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Thermal and Chemical Stability of Baseline and Improved Crystalline Silicotitanate[#]

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ABSTRACT

The U.S. Department of Energy (DOE) Savannah River Site (SRS) is evaluating technologies for removing radioactive cesium (^{137}Cs) from the supernate solutions stored in the high-level waste tanks at the site. Crystalline silicotitanate (CST) sorbent (IONSIV[®] IE-911, UOP LLC, Des Plaines, IL), which is very effective at removing cesium from high-salt solutions, was one of three technologies that were tested. Small-scale batch and column tests conducted last year using samples of production batches of CST showed potential problems with CST clumping and loss of cesium capacity after extended contact with the simulant solutions. Similar tests using samples of a baseline and improved granular CST and

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the CST powder used to make both granular samples were performed this year to compare the performance of the improved CST.

The column tests showed that the baseline CST generated more precipitates of sodium aluminosilicate than the improved CST. The sodium aluminosilicate formed bridges between the CST granules, causing clumps of CST to form in the column. Clumps were visible in the baseline CST column after 1 month of operation and in the improved CST column after 2 months. The cesium capacity of the CST samples from the column tests with recirculating simulant decreased slightly as the run time increased. Most of this decrease could be attributed to the weight of cancrinite (a sodium aluminosilicate) on the CST samples. Tests conducted last year using production batch samples of CST showed a more pronounced drop in cesium capacity under comparable conditions. A column test using the improved CST and once-through simulant showed few problems during 5 months of operation. The pressure drop through the column remained low; however, the CST in the column was clumped together when the final samples were taken after 5 months. The final sample taken from the top 1 cm of the column showed a 65% drop in cesium capacity compared with all the other samples from this column. This sample also contained the highest concentration of cancrinite, but the weight of cancrinite would only account for a small fraction of the drop in cesium capacity by simple dilution of the CST.

The CST in the batch tests stored at elevated temperatures in average simulant formed clumps, but this occurred at a slower rate than that observed last year during comparable tests using production batch samples of CST. Storage at elevated temperatures caused a gradual decrease in cesium capacity as the storage time increased, with a loss in capacity of up to 20% after 5 to 6 months at 80°C. The results for the baseline and improved CST samples were essentially the same for these batch tests.

Key Words: Crystalline silicotitanate; CST; Cesium; Chemical stability; Thermal stability; Clumping.

INTRODUCTION

The U.S. Department of Energy (DOE) Savannah River Site (SRS) is evaluating technologies for removing ^{137}Cs from the supernate solutions stored in high-level waste tanks at the site. IONSIV IE-911 (UOP, LLC, Des Plains, IL), an inorganic crystalline silicotitanate (CST) ion-exchange material with a high affinity for cesium, is the key material in one of the processes that was tested. Because of the extremely high inventory of ^{137}Cs expected for



the large columns of crystalline silicotitanate (CST) that would be used for treating the SRS supernate, any loss of flow or cooling to the columns could result in high temperatures from radiolytic heating. Also, even under normal operating conditions, the CST would be exposed to the supernates for up to a year before being removed. Results obtained from previous studies at Oak Ridge National Laboratory (ORNL)^[1] showed that higher temperatures (50 to 120°C) could cause desorption of previously loaded cesium from CST in simulant solutions and that the CST would not reload the cesium when the temperature was reduced following 60 days of contact at the higher temperatures.

Previous long-term batch- and flow-through-leaching tests using samples from production batches of IONSIV IE-911 showed potential problems with clumping of the CST particles.^[2] Work at other DOE laboratories showed that niobium and silicon leach from the CST^[3,4] and that aluminosilicates precipitate from the SRS simulants onto the CST particles.^[5] UOP has supplied preproduction samples of an improved IE-911 product that was treated to reduce the amount of leachable niobium and silicon. Batch- and flow-through-leaching tests, similar to the earlier tests, were conducted to determine the performance of this new material.

MATERIALS AND METHODS

Two samples of granular CST, and the CST powder used to prepare them, were received from UOP in November 2000 and January 2001. The first granular sample is a baseline material (labeled as 9090-76) that was prepared using the same process as the commercial CST available from UOP but with a higher level of documentation and quality control. The second granular sample (designated as improved, or MH-9098-9) was treated by UOP to remove most of the leachable material (mainly niobium) from the CST. The CST powder sample, which had been used to make both of the granular CST samples, was designated as 30950-48. Batch-leaching tests with all three samples were carried out, and column-leaching tests were performed using the two granular samples. The baseline CST was pretreated by pumping 3-M NaOH through a column of the CST for 24 hours (10-L NaOH for 400-g CST) and then backwashing with deionized water to remove any fines prior to use. The MH-9098-9 and 30950-48 samples were used as received for the batch tests. The MH-9098-9 sample used in the column tests was pretreated with recirculating 1.9-M NaOH for 24 hours to ensure that the alkalinity of the CST had stabilized prior to starting the tests.



Table 1. Composition of SRS average simulant.

