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Cesium Batch Contact Equilibrium Testing of Crystalline Silicotitanate (CST) Sieve Cuts in SRS Average Simulant and Examination of CST Samples Aged in Caustic and Simulant in Support of Tank Closure Cesium Removal 1A (TCCR-1A)

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Cesium Batch Contact Equilibrium Testing of Crystalline Silicotitanate (CST) Sieve Cuts in SRS Average Simulant and Examination of CST Samples Aged in Caustic and Simulant in Support of Tank Closure Cesium Removal 1A (TCCR-1A)

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EXECUTIVE SUMMARY

Batch contact testing to determine cesium equilibrium loading on Crystalline Silicotitanate ion exchange media in Savannah River Site Average Waste Simulant at 25 °C indicated that smaller diameter particles isolated by sieving pretreated CST media may load slightly higher (<10%) amounts of cesium, though the differences are within analytical uncertainty. In addition, ion exchange media sub-samples stored in 2-4 M NaOH and caustic simulant solutions for ~2.5 years were examined by optical microscopy and the 3 M NaOH sample was also analyzed to determine whether changes in the particle size distribution occurred during storage. No visual indications of particle attrition or agglomeration were observed for any sample. Particle size analysis indicated that a slight decrease occurred in the average particle diameter following contact with 3 M NaOH (541 µm average diameter versus 566 µm for the pretreated CST prior to contact). A small increase (from 0 to <0.5 wt. %) in the number of particles ranging from 271 and 322 µm was also observed for the CST sample contacted with 3 M NaOH relative to a sample of the original pretreated material. However, this small change could be due to sub-sampling differences or analytical uncertainty. It does not appear that small particles are formed to a significant degree during CST caustic contact or that small particles which do form (presumably from attrition of larger particles during pretreatment) load significantly more cesium than the bulk material. Minimal other negative consequences were observed associated with CST extended caustic or simulant contact, except for the tendency for more concentrated salt solutions to form some salt crystals which deposit on the media over time.

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LIST OF ABBREVIATIONS

CST	Crystalline Silicotitanate
ICP-ES	Inductively Coupled Plasma - Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma - Mass Spectroscopy
ISS	Interim Safe Storage
K_d	Distribution Coefficient
PT1	Pretreatment #1
RPM	Rotations per Minute
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TCCR	Tank Closure Cesium Removal
TGA	Thermal Gravimetric Analysis

1.0 Introduction

The Tank Closure Cesium Removal (TCCR) Process utilizes Crystalline Silicotitanate (CST) ion exchange media in column configuration to remove cesium from radioactive dissolved saltcake solutions at the Savannah River Site (SRS). The columns from the first TCCR unit (TCCR Demo) have been removed and transferred to an Interim Safe Storage (ISS) pad at SRS. A new batch of CST media (R9120-B 30x60 Lot #2102020756) with a smaller particle size has been received from the supplier and a small sample of the CST has been pretreated at the Savannah River National Laboratory (SRNL) to determine the requirements for conversion to the sodium media form and prepare material for testing. In the field, the new CST media will be loaded into new columns, and the columns will be loaded into the TCCR unit where the media will be pretreated in preparation for decontaminating radioactive waste solutions. Dissolved saltcake waste from SRS Tank 9H has been transferred to Tank 10H, which serves as the feed tank for the TCCR unit. The processing campaign using the new media and columns will be referred to as TCCR 1A.

Sieve cuts of sodium-form TCCR 1A CST media following pretreatment (water up flow fines elutriation, downflow NaOH conditioning, and water washing in a column configuration followed by media removal from the column and air drying to constant mass) were isolated as described in a previous report.[i] Smaller particles than expected (passing through 60 mesh or smaller standard screens) were observed and subsequently removed from the bulk media by sieving. This resulted in three particle size fractions of pretreated CST media including two cuts below 60 mesh. These sieve cuts were evaluated by batch contact testing with waste simulant solution to determine if the cesium loading characteristics of the small diameter CST particles differed from the bulk media.

