LETTER REPORT - CESIUM LEACHING RESULTS FROM LOADED CRYSTALLINE SILICOTITANATE IN CONTACT WITH SRS TANK 51 SLUDGE AND SUPERNATE SIMULANTS

P. A. Taylor

ABSTRACT

A small column ion-exchange system (SCIX), using crystalline silicotitanate (CST) sorbent, is being designed to remove radioactive cesium from low activity dissolved salt at the Savannah River Site (SRS). The spent CST would be discharged to Tank 51, the sludge washing tank, and combined with the sludge. Small-scale tests were conducted to determine if cesium would leach from the CST during washing or storage. The CST was loaded with cesium using a dissolved salt simulant solution, rinsed, sized reduced, and then mixed with simulant slurries that represent the sludge and supernate in Tank 51. The samples were stored at room temperature and at 50°C, and samples of the supernate were collected periodically and analyzed for dissolved cesium to determine the amount of cesium that leached from the CST.

All of the conditions tested showed that only a very small fraction of the cesium that was originally loaded on the CST (0.005% to 1.6%) leached into the supernate simulants. These results show that dumping spent CST into Tank 51 would not result in significant leaching of cesium from the CST.

BACKGROUND

The Savannah River Site is evaluating acceleration of the treatment schedule for the waste in their High Level Waste Tanks by treating the low activity liquid from dissolved saltcake in an alternate treatment facility from the Salt Waste Processing Facility, which will handle the higher activity liquid wastes. Treatment to reduce the level of ^{137}Cs will be required for the low activity wastes in order to meet the waste acceptance criteria for the Saltstone Processing Facility. One treatment method being developed is an SCIX system using CST sorbent, located in the riser of a high-level waste tank. Current plans call for the cesium-loaded CST from the ion-exchange column to be rinsed and then sluiced from the column into a grinder vessel with inhibited water. After being sized-reduced in the grinder, the CST will be discharged to Tank 51 (the sludge-washing tank), where it will be mixed with the sludge in that tank. Earlier work at Oak Ridge National Laboratory (ORNL) has shown that previously-loaded cesium could leach from CST under some conditions.[1] Small-scale tests were conducted to determine if cesium leaching is likely to occur during storage of cesium-loaded CST in Tank 51. CST was loaded with cesium and then placed in simulant slurries that represented the range of composition of the material in Tank 51.

MATERIALS AND METHODS

The CST used in these tests was caustic washed crystalline silicotitanate (IONSIV™ IE-911, lot #2081000056) from UOP, LLC (Des Plaines, IL). The CST was loaded with cesium (Cs) by batch contact with an average composition SRS dissolved salt simulant solution (5.6 *M* sodium), which initially contained 3170 mg/L of nonradioactive cesium. The simulant was prepared by adding analytical-grade chemicals to deionized water. There was some solid material that did not dissolve and was removed by filtration. The filtered simulant was analyzed by inductively-coupled plasma – emission spectroscopy (ICP–ES) for selected cations, by ion chromatography for anions, and by ICP– mass spectroscopy (ICP–MS) for cesium. The target composition and the corresponding analytical results (shown as the appropriate compound) for the simulant are shown in Table 1. From the analytical results, it appears that at least some of the insoluble material was aluminum fluoride. The CST (50 g) was contacted with 500 mL of the simulant solution on a bottle roller for 2 days. After contact, the simulant solution was decanted from the CST, and the CST was rinsed three times, for 5 minutes each, with 500 mL portions of inhibited water (SRS formulation containing 0.015 *M* NaOH and 0.015 *M* $NaNO_2$ in deionized water) to remove the simulant solution and any unadsorbed cesium from the CST. The cesium-loaded CST was air dried overnight and ground to a powder with a mortar and pestle. Two samples of the CST were digested and analyzed for cesium, giving concentrations of 32.1 and 29.3 mg Cs/g CST. The target loading was 30 mg Cs/g CST, which is the predicted maximum loading for spent CST that had treated a dissolved salt solution containing 2.0 Ci/gal of ^{137}Cs. The simulant solution after contact with the CST had a cesium concentration of 21.9 mg/L, compared to the starting concentration of 3140 mg/L. The sequential rinse solutions had cesium concentrations of 0.87 mg/L, 0.13 mg/L and 0.087 mg/L, respectively.

