

# Chemical and Thermal Stability of Crystalline Silicotitanate Sorbent

**P. A. Taylor and C. H. Mattus**  
**Oak Ridge National Laboratory**

(Managed by UT-Battelle for the U.S. Department of Energy)

The Savannah River Site (SRS) (Aiken, SC) is evaluating technologies for removing  $^{137}\text{Cs}$  from the supernate in their high-level waste tanks. Crystalline silicotitanate (IONSIV IE-911<sup>®</sup>, UOP LLC) is very effective for removing cesium from high-salt solutions. Because of the high loading of  $^{137}\text{Cs}$  that would be expected for columns of crystalline silicotitanate (CST) used to treat the SRS supernate, radiolytic heating would be significant. The ability of CST to load and retain  $^{137}\text{Cs}$  at various temperatures was determined. At 80 and 120°C, the amount of cesium loaded on the CST was reduced by 72 and 83%, respectively, from room temperature results. CST that was loaded with cesium at room temperature and then heated to higher temperatures leached cesium back into the simulant solution. The final cesium loadings on the leached CST were similar to those for the corresponding loading tests. Following storage in the simulant at 50 to 120°C for 60 days, the CST did not reload any cesium after the temperature was reduced to 22°C. CST stored in simulant solutions without cesium for up to 6 months at 50 and 80°C showed only a small loss in cesium capacity when tested at room temperature. Silicon was leached from the CST into the simulants during storage, and then precipitated with aluminum from the solutions to form particles of sodium aluminosilicate on the CST.

## MATERIALS AND METHODS

The CST used in all of these tests was the commercial, granular form of the sorbent, IONSIV<sup>®</sup> IE 911 (UOP LLC, Mt. Laurel, NJ). The as-received sorbent is slightly acidic, so dilute sodium hydroxide was used to stabilize its pH at 13 before use. Four different simulant solutions were used for these tests. The compositions are shown in Table I. Samples of CST and simulant were placed in Teflon flasks and mixed in Model 3527-5 Environ Shakers (Lab-Line Instrument, Inc., Melrose Park, IL) at 120 rpm for 4 days. The temperature of the samples was maintained within  $\pm 0.2^\circ\text{C}$  by a built-in, forced-air convection heater with a temperature controller.

Batch loading tests were performed at temperatures of 25, 30, 35, 40, 45, 50, 60, 70 and 80°C, using 0.1 g of CST and 100 mL of supernate simulant, which contained 50 mg/L Cs and 0.1  $\mu\text{Ci/L}$   $^{137}\text{Cs}$ . Two samples of the supernate from each flask were filtered through 0.2- $\mu\text{m}$ -pore size, nylon syringe filters. A 2.00-mL portion of each filtered sample was transferred into a polyethylene counting tube, centrifuged for about 30 s to ensure that no droplets were left on the sides of the tubes, and then gamma counted for 1000 s. The samples were counted at an energy level of 664.7 keV, using a Canberra Industries, Inc. (Meriden, CT) series 90 gamma spectrometer, with a shielded germanium detector, to determine the

concentration of  $^{137}\text{Cs}$ . Three samples of the starting supernate simulant and three background rates were counted for each series of samples.