In addition, samples of CST from the batch used in the TCCR Demo (R9120-B CST Lot #2099000034) have been stored in caustic solution and SRS Average Simulant for nearly 2.5 years. A report describing studies evaluating the impacts of CST storage in caustic was issued previously after 8 months of contact.[ii] Sub-samples of these CST samples were retrieved and evaluated by optical microscopy and the particle size of one sample was determined for comparison to previously reported data for the pretreated CST prior to caustic contact. The caustic solution from this sample was also analyzed to determine the concentrations of various metals known to leach from CST.

2.0 Experimental Procedure

2.1 Batch Contact Equilibrium Testing of Various CST Sieve Cuts

Samples of sodium-form, pretreated CST sieve cuts (R9120-B 30x60 Lot #2102020756) isolated as described in a previous report[i] were used for CST batch contact equilibrium testing in SRS Average Simulant to determine the cesium distribution coefficients (K_d) for each particle size range. The CST sub-samples had been isolated following media Pretreatment #1 (PT1) in the earlier report. The as-received hydrogen-form media (prior to pretreatment) was expected to be in the sieve mesh size range +30 to -60 and CST does not shrink or swell significantly upon conversion to the sodium ionic form. However, following pretreatment small particles were observed and subsequently removed using 60 and 120 mesh U.S. Standard stainless steel screens. This resulted in three particle size fractions of pretreated CST media: -120 mesh, +120 to -60 mesh, and +60 mesh (where "-" and "+" indicate particles passing and not passing, respectively, through a given screen size opening). A sample representing the pretreated CST media particle size distribution prior to sieving was also reconstituted by blending known masses from each of these sieve fractions at the reported mass ratios of each sieve cut. The mass ratio of the reconstituted composite CST blend was 0.056 g:0.2697 g:1.6085 g (corresponds to 2.9, 13.9, and 83.2 wt. %, respectively) for the -120 mesh, +120 to -60 mesh, and +60 mesh cuts, respectively. This sample was referred to as the RECONST-COMP.

Thermal Gravimetric Analysis (TGA) was conducted in duplicate on small sub-samples (collected at the same time as batch contact sub-samples) of each CST sieve cut and the reconstituted composite to determine the water content of each material. The thermal analysis involved heating reference-state, sodium-form CST sub-samples at a rate of 5 °C per minute to 400 °C and holding the sample at that temperature for 240 minutes followed by a second heating period up to 700 °C. The total mass loss was determined as the sum of several successive mass losses believed to be associated with both physiosorbed and chemisorbed water. Cumulative mass loss data for each CST sample up to 400 ºC is summarized and average F-factor (water content mass correction factor; F-factor = dry CST mass/reference-state hydrated mass) values are provided in Table 2-1. Percent relative standard deviation values were below 0.25% for all four samples based on the duplicate sample data. Small mass losses (<0.5 wt %) were observed between 400 and 700 ºC for all samples. A mass loss versus temperature profile for one reconstituted composite R9120-B 30x60 CST sub-sample is provided in Figure 2-1. This mass loss profile was typical of all of the sub-samples from the various sieve cuts analyzed and is very similar to profiles reported elsewhere for R9120-B (TCCR Demo) CST.[iii] The average F-factor for each CST sample was used to convert the hydrated, reference-state CST mass to a dry mass basis.

An archived sample of SRS Average Simulant with the target simulant composition provided in Table 2-2 was used for batch contact equilibrium testing. This simulant was used in previous batch contact testing described in an earlier report,[iv] although the cesium concentration used in the current testing differed from the previous testing since the solution was prepared by blending three previous simulant batches. The simulant was filtered prior to use with 0.45 µm filters. The filtered simulant density was determined to be 1.251 g/mL (mass of 25 mL at 22 °C: 31.2847 g). The simulant was analyzed by Inductively Coupled Plasma - Emission Spectroscopy (ICP-ES) to confirm that the concentrations of the major metals had not changed significantly. The measured concentrations of metals above detection were: 5.22 M Na^+, 0.29 M Al, 0.16 M S, 0.015 M K^+, 0.011 M P, 0.0016 M Si, and 0.00021 M Mo. The analysis results confirmed that the metals were in the expected range based on the measurement uncertainty, except for silicon which was 60% lower than the target value of 0.004 M.