Table 1. Composition of SRS Average Dissolved Salt Simulant

Component	Concentration (*M*)	
	Target	Analysis
NaOH	1.10	NA*
$NaNO_3$	2.40	2.03
$NaNO_2$	0.34	0.34
$NaAlO_2$	0.54	0.50
Na_2SO_4	0.30	0.28
Na_2CO_3	0.55	NA
NaCl	0.035	0.056
NaF	0.033	<0.001
Na_2HPO_4-$7H_2O$	0.003	0.0034
Na_2SiO_3-$9H_2O$	0.005	NA
KNO_3	0.006	0.0085
CsCl	0.0228	0.0236

*NA = Not analyzed

Three supernate simulants were prepared, which represent the minimum, average and maximum concentrations measured in Tank 51 since 1989. These compositions were supplied by SRS personnel, who also stated that future solutions in Tank 51 are expected to most closely resemble the minimum composition. The target concentrations for these simulant solutions are shown in Table 2.

Table 2. Composition of Tank 51 Simulant Solutions

	Concentration (*M*)		
Component	Minimum	Average	Maximum
NaOH	0.01	0.38	1.96
$NaNO_3$	0.017	0.32	1.02
$NaNO_2$	0.092	0.65	1.82
$NaAlO_2$	0.005	0.030	0.15
Na_2SO_4	0.002	0.021	0.11
NaCl	0.0003	0.004	0.05
NaF	0.0009	0.006	0.06
Na_2CO_3	0.01	0.082	0.44
Na_2HPO_4-$7H_2O$	0.0003	0.001	0.003
Na_2SiO_3-$9H_2O$	0.001	0.002	0.005
KNO_3	0.001	0.003	0.006
$Na_2C_2O_4$	0.002	0.014	0.051

Portions of the ground, cesium-loaded CST were placed in a series of Teflon flasks, along with 50 mL of one of the Tank 51 simulant solutions (see Table 3). An SRS sludge simulant slurry, containing 180 g/L of suspended solids, was added to all but one of the flasks. The sludge simulant was originally obtained from SRS in 1999, and is a mixture of two simulants representing H-Area Modified and PUREX sludge at SRS[2]. The flasks were stored stagnant at room temperature (XXX-XXX-25 Container I.D.s, see Table 3) or in an environmental chamber at 50°C (XXX-XXX-50 I.D.s). Small samples of the supernate were removed after 1 day, 1 week, 3 weeks, 1 month, 2 months, 4 months, and 7 months, filtered and analyzed for cesium by ICP-MS. If all of the cesium that was loaded on the CST leached into the solution, the resulting concentration would have been 1500 mg/L. Two of the flasks contained the minimum simulant solution and sludge, but no CST. Cesium chloride was added to these two flasks to give a concentration of 120 mg/L Cs in the simulant solution. The purpose of these control flasks was to check for adsorption of cesium by the components in the sludge simulant. One flask contained the minimum simulant and CST but no sludge, to determine any influence of the sludge in cesium leaching from the CST.

RESULTS AND DISCUSSION

The storage temperature of the flasks was measured periodically using a digital thermometer, which was factory calibrated using a National Institute of Standards and Technology traceable standard. The temperature of the flasks stored at room temperature varied between 21.7 and 25.1^{o}C, with an average of 22.3^{o}C, and the flasks stored in the environmental chamber varied between 48.7 and 50.3^{o}C, with an average of 49.1^{o}C.

Table 3. Composition of Test Slurries

Container I.D.	Simulant Type	CST (g)	Sludge Simulant (mL)
T51-Min-25	Minimum	5.00	50
T51-Min-50	Minimum	5.00	50
T51-Min-25-dup	Minimum	5.00	50
T51-Min-50-dup	Minimum	5.00	50
T51-Avg-25	Average	5.00	50
T51-Avg-50	Average	5.00	50
T51-Max-25	Maximum	5.00	50
T51-Max-50	Maximum	5.00	50
T51-Min-C-25	Minimum	0	50
T51-Min-C-50	Minimum	0	50
T51-Min-CST-50	Minimum	5.00	0

A sample of the solids in the SRS sludge simulant was analyzed using ICP-ES to characterize the simulant. The results are shown in Table 4.