**Table I. Composition of Simulated Waste Solutions**

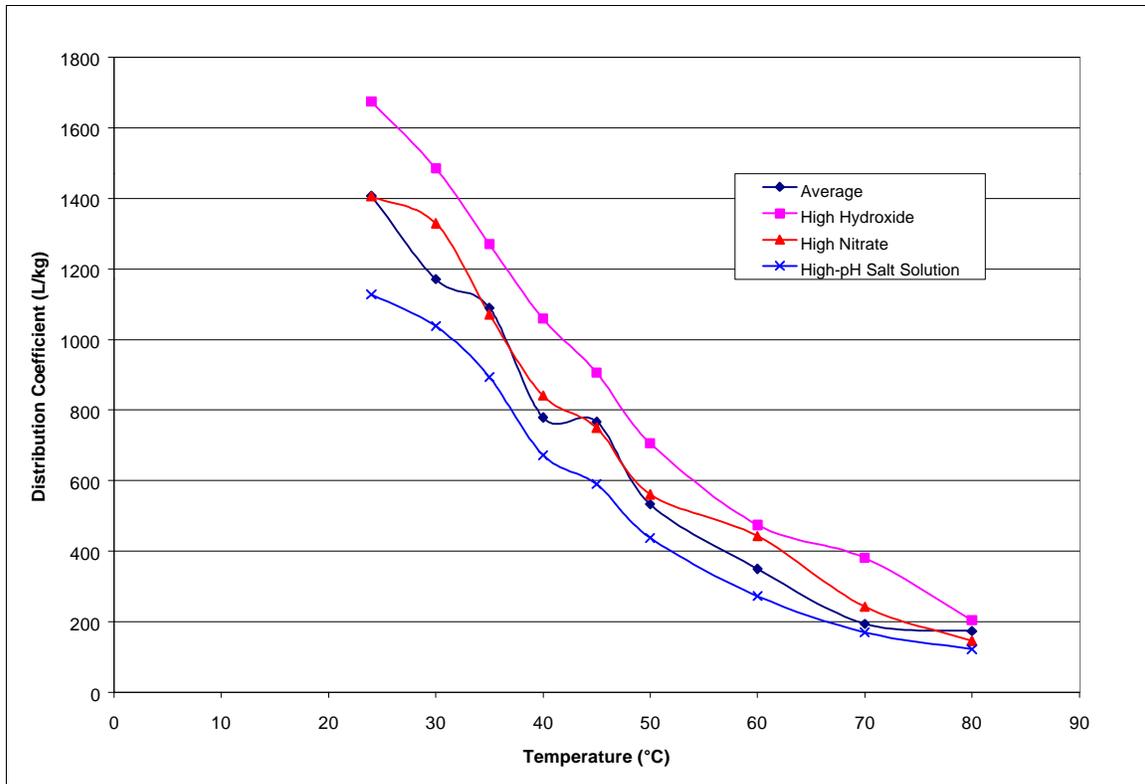
Component	Concentration (molar)			
	Average	High OH <sup>-</sup>	High NO <sub>3</sub> <sup>-</sup>	High-pH Salt
Na <sup>+</sup>	5.6	5.6	5.6	5.6
K <sup>+</sup>	0.015	0.030	0.0041	
OH <sup>-</sup>	1.91	3.05	1.17	1.91
NO <sub>3</sub> <sup>-</sup>	2.14	1.10	2.84	3.69
NO <sub>2</sub> <sup>-</sup>	0.52	0.74	0.37	
AlO <sub>2</sub> <sup>-</sup>	0.31	0.27	0.32	
CO <sub>3</sub> <sup>2-</sup>	0.16	0.17	0.16	
SO <sub>4</sub> <sup>2-</sup>	0.15	0.030	0.22	
Cl <sup>-</sup>	0.025	0.010	0.040	
F <sup>-</sup>	0.032	0.010	0.050	
PO <sub>4</sub> <sup>3-</sup>	0.010	0.008	0.010	
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	0.008	0.008	0.008	
SiO <sub>3</sub> <sup>2-</sup>	0.004	0.004	0.004	
MoO <sub>4</sub> <sup>2-</sup>	0.0002	0.0002	0.0002	

The 1999 leaching tests were performed in a similar manner to the loading tests, except that the CST and supernate containers were contacted at room temperature for 4 days to load the CST with cesium. The containers were then heated to 50, 80, or 120°C and stored, while being mixed, for a total of 60 days to determine how much cesium would leach from the CST back into the simulants. Samples of supernate were removed, filtered, counted to measure the soluble cesium concentration, and then returned to their original container, after storage times of 1, 2, 4, 16, 29, and 60 days. Following completion of the leaching tests, all of the containers were mixed at room temperature for 4 days and then sampled to determine how much of the cesium previously leached from the CST had been reloaded. Batch leaching tests are currently in progress at temperatures of 25, 30, 35, 50 and 80°C, using simulant solutions that do not contain cesium. Samples of the simulant and CST are withdrawn periodically for elemental analysis. A portion of each CST sample is used for a cesium loading test, using average simulant containing 50 mg/L Cs and 0.1 μCi/L  $^{137}\text{Cs}$ .