Table 2-1. F-Factor Mass Correction Data for R9120-B 30x60 CST (Lot #2102020756) Samples Used for Batch Contact Testing.

Sample	Mesh Range[a,b]	Mesh Opening µm Range[a,b]	F-Factor[c]	Average F-Factor	F-Factor %RSD
LT120 Rep. 1	-120	<125	0.8131	0.8127	0.07
LT120 Rep. 2			0.8123		
GT120TOLT60 Rep. 1	+120 to -60	125-250	0.8103	0.8099	0.08
GT120TOLT60 Rep. 2			0.8094		
GT60 Rep. 1	+60	>250	0.8063	0.8074	0.19
GT60 Rep. 2			0.8084		
RECONST-COMP Rep. 1[c]	original mesh size range following pretreatment		0.8093	0.8080	0.24
RECONST-COMP Rep. 2[c]			0.8066		

[a] U. S. Standard mesh sieves

[b] As-received, hydrogen-form media was specified to be 30x60 mesh (250-595 µm). All samples in this table were previously pretreated to convert the media to sodium form.

[c] The F-factor is the multiplication factor required to convert the measured hydrated, reference-state CST mass to a dry mass basis based on TGA mass loss up to 400 °C.

[d] RECONST-COMP = reconstituted composite CST prepared by mixing the three sieve cuts at the initial measured mass ratios to reconstitute the original mixture

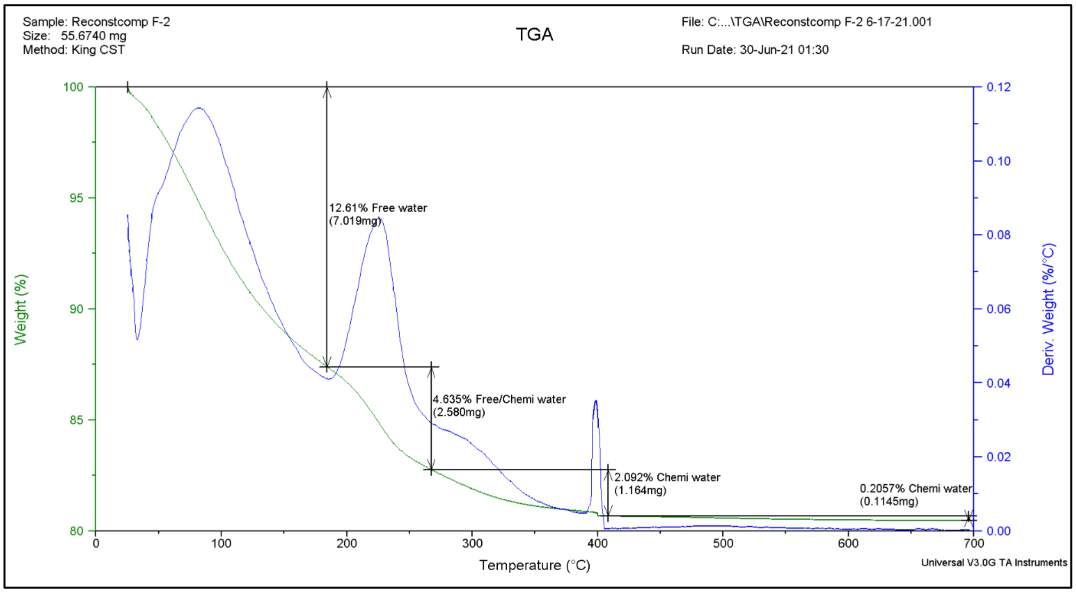


Figure 2-1. TGA Mass Loss Profile for Sodium-Form, Reconstituted Composite CST from Batch R9120-B 30x60 Lot #2102020756.

Table 2-2. SRS Average Simulant Target Composition.