Component	Concentration (M)
Na ⁺	5.6
K ⁺	0.015
OH ⁻	1.91
NO ₃ ⁻	2.14
NO ₂ ⁻	0.52
AlO ₂ ⁻	0.31
CO ₃ ²⁻	0.16
SO ₄ ²⁻	0.15
Cl ⁻	0.025
F ⁻	0.032
PO ₄ ³⁻	0.010
C ₂ O ₄ ²⁻	0.008
SiO ₃ ²⁻	0.004
MoO ₄ ²⁻	0.0002

Simulant Solutions

The average supernate simulant was prepared at ORNL using a recipe supplied by SRS.^[6] The composition of the simulant is shown in Table 1. The simulant was prepared using reagent-grade chemicals and deionized water in 20-L batches, without any cesium. A portion of each batch was then spiked with 50-mg/L cesium (added as CsCl) and 1- μ Ci/L ¹³⁷Cs for use in the cesium-loading tests. Each large batch of simulant was analyzed for metals by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and for anions by ion chromatography. The spiked batches of simulant were analyzed for cesium by ICP-mass spectroscopy (ICP-MS) and for ¹³⁷Cs by gamma counting at the ORNL Radioactive Materials Analysis Laboratory.

Column-Leaching Tests

Cesium-free average supernate simulant was recirculated through small polyvinyl chloride columns (1.6-cm ID by 120-cm tall) containing pretreated granular CST at room temperature. The columns were initially filled with 200 g of the CST, which gave a bed height of 90 cm. The flow rate of each solution was 6 mL/min. The solutions were pumped through 0.45- μ m-pore-size filter cartridges



before entering each column, using a dual-head peristaltic pump and silicon rubber tubing. Pressure gauges on the inlet of the filters were used to monitor column plugging. Samples of the solutions were analyzed periodically for dissolved metals to measure CST leaching and precipitation of simulant components. The solutions were replaced when their concentrations changed significantly (>0% change or >200 mg/L, whichever was larger). Samples of the CST (~1 g) were removed from the top and bottom of the columns each month and tested for cesium sorption and elemental composition. The baseline (9090-76) CST ran for 6 months, and the improved CST (MH-9098-9) column ran for 5 months.

A 1.6-cm ID column with a CST bed height of 115 cm was used to test the improved CST and average simulant in a once-through flow mode. The purpose of this test was to determine if continuous exposure of the CST to fresh simulant would result in the collection of higher amounts of precipitated aluminosilicate in the column. The flow rate for this column was 2.0 mL/min, giving a fluid residence time within the CST bed of about 1 hour (which is comparable to conceptual designs for the full-scale SRS columns). Because the leaching and precipitation reactions have very slow kinetics, it was important to match the residence time for the full-scale columns, even though this meant that the fluid velocity would be lower. This test ran for 5 months.

Batch-Leaching Tests

Long-term batch-leaching tests were conducted using cesium-free average simulant to determine the effects of temperature on the stability of the CST. Teflon bottles containing 16 g of CST and 240 mL of simulant were stored at room temperature and 30, 35, 50, and 80°C. Samples of the solutions were analyzed each month for dissolved metals to measure CST leaching and/or precipitation of simulant components. Samples of the CST (~1 g) were removed each month and tested for cesium sorption and elemental composition.

Analytical Methods

The CST samples from the leaching tests were rinsed three times with a small volume of deionized water and then dried at room temperature in a desiccator prior to analysis. Samples of unused CST were contacted with the simulant solution for 10 minutes and then rinsed and dried following the same procedure used for the batch- and column-leaching test samples. These samples served as the baseline (zero time) for comparing all of the analytical results for the leaching test samples. The cesium-loading tests used 0.1-g



samples of CST and 100 mL of SRS average simulant containing 50-mg/L cesium and about 1- μ Ci/L ^{137}Cs . The CST samples and simulant were contacted in Teflon flasks for 7 days at room temperature (21 to 23°C). Simulant samples were collected and filtered (0.2- μ pore-size, nylon syringe filters) and then gamma counted on a Cobra II (Packard Instrument Co., Downers Grove, IL) counter with a sodium-iodide detector.

The ICP-ES analyses were performed using a model 61E Trace ICP from Thermo Jarrell Ash, following standard EPA method SW846-6010B. Standard reference samples from the National Institute of Standards and Technology (NIST) were analyzed, along with the test samples to verify the accuracy of the results. The NIST standard was analyzed 11 times, once for each batch of CST samples analyzed, and the coefficient of variation (mean/standard deviation) was 3 to 4% for Al, Na, Si, and Ti. Both simulant solutions and CST samples were digested using nitric and hydrofluoric acids in a microwave oven to solubilize the materials; boric acid was then added to complex the fluoride ion prior to analysis.

RESULTS AND DISCUSSION

Column-Leaching Tests

During the first 3 months of operation for the column with the baseline (9090-76) CST, there was a continual buildup of an aluminosilicate precipitate on the inside of the silicon rubber tubing leading to and from the column. The precipitate restricted flow through the tubing and caused the back pressure in the column to increase. The tubing was replaced seven times during this period, resulting in a reduction in the back pressure each time. By comparison, the tubing for the column using the improved (MH-9098-9) CST did not show any precipitate formation until after 2 months of operation, at which point, the tubing was replaced one time. A control test was performed by recirculating average simulant through a section of the silicon rubber tubing without any contact with CST. Small amounts of precipitate were visible after 8 weeks of operation, in quantities similar to those observed in the tubing for the improved CST column. These results demonstrated that the simulant solution was not stable and would produce aluminosilicate precipitates; however, contact with the baseline CST greatly increased the amount of precipitate formed. The pressures and flow rates for both columns during the first 110 days of operation are shown in Fig. 1. The baseline CST column contained several weak agglomerations of CST after 1 month of operation. Backwashing the column after each sampling campaign helped break up the clumps of CST.