Column leaching tests are also in progress using two 1.6 cm I.D. by 100 cm tall plastic columns. Average simulant is recirculated through the first column and high-pH salt solution through the second at flow rates of 6.0 mL/min. Samples of simulant and CST are withdrawn periodically and analyzed the same as for the batch leaching tests.

## RESULTS

The results of the cesium loading tests are shown in Figure 1. Temperature has a strong effect on the distribution coefficient ( $K_d = [Cs]_{\text{CST}}/[Cs]_{\text{simulant}}$ ) for cesium loading on the CST. The high hydroxide simulant shows the highest  $K_d$ , followed by the average and high nitrate simulants, and then by the high-pH salt solution.

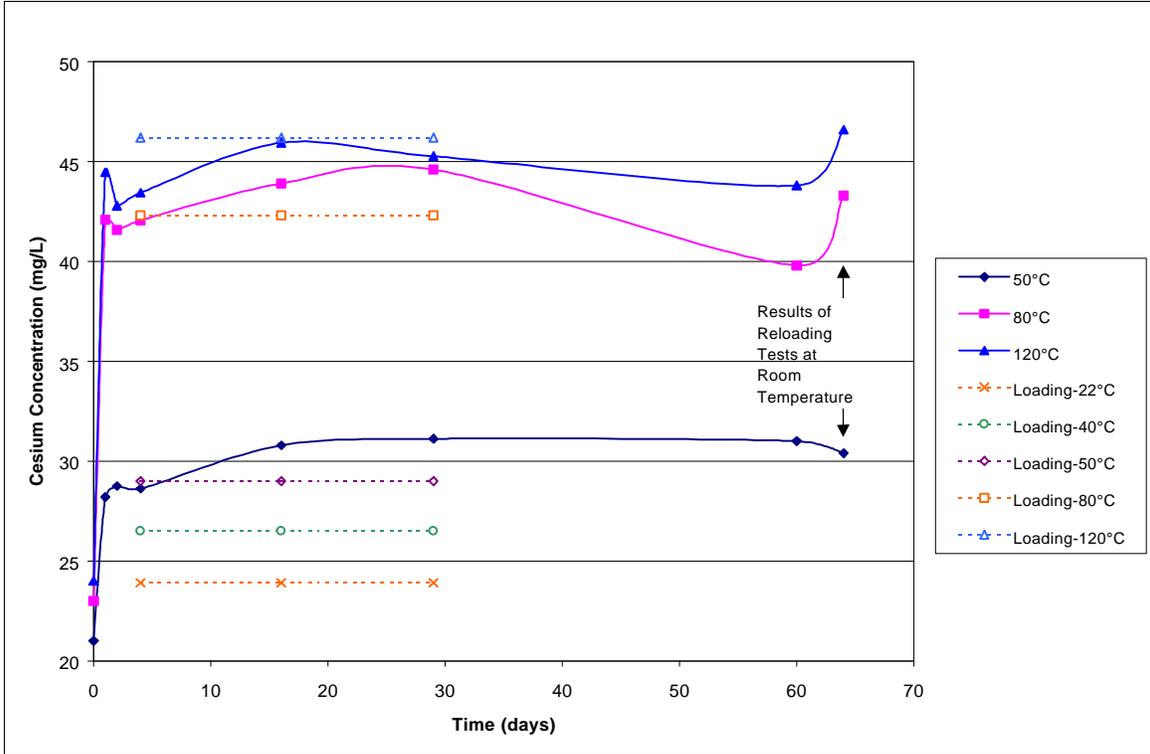


**Fig. 1. Results of cesium loading tests CST and simulant solutions.**

Figure 2 shows a plot of the cesium concentration in the average simulant solutions at each temperature for the leaching tests, and also shows the comparable results from the 4-day loading tests. The loading results are displayed as short line segments so that they will be more visible; however, the data are actually single points at 4 days. The simulants originally contained 50 mg/L cesium, and the soluble concentration was reduced to 23 mg/L during the initial 4-day, room temperature loading phase. When the temperature of the CST and simulants was increased, some of the sorbed cesium rapidly leached from the CST back into the simulants. The distribution coefficients for the CST in the leaching tests at each temperature were about the same as for the loading tests performed at that temperature.