Component	Molarity
Na^+	5.60
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-}	0.01
$C_2O_4^{2-}$	0.008
SiO_3^{2-}	0.004
MoO_4^{2-}	0.0002
Cs^+	4.0E-05

Batch contact equilibrium tests were conducted by collecting representative ~0.1 g samples (hydrated, reference-state mass) of each CST sieve cut and the reconstituted sample by combining 4-5 smaller portions of CST particles in a 60 mL plastic test vial. Duplicate test samples were prepared of each sieve cut. Approximately 10 mL of filtered simulant were added to each bottle. The bottles were capped and placed in an incubated shaker oven and maintained at a set temperature of 23 °C for 5.9 days with continuous orbital agitation at a rotation rate of 150 RPM. The bottles were subsequently removed from the oven and the samples were immediately filtered through 0.45 μm syringe filters into a second plastic bottle and submitted for cesium analysis by Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS). Duplicate samples of the simulant feed solution without added CST were handled in an identical manner (plastic bottles agitated in the oven and filtered) and analyzed along with the samples contacted with CST. Equilibrium cesium distribution coefficients ($K_d = [(C_i/C_f)-1][V/(M*F)]$; where C_i and C_f correspond to initial and final simulant cesium concentrations, V = simulant volume in milliliters, M = CST reference-state mass in grams, and F is the F-factor mass correction for CST water content) were calculated based on analytical results and CST and simulant masses.

2.2 Examination and Analysis of the CST Samples Aged in Caustic Solutions

R9120-B CST samples (Lot# 2099000034) stored in 2-4 M NaOH solutions and SRS Average Simulant for approximately 2.5 years in plastic bottles were examined and photographed by optical microscopy. The preparation and initial examination of these samples were described in an earlier report.[ii] These samples were returned to the original bottles following examination.

In addition, approximately half of the CST sample stored in a plastic bottle in 3 M NaOH was subsequently retrieved along with a portion of the caustic solution. The CST was submitted for particle size analysis and a portion of the liquid was filtered and analyzed by ICP-ES to determine the concentrations of selected species known to leach from CST. The remaining portion of the sample was returned to storage.

2.3 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.0 Results and Discussion

3.1 Batch Contact Equilibrium Testing of Various CST Sieve Cuts

Analysis results for SRS Average Simulant samples prior to and after batch contact with sieve cuts of CST media batch R9120-B 30x60 are provided in Table 3-1. Duplicate tests were conducted with sub-samples of four different sieve cuts of CST media isolated and prepared as described in a previous report**Error! Bookmark not defined.** and in Section 2.1 of this report. The initial concentration of cesium in the SRS Average Simulant used for testing was 5.16 mg/L (average of analytical results in Table 3-1) which corresponds to 3.85 E-05 M. The samples were agitated for 5.9 days, filtered to remove the CST, and analyzed to determine the cesium concentration. The final cesium concentrations for all samples ranged from 0.038 to 0.041 mg/L which is greater than an order of magnitude lower than the initial cesium concentration and corresponds to 92-93% Cs^+ removal. Average cesium distribution coefficients ranged from 1429 mL/g for the CST particles greater than 60 mesh (>250 μm) to 1527 mL/g for particles less than 120 mesh (<125 μm). For comparison, previous batch contact testing with the TCCR Demo CST batch and this simulant at initial cesium concentrations ranging from 5.1 E-6 to 9.9 E-04 M resulted in distribution coefficients ranging from 1273 to 1812 mL/g.[iv] These results indicate that the maximum cesium loading on the particles below 125 μm may be 6.9% higher than the maximum loading for particles greater than 250 μm. The average distribution coefficient for particles in the size range 125 to 250 µm of 1512 was 5.8% higher than the K_d for particles greater than 250 µm. The distribution coefficient for the reconstituted composite CST sample (which contains 16.8 wt. % particles below 250 µm) was slightly higher (0.3%) than was observed for the particles greater than 250 µm. The distribution coefficients for the particles below 125 and 250 µm are 6.5 and 5.5% higher, respectively, than the reconstituted composite sample which represents pretreated and unsieved CST. The data trends indicate that smaller particles load a slightly larger amount of cesium than the bulk material, although the differences in the results are not statistically significant (ICP-MS uncertainty: ±20%).

Table 3-1. Analysis Results for CST Batch Contact Samples.