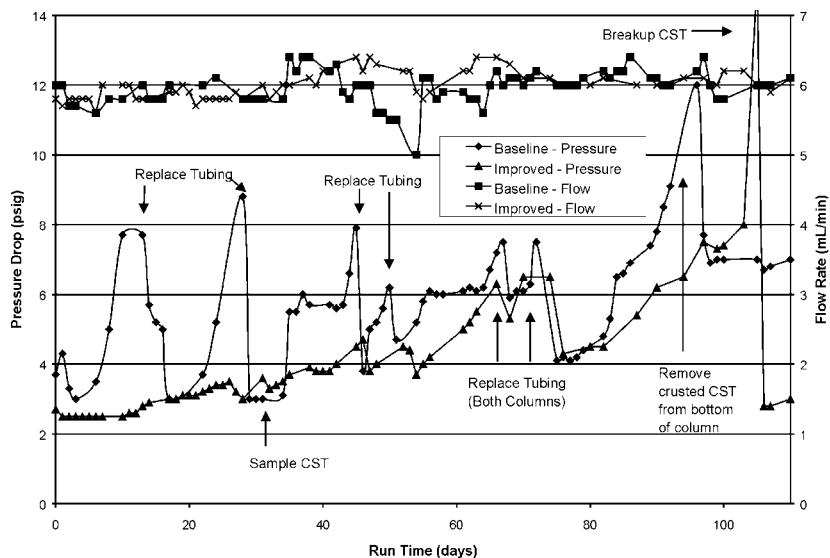


Figure 1. Operational data for column-leaching tests using baseline (9090-76) and improved (MH-9098-9) CST.

After 3 months of operation, the back pressure for the column with the baseline CST started to increase without any visible buildup of precipitate in the lines. Backwashing the column did not reduce the pressure, even after all the visible clumps of CST had broken up. The back pressure increased to 12 psig after 96 days of operation. The column was then inverted, and the bottom cap was removed to diagnose the problem. A thin layer (about 0.5 cm) of crusty CST was stuck to the bottom screen of the column. After removing this CST layer and placing the column back in operation, the back pressure was reduced and stayed in a range of 5 to 7 psig for the remainder of the test. Only very small amounts of precipitate collected in the tubing for this column during the final 3 months of operation.

For the column using the improved (MH-9098-8) CST, no precipitate was visible in the tubing during the first month of operation, but small amounts started to collect during the second month. The amount of precipitate that did collect in the tubing was much less than was seen in the tubing for the column using the baseline CST. The pressure drop for this column stayed quite low (2.5 to 5 psig) during the first 2 months of operation, although a slow, steady increase was observed during this time. After 66 days of operation, the pressure drop had increased to 6.3 psig, and significant amounts of white



precipitate were visible in the tubing leading to and from the column. After replacing the tubing, the back pressure dropped back to 4.3 psig. There was no further buildup of precipitate in the lines for this column.

After almost 2 months of operation, there were only a few weak clumps of CST visible in the top portion of the column using the improved CST. When the column was backwashed after almost 3 months of operation, the entire bed of CST was clumped together and could not be moved, even after shaking the column. The back pressure through the column was still relatively low (5.5 to 7.5 psig), and the column continued to operate normally, even with the CST clumped together. After 105 days of operation, the back pressure increased to over 15 psig, and the flow through the column almost stopped. Both end caps of the column were removed, and a thin metal rod was used to break up the bed of CST, which was lightly cemented together throughout the column, and remove it from the column. The column was then reassembled and backwashed to remove the fines generated by breaking up the bed of CST. The column operated normally for the remainder of the test.

The ICP results for dissolved Al, Si, and Nb in the recirculating simulant solutions showed very little change in the concentrations of aluminum and silicon in the solutions. Initially, there was no niobium in the simulant solutions, but the concentration increased quickly as niobium leached from the CST into solution. The simulant from the baseline CST column showed niobium concentrations of 200 to 400 mg/L. The simulant from the improved CST column stabilized at about 100 mg/L.

Slow increases were noted in the aluminum concentrations of the CST samples from both columns, particularly for the samples from the top of the bed (Fig. 2). Work at Sandia National Laboratory^[7] indicated that cancrinite, $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, forms on the CST particles during storage in SRS simulant solutions. The variation in aluminum concentrations between the top and bottom samples was much more pronounced for the column using the baseline CST. No other metal contaminants were detected at significant concentrations, and the concentrations of the CST components (Na, Si, Ti, Zr, and Nb) decreased very slightly as the aluminum concentration increased.