After the leaching tests had been completed, the samples were mixed at room temperature for 4 days. Analyses of these samples showed that the cesium in the simulant solutions did not

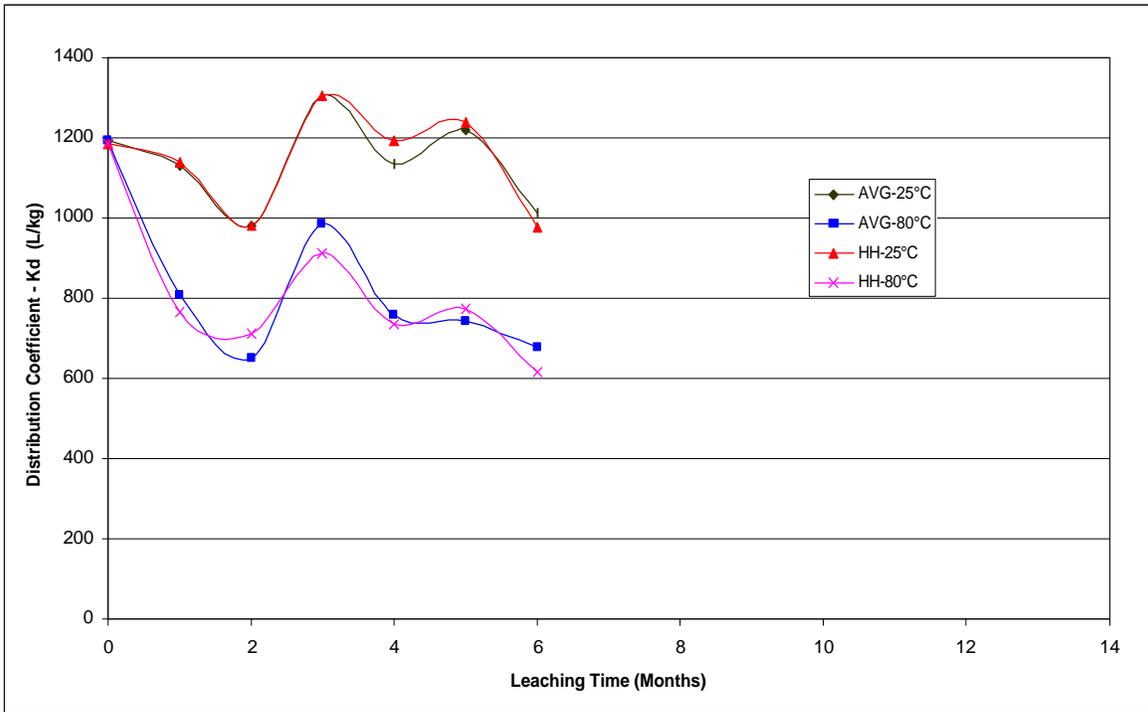
reload onto the CST. The cesium concentrations were actually a little higher than those for the 60-day leaching samples; however, the control samples were also higher, so the increase is probably just analytical variation.



**Fig. 2. Results of leaching tests in average simulant. Loading results are shown for comparison.**

The results for the batch leaching tests that are currently in progress are shown in Figure 3 for the average and high hydroxide simulants. In these tests the simulant solutions, and therefore the CST, does not contain any cesium during exposure to the higher temperatures. Samples of the CST are removed periodically and contacted with average simulant containing 50 mg/L Cs to determine any change in cesium loading capacity. After one month of exposure at 80°C the  $K_d$  for cesium loading on the CST dropped by about 30%, compared to CST stored in the simulants at 25°C. After the initial drop, the difference in  $K_d$  between the CST stored at 25 and 80°C did not change during the next five months. There was month-to-month variation in all of the  $K_d$ s measured, but within each set of samples the results were very consistent. The results for the intermediate temperatures (30, 35 and 50°C) fell between the results shown. These results are very different from the earlier leaching tests, where the CST contained some cesium during exposure to the higher temperatures. It appears that the sodium form of the CST is more stable than the cesium form.