Analytical Sample ID	Sample Description[a]	CST (g)[b]	SRS Average Simulant (mL)	Cs^+ (µg/L)	Cs^+ K_d (mL/g)[c]	Average Cs^+ K_d (mL/g)[c]	Cs^+ K_d %RSD
LW22807	CST-PT1-LT120-1	0.1001	9.93	3.86E+02	1507	1527	1.80
LW22808	CST-PT1-LT120-2	0.1000	9.91	3.77E+02	1546		
LW22809	CST-PT1-GT120TOLT60-1	0.1000	9.90	3.87E+02	1507	1512	0.49
LW22810	CST-PT1-GT120TOLT60-2	0.0999	9.91	3.85E+02	1517		
LW22811	CST-PT1-GT60-1	0.1006	9.91	4.06E+02	1427	1429	0.22
LW22812	CST-PT1-GT60-2	0.1003	9.88	4.05E+02	1431		
LW22813	CST-PT1-RECONST-COMP-1	0.1001	9.85	4.04E+02	1432	1434	0.15
LW22814	CST-PT1-RECONST-COMP-1	0.1003	9.86	4.03E+02	1435		
LW22815	Feed-1	---	10.01	5.09E+03	---		
LW22816	Feed -2		10.05	5.23E+03			

[a] CST = crystalline silicotitanate, PT1 = Pretreatment #1, LT120 = <120 mesh, GT120TOLT60 = >120 to <60 mesh, GT60 = >60 mesh, RECONST-COMP = reconstituted composite

[b] hydrated, reference state, sodium-form mass (All batch contact test samples utilized hydrated R9120-B 30x60 CST Lot #2102020756.)

[c] Calculated based on F-factor data for each sieve cut provided in Table 2-1.

3.2 Examination and Analysis of the CST Samples Aged in Caustic Solutions

In November of 2019, sub-samples of sodium-form, pretreated R9120-B CST (major media batch used for initial SRS TCCR Demonstration) were placed in NaOH solutions ranging from 2 to 4 M and in a sample of SRS Average Simulant. The samples were stored in sealed plastic and glass bottles. Observations on these samples over an 8-month time period were reported in SRNL-STI-2019-00463.[ii] Although the report was issued in 2019, the samples have remained in storage since that time. After approximately 2.5 years (29-32 months) in storage with no agitation, selected samples in the plastic bottles were retrieved and examined by optical microscopy and measured by Microtrac particle size analysis. A sample of the liquid phase from the 3 M NaOH contact was also analyzed to determine the concentrations of Si, Ti, Zr, and Nb.

Optical micrographs of the CST samples stored in 2, 3, and 4 M NaOH and in simulant solution in plastic bottles are provided in Figure 3-1, Figure 3-2, Figure 3-3, and Figure 3-4, respectively. There was little indication of particle attrition, cracking, or agglomeration after extended storage in these solutions. The particle shapes observed were typical of CST media. A few salt crystals were observed in the samples stored in 4 M NaOH (Figure 3-3) and SRS Average simulant (crystals not shown in Figure 3-4). The crystal shapes in both of these solutions appeared to be hexagonal. In simulant solution a hexagonally shaped crystal might correspond to sodium nitrate which crystallizes in the hexagonal system. Hexagonally shaped crystals should not be observed in sodium hydroxide solution, since the crystal system is orthorhombic. No crystals were observed in 2 and 3 M NaOH solutions containing CST. The crystals appeared to adhere to the CST particles, but no indication of bridging or agglomeration of CST particles was observed. Otherwise, no apparent negative consequences from extended storage in caustic solutions were observed.

A portion of the CST stored in 3 M NaOH in a plastic bottle was submitted for Microtrac particle size analysis to determine whether particle attrition occurred during storage. Results are provided in Figure 3-5 and Figure 3-6 for the two replicate samples analyzed. The average volume-based mean particle diameter observed for the two sub-samples of CST stored in caustic for 2.5 years was 540.6 μm (%RSD for two replicates of 5.2%). The measured particle diameters ranged from 271 to 1408 μm, which is the upper limit of the instrument (upper data channel ranged from 1291 to 1408 μm and contained <0.25% of the particles for each replicate). For comparison, the mean volume-based diameter (based on Mictrotrac data) of the pretreated particles from this CST batch prior to extended contact with NaOH solution was 566 μm, which is 4.7% larger than the mean value determined after caustic aging.[v] The range of diameters observed for the pretreated CST particles from Lot #2099000034 prior to caustic contact was 322 to 1408 μm. The percentage of particles below 322 μm (in the range from 271 and 322 μm) in the samples aged in caustic was <0.5% for the two sub-samples. This comparison indicates that a minor shift toward smaller particle diameters may have occurred during CST caustic contact, but the differences between the caustic-aged sample and the original pretreated sample are believed to be within the measurement and sub-sampling uncertainties.