The cesium-loading results for the CST samples from the column-leaching tests are summarized in Fig. 3. There was a slight decrease in the cesium capacities of the samples from both columns as the run time increased, but the change was much smaller than had been measured previously in similar tests using production batch samples of CST.^[2] The “reference” results are for unused samples of baseline (9090-76) CST that were analyzed with each batch sample from the leaching tests. These results showed good repeatability, which indicates that the loading tests were consistent with a very small decrease measured for the 5- and 6-month tests. Generally, there was only a small difference between

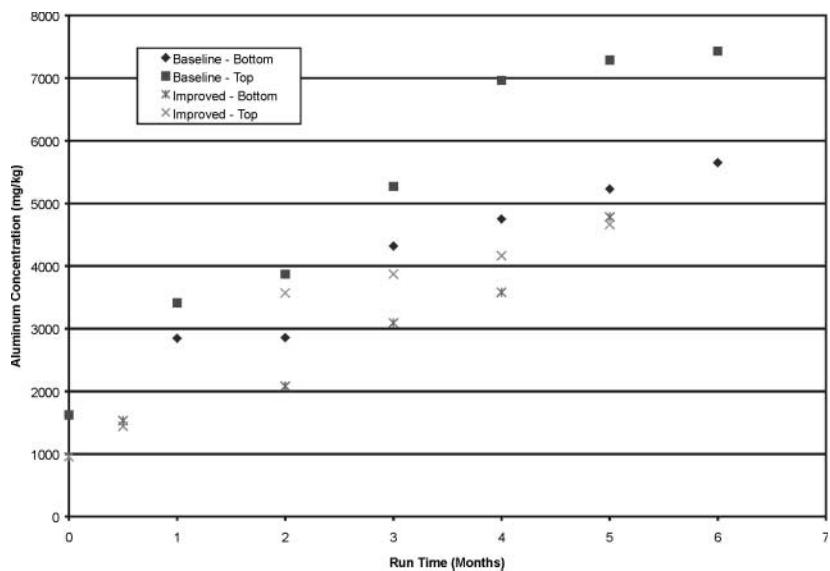


Figure 2. Aluminum concentrations in CST samples from column-leaching test using baseline (9090-76) and improved (MH-9098-9) CST.

the cesium capacities of the top and bottom samples from each column. The column with the improved (MH-9098-9) CST showed an increasing difference between the top and bottom samples after 3 and 4 months of run time. When the column plugged and the CST was removed from the column, the CST was mixed as it was reloaded, so the difference between the top and bottom samples disappeared for the 5-month samples.

The buildup of cancrinite on the CST would reduce the actual amount of CST in the samples used for the cesium-loading tests. By comparing the concentrations of aluminum and titanium in the CST samples, the ratio of CST to cancrinite can be calculated. Cancrinite is 14.8 wt% Al, and the granular CST contains 17.8 wt% Ti. These ratios can be used to calculate an adjusted cesium loading, using only the weight of CST in each sample. The adjusted results for the samples taken from the top of the baseline CST column are shown in Fig. 4. Dilution of the CST by cancrinite accounted for most of the loss in cesium capacity. There was a slight decrease in the adjusted cesium capacity for the CST samples taken after 5 and 6 months of column operation, but the reference sample (unused baseline CST) showed a similar trend. These results indicate that the decrease in cesium capacity was caused by some small variation in the loading tests, rather than a change in the CST for the last two tests. The samples taken

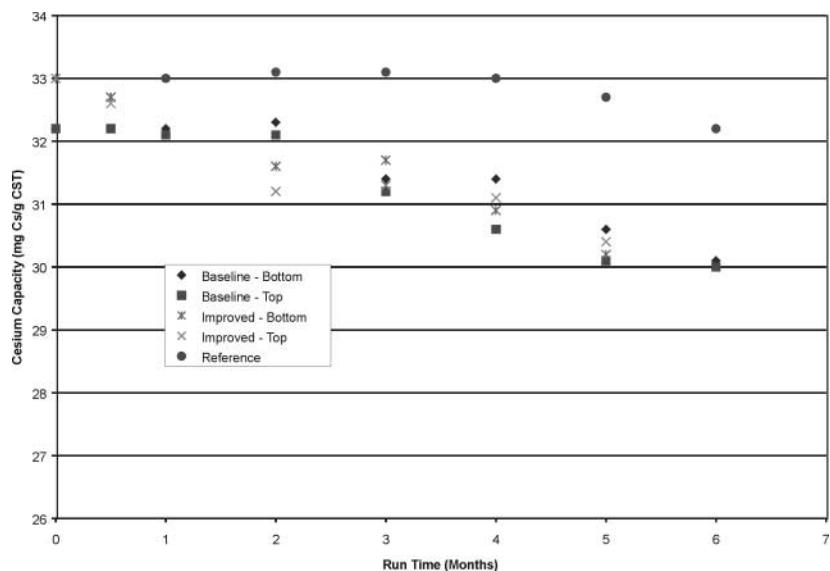


Figure 3. Cesium-loading results for CST samples from the column-leaching tests.

from the bottom of the baseline CST column and both sets of samples from the column with the improved CST showed similar results.

