$ 2	
	0.46		1.50 $\pm$ 0.10
	0.05	2.8 $\pm$ 0.1	
	0.430	50.8 $\pm$ 0.55	
	0.276	27.0 $\pm$ 0.26	
Untreated	0.138	9.00 $\pm$ 0.36	
	0.551	65.8 $\pm$ 2.2	
	0.354	39.4 $\pm$ 0.92	
Blender 60 Minutes	0.179	12.7 $\pm$ 2.1	
	0.426	43.2 $\pm$ 2.1	
	0.284	25.2 $\pm$ 1.4	
Blender 120 Minutes	0.140	7.60 $\pm$ 0.17	

Table V. Strontium Loadings on MST Before and After Treatment in High-Speed Blender

<u>Treatment Time</u> (min.)	<u>Sr Loading</u> ($\mu\text{mol/g}$)	<u>Loading Normalized</u> <u>to Untreated Sample</u>
Untreated	5.8	1.00
60 min.	5.0	0.86
120 min.	4.6	0.78

DISCUSSION

Competition Experiments

From the high decontamination factors, it is apparent that monosodium titanate effectively removes both strontium and plutonium from alkaline salt solution. Uranium, however, is not strongly adsorbed by the MST as evidenced by the low decontamination factors.

In order to assess if there exists a competition between strontium and plutonium for adsorption sites on the MST, the equilibrium distribution constants, K_d , were calculated for strontium and plutonium from the experimental data (see Table VI). K_d is defined as the ratio of the concentration of the adsorbing species on the MST to the concentration in solution at equilibrium (equation 2) and has units of mmol/g .

$$K_d = \{M\}_{\text{ads}}/[M] = (\text{DF}-1)/[\text{MST}] \quad (2)$$

where, $\{M\}_{\text{ads}}$ is the equilibrium concentration of adsorbing species, M , on the MST in mmol/g , $[M]$ is the equilibrium solution concentration of adsorbing species, M , in mmol/mL , DF is the decontamination factor, and $[\text{MST}]$ is the concentration of MST in g/mL .

Table VI. Equilibrium Distribution Constants

<u>Solution</u> <u>Type</u>	<u>K_d (mL/g)</u> <u>Sr</u>	<u>Pu</u>
Sr-doped	1.0×10^5	-
Pu-doped	-	7.9×10^4
Sr & Pu-doped	9.2×10^4	1.2×10^5
Sr, Pu & U-doped	1.2×10^5	4.8×10^4

The equilibrium distribution constants for strontium and plutonium are both quite high. Using the measured decontamination factors and assuming a strontium concentration of 2.0×10^{-7} M and a plutonium concentration of 3.3×10^{-6} molar, a total loading of plutonium and strontium is calculated to be $11.3 \mu\text{mol/g}$ at a MST concentration of 0.30 g/L . This result indicates only about 0.2% of the theoretical adsorption capacity of the MST is tied up with plutonium and strontium. At this low loading, competition between ionic species for adsorption sites would not be expected to be significant.

The presence of strontium and plutonium did not appear to significantly affect the adsorption of uranium (see Figure 2). In the presence of uranium, the adsorption of plutonium but not strontium is decreased. This result may be due to the higher loading on the MST when uranium is present and to differences in the sizes of the strontium and plutonyl ions.

At the uranium concentration tested (8.5×10^{-5} M), the total loading on the MST is about 10 times higher than that in the experiments with only strontium and/or plutonium present. Thus, the fraction of adsorption sites available to strontium or plutonium is significantly lower when uranium is present. Also, the size of the plutonyl ion is about four times that of the Sr^{2+} ion.² Thus, the smaller Sr^{2+} ion may be able to reach adsorption sites that the larger plutonyl ion may not be able to reach because of its much larger size.

Effect of Particle Size

During the ITP process, the particle size distribution of the MST may be changed by (1) breaking due to high shear forces in pumps or in the cross-flow filter and/or (2) separation due to differential settling in the tank. Smaller particles may exhibit higher adsorption due to increased surface area. However, experimental results indicated that changing the particle size distribution of the MST did not significantly affect the adsorption of uranium or strontium onto the MST. Thus, there is no identified mechanism by which the MST can be physically altered which would increase the adsorption of ionic species during the ITP process.