A portion of the caustic solution isolated from the CST sample stored in 3 M NaOH in a plastic bottle was filtered and analyzed to determine the concentrations of metals known to leach from CST. The results are provided in Table 3-2. The primary metal observed in the solution was silicon which was present at a concentration of 149 mg/L (5.3E-03 M). No detectable titanium or niobium was observed. Zirconium was observed at a low concentration of 2.4 mg/L (2.6E-05 M). For comparison, the maximum concentrations of these metals observed during caustic pretreatment of the TCCR Demo R9120-B CST batch were 250 mg Si/L, 10 mg Ti/L, 11 mg Zr/L, and 95 mg Nb/L.[iii] The maximum concentrations of these metals observed during caustic pretreatment and subsequent water washing of the R9120-B 30x60 TCCR 1A CST batch were 12 mg Ti/L, 4 mg Zr/L, and 214 mg Nb/L, with the latter two concentrations being observed in the water wash (silicon was not analyzed).[i] (Note: The above metal concentrations for each CST batch were measured during pretreatment under dynamic flow conditions in a column rather than from a batch contact sample.) The relatively high silicon concentration observed for the 3 M NaOH sample after extended contact with TCCR Demo CST indicates that some degree of dissolution of a media component has occurred. The fact that titanium and niobium were not observed above detection indicates that the soluble portions of these metals were removed during pretreatment.

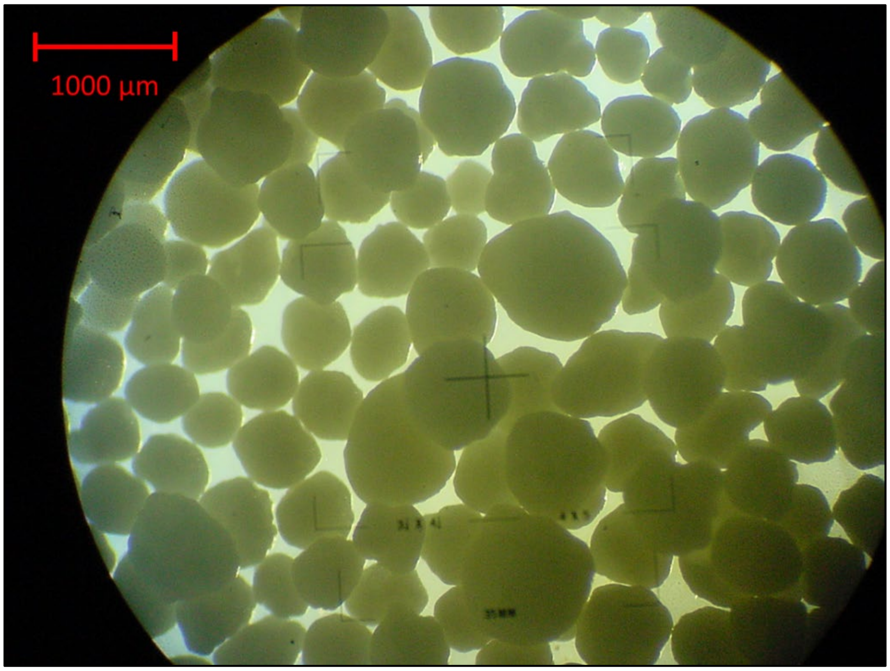


Figure 3-1. Optical Micrograph of CST Stored in 2 M NaOH for ~2.5 Years (back lighting).