Once-Through-Column Test

The column test using improved (MH-9098-9) CST and SRS average simulant that was pumped once through the column and then discarded and ran for 5 months with no operational problems. The simulant for this test was prepared in 100- to 200-L batches, and each batch was stored for at least 1 month before being used. A small amount of precipitate collected in the bottom of the drum, but the suction line for the pump feeding the column was kept above the settled solids. The measured flow rate of the simulant exiting the column ranged from 1.5 to 2.4 mL/min, and a total of 430 L of simulant was used during the test. The pressure drop through the column stayed below 5 psig for the entire test. At the end of the test, the flow rate was increased to 6.0 mL/min, and the pressure drop increased to 6 psig, which is similar to the results that were obtained for the columns using recirculating simulant (described previously) when they were operating normally at this flow rate.

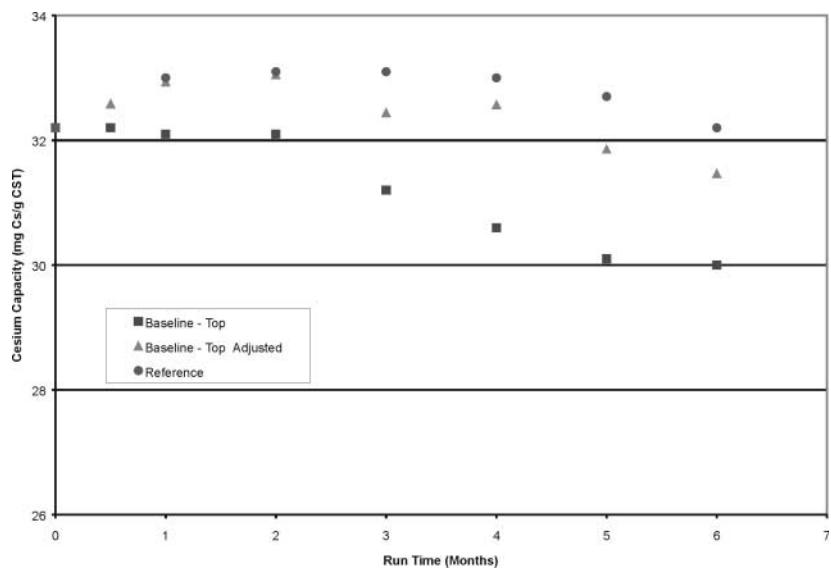


Figure 4. Measured and adjusted cesium capacity for CST samples from the top of the baseline column.

Samples of CST were collected from the top, middle, and bottom of the column after 1 month and 5 months of operation. For the 1-month samples, the CST moved easily through the sampling valves, but for the 5-month samples, a wire was used to break up the CST before it could be moved through the valves. When the CST was removed from the column at the end of the test, the entire bed was weakly clumped together.

Samples of column effluent and the simulant feed were analyzed periodically. Initially, the aluminum concentration in the effluent was less than that in the feed, indicating that some aluminum was precipitating within the column. For the middle portion of the test, the feed and effluent aluminum concentrations were about the same. During the last month of operation, the effluent concentrations were lower, again indicating precipitation of aluminum within the column. No niobium was added to, or detected in, the simulant feed, but the effluent concentration ranged from 4 to 13 mg/L, indicating slight dissolution of niobium from the CST. A total of 2.6 g of niobium was leached from the 250 g of CST in the column during the 5 months of operation.

Table 2 shows a summary of the aluminum concentration and the cesium capacity for the CST samples from the once-through column test. The sample



Table 2. Aluminum concentration and measured and adjusted cesium loading capacity for CST samples from the once-through-column test.

CST sample description	Aluminum (mg/kg)	Cesium capacity (mg Cs/g CST)	Adjusted cesium capacity (mg Cs/g CST)
Bottom—1 month	844	31.2	31.4
Middle—1 month	889	30.5	30.7
Top—1 month	1420	30.6	30.9
Bottom—5 month	1256	29.8	30.1
Middle—5 month	2575	29.7	30.3
Top—5 month	11005	10.2	11.1

taken from the top 1 cm of the CST bed after 5 months of operation showed a dramatic decrease in cesium capacity and an increase in aluminum concentration. This high-aluminum concentration indicates that about 10% of the CST sample from the top of the column was cancrinite; however, the loss in cesium capacity was much larger than what could have been caused by simple dilution of the sample by cancrinite. This effect has been seen in the past with other CST samples that contained significant amounts of cancrinite, and it is likely that the drop in cesium capacity was caused by the cancrinite blocking access to the inner pores of the CST.

Batch-Leaching Tests

The baseline and improved granular CST samples stored at 80°C in the average simulant were both weakly agglomerated after 1 month of storage. After 2 months of storage, the improved CST sample stored at 50°C was also weakly clumped together. After 3 months, the baseline and improved CST samples stored at 35°C had formed clumps. The baseline CST sample stored at 50°C and both CST samples stored at 23°C did not form any clumps. It is not clear why the baseline CST stored at 50°C responded differently from all of the other CST samples stored at elevated temperatures. The existing CST clumps did not become any more difficult to break apart as the storage time increased. While taking the monthly samples, portions of the clumped CST were broken up, and this CST did not reform into clumps during subsequent storage periods. The samples of CST powder did not form the hard clumps that were observed for the granular CST samples.