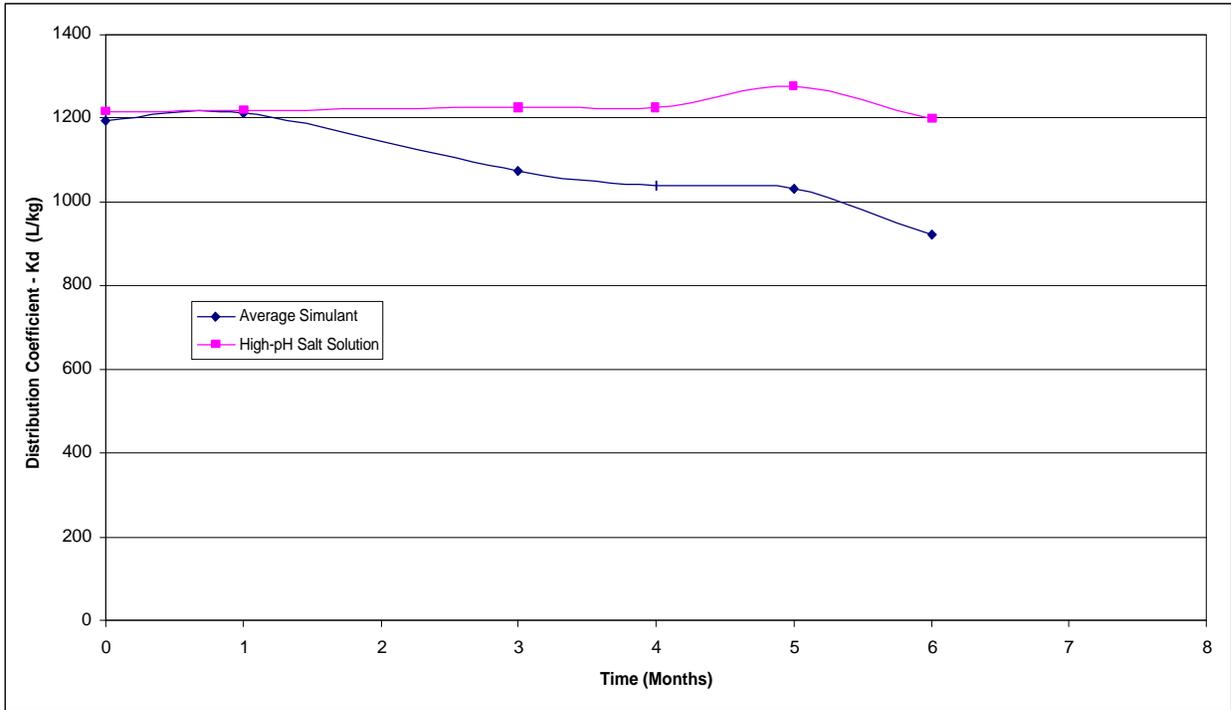
Chemical analysis of the simulants from the leaching tests shows that the concentration of silicon in solution initially increases and then decreases. Precipitates of sodium aluminosilicate are formed on the CST particles. The formation of the precipitates, and the decrease in soluble silicon concentration, is much faster at the higher temperatures.



**Fig. 3. Cesium loading results for CST from current batch leaching tests.**

The cesium loading results for the CST samples from the column leaching tests are shown in Figure 4. The CST from the column with high-pH salt solution has not shown any change in cesium capacity for the six months that the test has been in progress. The CST exposed to recirculating average simulant solution has shown a 23% decrease in  $K_d$  over six months.

The current design for the CST columns that could be used to treat the high-level waste supernates at the Savannah River Site uses three large columns in series (lead, lag and guard columns). The original guard column moves up to the lag and then the lead position as the CST in the lead column becomes fully loaded and is replaced with fresh CST. CST that originally started in the guard column could be exposed to supernate solution for up to a year before it was fully loaded with cesium in the lead column position. During most of this time it would be exposed to supernate that had already been treated to remove most of the cesium by the original lead and lag columns. The column leaching test simulates this exposure. The results to date show that there could be a small loss in cesium capacity from long-term exposure to the treated supernate. The batch leaching tests show that exposure to higher temperatures for one month, or less, will reduce the cesium capacity of the CST, but there is no further change for longer-term exposures.



**Fig. 4. Cesium loading results for CST samples from column leaching tests.**