Table 4. Analytical Results For the SRS Sludge Simulant

Component	Concentration (g/kg)
Aluminum	75.9
Calcium	22.3
Iron	255.2
Manganese	57.3
Nickel	24.0
Silicon	31.1
Zirconium	21.6

Table 5 shows the cesium results for the supernate samples that were taken from the test flasks. The samples from the flasks containing the minimum supernate simulant showed very low leaching of cesium from the loaded CST. The average supernate simulant showed slightly higher cesium leaching, while the maximum simulant showed the highest amount of leaching. In all cases, the flasks stored at 50°C showed higher cesium leaching than the flasks stored at room temperature. The control samples that contained supernate, sludge and cesium, but no CST (T51-Min-C-25 and T51-Min-C-50), showed significant sorption of the cesium, 57% sorbed at room temperature and 40% sorbed at 50°C. These results were unexpected, and it is not known which components of the sludge simulant are adsorbing the cesium. The control sample stored at 50°C is the only sample that showed a consistent change in soluble cesium concentration over time. The amount of cesium sorbed on the sludge slowly decreased as the storage time increased, which is probably caused by a slow change in the crystalline structure of the sludge components at this elevated temperature. The control sample with CST and supernate simulant, but no sludge simulant (T51-Min-CST-50), showed similar results to the comparable samples with sludge simulant (T51-Min-50 and T51-Min-50-dup), which suggests that the sludge is not adsorbing significant amounts of cesium at these low concentrations. The soluble cesium concentration for

the control sample did decrease with time, suggesting that part of the leached cesium readsorbed onto the CST.

Table 5. Measured Cesium Concentrations in Test Slurry Supernates

Container I.D.	Cesium Concentration (mg/L)						
	1 d	1 w	3 w	1 m	2 m	4 m	7 m
T51-Min-25	0.138	0.131	0.072	0.135	0.099	0.102	0.084
T51-Min-50	0.288	0.389	0.407	0.393	0.398	0.334	0.331
T51-Min-25-dup	0.143	0.144	0.117	0.138	0.135	0.124	0.116
T51-Min-50-dup	0.309	0.401	0.416	0.425	0.422	0.284	0.354
T51-Avg-25	2.19	2.04	2.00	1.96	2.01	1.48	2.02
T51-Avg-50	5.75	5.73	6.00	5.80	5.64	4.72	5.14
T51-Max-25	7.94	8.13	8.13	8.18	7.77	7.48	7.99
T51-Max-50	19.7	22.4	23.4	23.2	22.0	23.2	24.2
T51-Min-C-25	56.5	51.9	54.0	52.7	52.2	52.2	55.1
T51-Min-C-50	67.6	68.3	70.0	71.3	77.2	78.8	87.9
T51-Min-CST-50	0.352	0.291	0.351	0.283	0.280	0.235	0.149

d = day, w = week, and m = month

Table 6 shows the average soluble cesium concentration for each of the flasks that contained CST and the predicted concentration of soluble cesium from the ZAM model[3]. The resulting cesium concentration left on the CST, calculated by subtracting the amount of soluble cesium from the amount of cesium originally loaded on the CST, is also shown for each flask. The fraction of the cesium that was originally loaded on the CST that leached into the simulant ranged from 0.005% for the minimum simulant at 25°C to 1.6% for the maximum simulant at 50°C. Even for the maximum simulant solution, which showed the greatest amount of leaching, only a small fraction of the cesium that was originally loaded on the CST leached into the solution. A graph showing the percent of cesium leached from each of the samples at each time period is shown in figure 1.