In previous batch-leaching tests with production CST samples, all of the samples stored at elevated temperatures had formed clumps within the first

month, and the samples stored at room temperatures had formed clumps during the second month.^[2] The baseline CST was manufactured using the same process as the production samples from last year, but the pretreatment prior to use was slightly different. The production CST samples were pretreated to a pH of 13 (0.1-M NaOH) using recirculating sodium hydroxide, and the baseline CST sample was pretreated using 3-M NaOH in a once-through mode. The higher concentration of NaOH dissolves more impurities from the CST, and the once-through mode does not allow these impurities to reprecipitate within the bed of CST.

For all of the batch-leaching test conditions, the aluminum concentration in the simulants slowly decreased as the aluminum precipitated from the solution. A summary of the results for the three types of CST stored at 25 and 80°C is shown in Fig. 5.

Some niobium was leached from the CST samples into the supernate simulant, with higher concentrations of soluble niobium measured for the samples stored at lower temperatures. The soluble-niobium concentration depends on both the leaching rate from the CST and on any reprecipitation of the niobium. The amount of niobium leached from the CST powder sample at

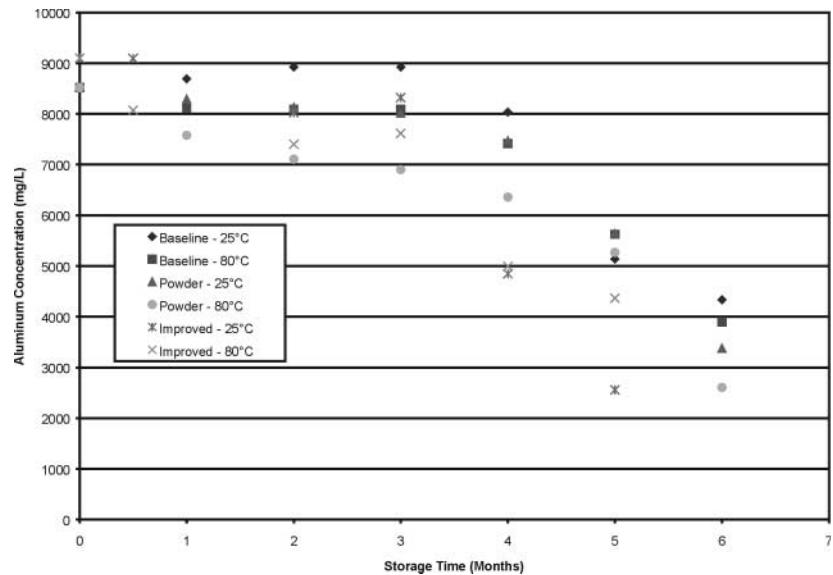


Figure 5. Aluminum concentration in simulant samples from batch-leaching tests using baseline and improved granular CST and CST powder.

room temperature was much higher than that leached from the granular CST samples, and the improved CST showed the lowest concentrations. The results for the samples stored at 25 and 80°C are shown in Fig. 6.

The CST in all of the batch tests showed increasing concentrations of aluminum over time, particularly at the higher temperatures. A summary of the results for samples stored at 25 and 80°C is shown in Fig. 7. No other metal contaminants were detected at significant concentrations in the samples of CST, and the concentrations of the CST components (Na, Si, Ti, Zr, and Nb) decreased very slightly as the aluminum concentration increased. The measured concentrations of Si showed much more scatter than was observed for the other elements, and this same effect was seen for the samples analyzed last year. The variation seems to be caused by the sample preparation (digestion and dilution) process, since there is less variation within each group of samples that are prepared at the same time, as compared with groups of samples prepared at different times. Fluorine from the hydrofluoric acid used in the digestion process can form volatile compounds with silicon, which could evaporate from the solubilized CST.

Storage temperature had a strong effect on the cesium capacity of the CST samples from the batch-leaching tests, with a drop of about 15% for

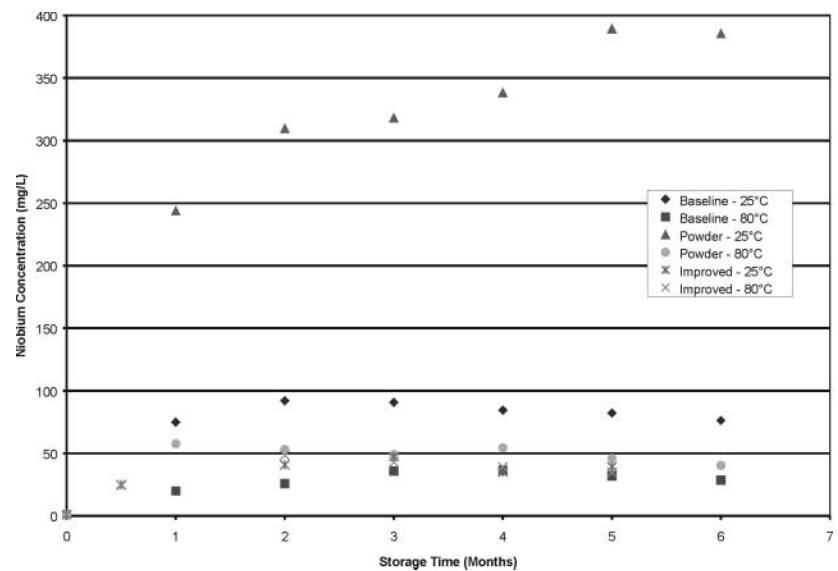


Figure 6. Niobium concentration in simulant samples from batch-leaching tests using baseline and improved granular CST and CST powder.