Maximum Possible Loading of Plutonium-239 and Uranium-235

The maximum possible loadings of plutonium-239 and uranium-235 were determined to be 0.68 wt% for plutonium-239 and 1.4 wt% for uranium-235. These loadings were determined from graphs of the experimental loading data as a function of the MST concentration. The experimental data were fitted to a linear expression and the y-intercept taken to be the maximum possible loading (infinitely dilute MST). The plots for plutonium and uranium are given in Figures 4 and 5, respectively.

The maximum possible plutonium-239 loading is below the ever-safe limit of 0.80 wt% previously calculated for plutonium-239³. The maximum possible uranium-235 loading is slightly above the ever-safe limit of 1.2 wt% uranium-235 calculated using the rule of fractions⁴. The ever-safe limits assume a dry solid, and therefore, are conservative for the aqueous MST suspensions.

The concentration of plutonium in the Pu-doped salt solution was 3.29×10^{-6} M (0.79 mg/L), which is consistent with that reported for plutonium in alkaline salt solutions⁵. The solubility of plutonium is lower with uranium present, 8.39×10^{-7} M (0.20 mg/L), and competition for sites on the MST reduces the amount of plutonium on the MST. With strontium present, the maximum loading decreased to 0.52 wt%, and with strontium and uranium present the maximum loading decreased to 0.16 wt%.

Using all of the experimental data, the maximum loading of U-235 is determined to be 1.3 wt%. Because of the relatively high experimental error in measuring the concentration of uranium in alkaline salt solutions at the milligram-per-liter levels, there is considerable scatter in the data from Tests #1 and #2. The two data points from Test #3 were determined by isolating and measuring the uranium content of the MST solids. This experimental method has a much lower experimental error than the solution method used in Test #1 and #2. Fitting these two data points to a linear equation gives a line which has a y-intercept of 1.4 wt% and is parallel to a line obtained by linear regression analysis of all of the data.

The uranium concentration was 6-7 mg/L in Tests #1 and #2 and 20 mg/L in Test #3. Also, in test #3, the strontium decontamination factor of the MST sample was approximately a factor of four greater than that used in Tests #1 and #2. Thus, even though the uranium concentration was increased by a factor of about three and a higher strontium-capacity MST sample was used in the experiment, the uranium loading did not increase.

The highest reported concentration of uranium in supernate is 16 mg/L.⁶ Literature data are not complete for the solubility of uranium and plutonium over the full range of alkaline salt solutions which will be processed in the ITP process. Therefore, it is recommended that solubility tests be conducted to determine the maximum possible concentrations of uranium and plutonium to ensure that the concentration of fissile materials cannot exceed nuclear safety limits.

Figure 4. Pu-239 Loading onto Monosodium Titanate

Figure 5. U-235 Loading onto Monosodium Titanate

Analysis of Experimental Errors

Experimental errors in the data reported in this document arise from three sources; (1) from gamma and alpha counting measurements, (2) from the transfer of small quantities of MST slurry and (3) from pipetting solutions. The total maximum experimental error is estimated to be the sum of these three types or errors. Based on the maximum reported error in the counting measurements, the average relative error determined from cross-check experiments, and maximum error of the pipets, the combined error is estimated to be 42%.

The maximum error reported in any of the counting analyses was 16%. The concentration of MST slurry used in the experiments is 4.6 % by weight. Upon standing, the MST solids will settle. Therefore, the slurry must be mixed to obtain a representative sample. Because of the small quantity of MST slurry needed in the experiments, uncertainty in the quantity of MST in the experiment may give rise to a significant error. This error would be dependent on the technique used to make the transfer. In order to assess this type of error, cross-check experiments were performed with the same solutions and MST samples by two different analysts. The average relative error for three cross-check experiments was 24%. All pipets used in these experiments were verified for accuracy before use. For the volumes of solutions pipetted, the accuracy of the pipets is better than 2%.

QUALITY ASSURANCE

All experimental work reported in this document was obtained in accordance with the QA controls and procedures given in WSRC-1Q and Interim Waste Technology Section Operating Procedures Manual L12.1. Experimental data are recorded in laboratory notebooks WSRC-NB-91-151 and WSRC-NB-91-201.

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