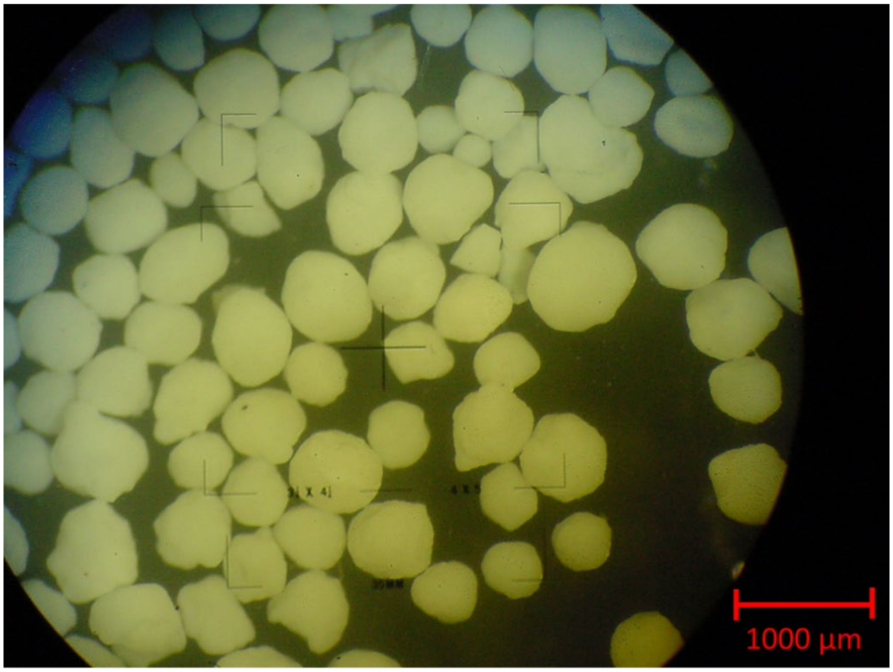


Figure 3-2. Optical Micrograph of CST Stored in 3 M NaOH for ~2.5 Years (front lighting).

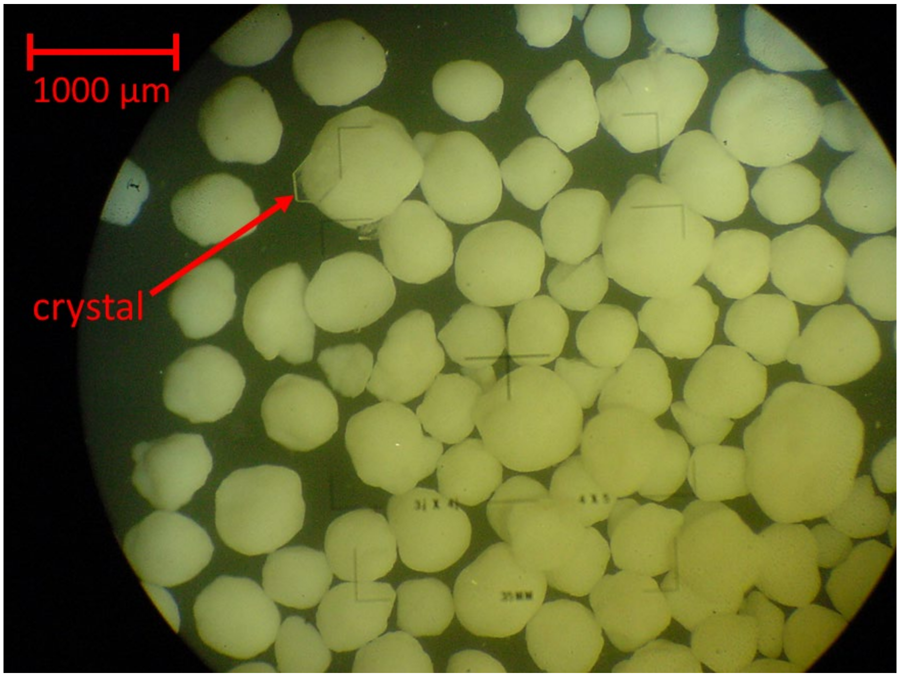
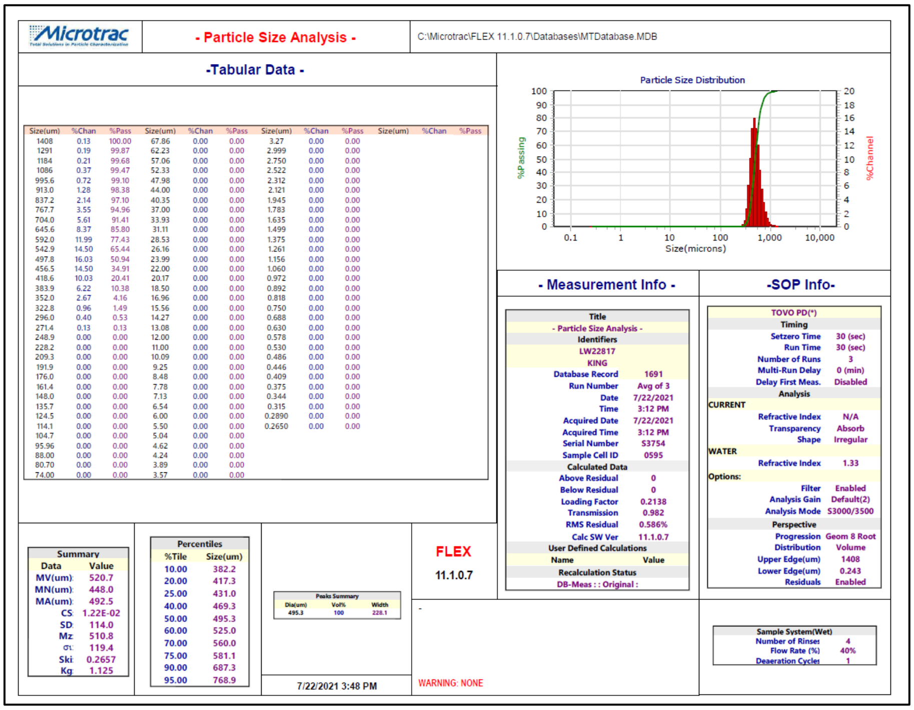