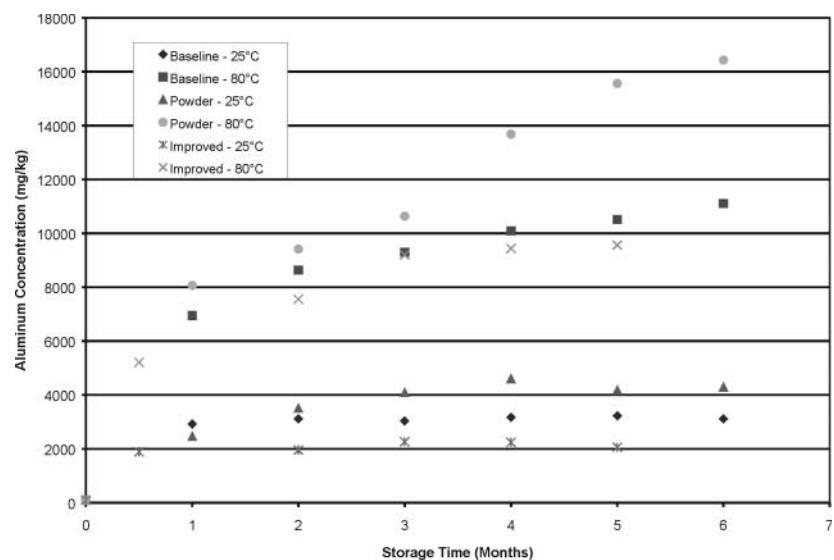


Figure 7. Aluminum concentration in CST samples from batch-leaching tests using baseline and improved granular CST and CST powder.

samples stored at 80°C compared with samples stored at 23°C (Table 3). The cesium capacity of the baseline and improved CST samples was almost the same. The CST powder shows a higher capacity because it lacks the zirconia binder that dilutes the CST in the granular samples. The samples stored at 23°C showed only a very small decrease in cesium

Table 3. Average cesium-loading capacities for CST samples stored at 23 and 80°C for up to 6 months.

CST		Cesium capacity (mg Cs/g CST) \pm SD		
		Stored at 23°C	Stored at 80°C	Change (%)
9090-76	Baseline	31.5 \pm 0.28	26.6 \pm 1.0	15.5
30950-48	Powder	36.1 \pm 0.34	30.6 \pm 2.0	15.2
MH-9098-9	Improved	31.6 \pm 0.53	26.8 \pm 1.5	15.2

All of the cesium-loading tests were performed at 23°C using average simulant that initially contained 50 mg/L cesium.

capacity as the storage time in the simulant increased up to 6 months, whereas the samples stored at 80°C showed a slow, steady decrease in cesium capacity (Fig. 8). The results of the cesium-loading tests on the reference samples (unused baseline CST) were very consistent, with a very slight decrease for the 5- and 6-month samples, which indicates that the loading tests were reproducible. Figure 8 also shows the results for an adjusted cesium capacity that was calculated by eliminating the weight of cancrinite from the measured sample weights. The amount of cancrinite was calculated from the measured concentrations of aluminum and titanium in each CST sample. The weight of cancrinite does not account for all of the drop in cesium capacity, so an additional mechanism, such as blocking access to the CST pores, is also involved in the loss of cesium capacity. Samples of production batches of CST tested last year showed more pronounced losses in cesium capacity, with drops of 18 to 20% for samples stored at 80°C for 2 months and longer.

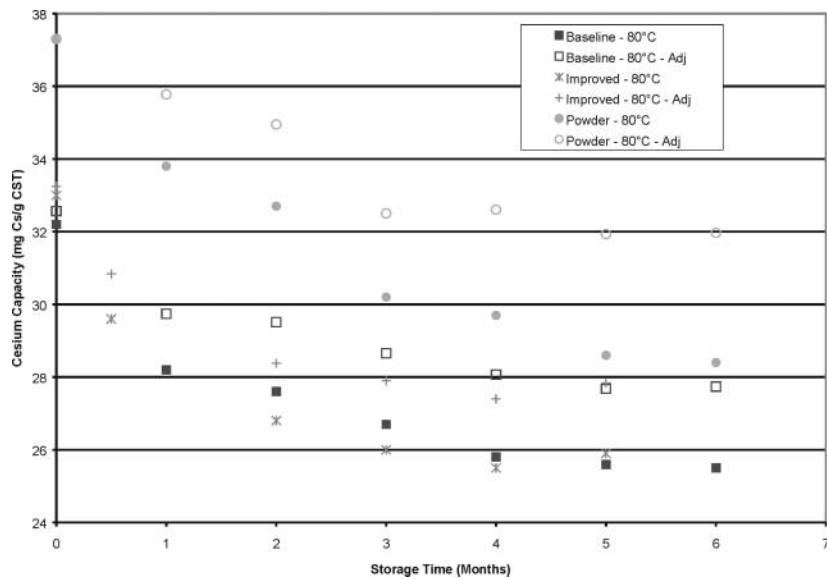


Figure 8. Results of cesium-loading tests for CST samples from batch-leaching tests stored in SRS average simulant at 80°C. The adjusted capacities were calculated by eliminating the weight of cancrinite in each sample.