Table 6. Comparison of Average Cesium Concentrations With ZAM Model Predictions

Container I.D.	Average [Cs] (mg/L)	ZAM Prediction (mg/L)	Cesium on CST (mg Cs/g CST)
T51-Min-25	0.11	0.39	30.00
T51-Min-50	0.37	0.70	29.99
T51-Avg-25	1.95	3.44	29.96
T51-Avg-50	5.60	5.94	29.89
T51-Max-25	7.94	22.2	29.84
T51-Max-50	20.6	23.2	29.59
T51-Min-CST-50	0.28	0.70	29.99

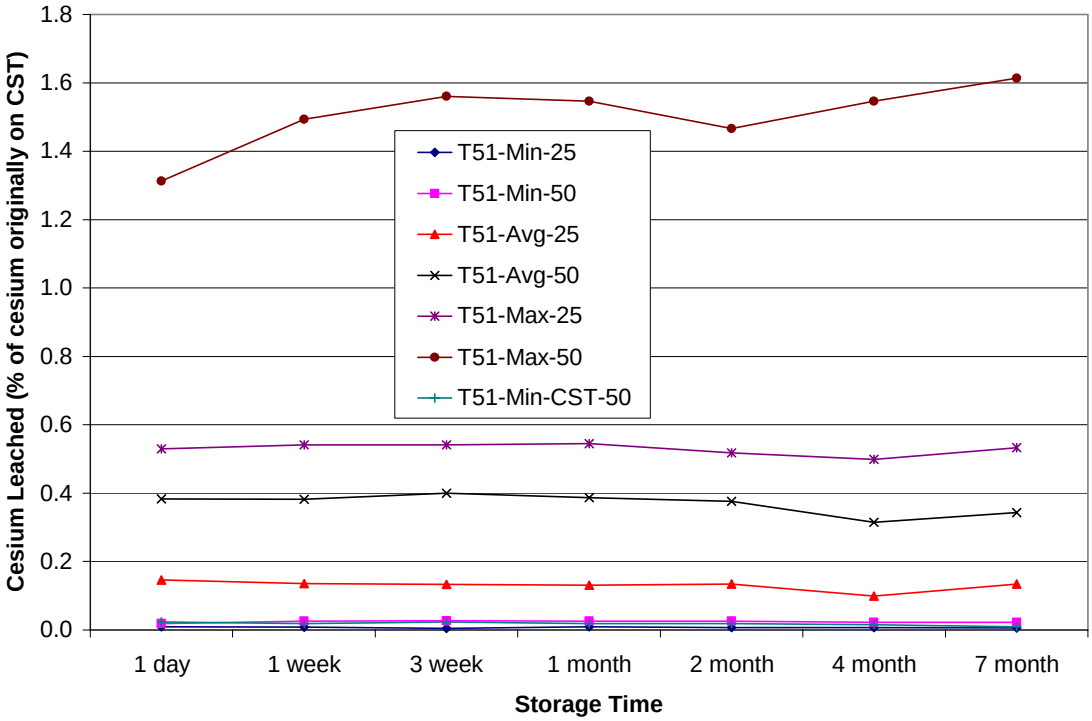

Fig. 1. Cesium leaching results for the samples that contained cesium-loaded CST.

The ZAM model predicts higher soluble cesium concentrations than were measured in all cases. There are two potential explanations for the measured cesium concentrations being lower than the predicted concentrations. First, the sorption process for cesium in the CST crystal is unlikely to be completely reversible. The ZAM model was developed from measurements of soluble cesium loading onto CST, and the reverse process of cesium leaching from previously loaded CST was not considered. The second potential explanation is that the sludge may be sorbing some of the cesium that was leached from the CST. The control samples that did not contain CST (T51-Min-C-25 and T51-Min-C-50) showed some sorption of soluble cesium, particularly at room temperature. The fact that the measured cesium concentrations are closer to the predicted values for the samples stored at 50°C, where sorption by the sludge was lower, supports this explanation. The control sample with CST but no sludge in the minimum simulant (T51-Min-CST-50) also showed a lower soluble cesium concentration than the predicted value, which does not support the sludge sorption explanation; however, the soluble cesium concentration was very low in all of the samples that contained minimum simulant. The samples that contained the average or maximum simulants, where the soluble cesium concentrations were higher, would be more likely to show sorption of cesium by the sludge.

All of the conditions tested showed that only a very small fraction of the cesium that was originally loaded on the CST (0.005% to 1.6%) leached into the supernate simulants. These results show that dumping spend CST into Tank 51 would not result in significant leaching of cesium from the CST.

REFERENCES

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