CONCLUSION

Experimental determination of the chemical stability of baseline and improved granular CST and the CST powder used to make both granular samples has been completed. The work was performed to evaluate the long-term chemical stability of these CST samples when exposed to supernate simulant using a range of possible operating conditions and temperatures and to compare the results to similar tests performed last year on production samples of CST.

The column tests using recirculating simulant showed that the baseline CST generated more precipitates of sodium aluminosilicate than the improved CST. The precipitates were particularly evident in the tubing that carried the simulant solution to and from the column, but the baseline CST also showed higher concentrations of aluminum on the CST than was observed for the improved CST. The sodium aluminosilicate formed bridges between the CST granules, causing clumps of CST to form in the column. Clumps were visible in the baseline CST column after 1 month of operation and in the improved CST column after 2 months. For the baseline CST column, the clumps were routinely dispersed by backwashing the column with simulant. After 96 days of operation, a thin, hard layer of CST formed on the bottom screen of the baseline column that restricted flow through the column. The bottom cap was removed, and the CST was scraped from the screen to restore the column to normal operation. After 3 months of operation, the improved CST column had completely clumped together and could not be dispersed by backwashing. The pressure drop through the column was still relatively low, so the test was continued until the pressure drop increased to > 15 psig, which occurred after 105 days of operation. The column was then disassembled, and the CST was physically removed from the column and broken up. These results show that when in contact with the supernate simulant, both the baseline and improved CST have the potential to form clumps that can restrict the flow through the small columns used in these tests.

The cesium capacity of the CST samples from the column test decreased slightly as the run time increased. Most of the drop was caused by the weight of cancrinite (a sodium aluminosilicate) that precipitated on the CST samples. Earlier tests using samples of production batches of CST showed a more pronounced drop in cesium capacity under comparable conditions.

The column test with improved CST and once-through simulant showed few problems during 5 months of operation. The pressure drop through the column remained low; however, the CST in the column was clumped together when the final samples were taken after 5 months. The final sample taken from the top of the column showed a 65% drop in cesium capacity as compared with the other samples taken from this column. This sample also contained



the highest concentration of cancrinite, but the weight of cancrinite could only account for a small fraction of the drop in cesium capacity by simple dilution of the CST, suggesting that an additional mechanism is involved in the drop in cesium capacity. The cancrinite may block access to the pores of the CST particles, limiting transport of cesium to the exchange sites.

The CST in the batch tests stored at elevated temperatures in average simulant formed clumps, but this occurred at a slower rate than was observed for earlier tests using production batch samples of CST. Storage at elevated temperatures caused a gradual decrease in cesium capacity as the storage time increased, with a loss in capacity of up to 20% after 5 to 6 months at 80°C. The results for the baseline and improved CST samples were essentially the same for the batch tests.

REFERENCES

1. Taylor, P.A.; Mattus, C.H. *Thermal and Chemical Stability of Crystalline Silicotitanate Sorbent*; ORNL/TM-1999/233; Oak Ridge National Laboratory: Oak Ridge, TN, 1999; 1–31.
2. Taylor, P.A.; Mattus, C.H. *Thermal and Chemical Stability of Crystalline Silicotitanate Sorbent*; ORNL/TM-2000/307; Oak Ridge National Laboratory: Oak Ridge, TN, 2001; 1–29.
3. Wilmarth, W.R.; Dukes, V.H.; Mills, J.T.; Fondeur, F.F. *Effect of Sodium Hydroxide Pretreatment of UOP IONSIV® IE-911 Crystalline Silicotitanate Sorbent*; WSRC-TR-2000-00167; Westinghouse Savannah River Company: Aiken, SC, 2000; 1–28.
4. Krumhansl, J.L.; Zhang, P.C.; Jove-Colon, C.; Anderson, H.L.; Moore, R.C.; Salas, F.M.; Nenoff, T.M.; Lucero, D.A. *A Preliminary Assessment of IE-911 Column Pretreatment Options*; SAND2001-1002; Sandia National Laboratory: Albuquerque, NM, 2001; 1–33.
5. Su, Y.; Li, L.; Young, J.S.; Balmer, M.L. *Investigation of Chemical and Thermal Stabilities of Cs-Loaded UOP IONSIV® IE-911 Ion Exchanger (Final Report)*; PNNL-13392-2; Pacific Northwest National Laboratory: Richland, WA, 2001; 1–35.
6. Walker, D.D. *Preparation of Simulated Waste Solutions*; WSRC-TR-99-00116, Rev. 0; Westinghouse Savannah River Company: Aiken, SC, 1999; 1–12.
7. Nyman, M.D.; Headley, T.J.; Nenoff, T.M.; Bustard, L.D. *Performance of IE-911: Characterization of As-Received, NaOH-Treated and Simulant-Treated CST*; SAND2001-0435P; Sandia National Laboratories: Albuquerque, NM, 2001; 1–33.