Figure 3-3. Optical Micrograph of CST Stored in 4 M NaOH for ~2.5 Years (front lighting).

Figure 3-4. Optical Micrograph of CST Stored in SRS Average Simulant for ~2.5 Years (front lighting).



- Particle Size Analysis -

C:\Microtrac\FLEX 11.1.0.7\Databases\MTDatabase.MDB

-Tabular Data -

Size(um)	%Chan	%Pass	Size(um)	%Chan	%Pass	Size(um)	%Chan	%Pass	Size(um)	%Chan	%Pass
1408	0.13	100.00	67.86	0.00	0.00	3.27	0.00	0.00			
1291	0.19	99.87	62.23	0.00	0.00	2.999	0.00	0.00			
1184	0.21	99.68	57.06	0.00	0.00	2.750	0.00	0.00			
1086	0.37	99.47	52.33	0.00	0.00	2.522	0.00	0.00			
995.6	0.72	99.10	47.98	0.00	0.00	2.312	0.00	0.00			
913.0	1.28	98.38	44.00	0.00	0.00	2.121	0.00	0.00			
837.2	2.14	97.10	40.35	0.00	0.00	1.945	0.00	0.00			
767.7	3.55	94.96	37.00	0.00	0.00	1.783	0.00	0.00			
704.0	5.61	91.41	33.93	0.00	0.00	1.635	0.00	0.00			
645.6	8.37	85.80	31.11	0.00	0.00	1.499	0.00	0.00			
592.0	11.99	77.43	28.53	0.00	0.00	1.375	0.00	0.00			
542.9	14.50	65.44	26.16	0.00	0.00	1.261	0.00	0.00			
497.8	16.03	50.94	23.99	0.00	0.00	1.156	0.00	0.00			
456.5	14.50	34.91	22.00	0.00	0.00	1.060	0.00	0.00			
418.6	10.03	20.41	20.17	0.00	0.00	0.972	0.00	0.00			
383.9	6.22	10.38	18.50	0.00	0.00	0.892	0.00	0.00			
352.0	2.67	4.16	16.96	0.00	0.00	0.818	0.00	0.00			
322.8	0.96	1.49	15.56	0.00	0.00	0.750	0.00	0.00			
296.0	0.40	0.53	14.27	0.00	0.00	0.688	0.00	0.00			
271.4	0.13	0.13	13.08	0.00	0.00	0.630	0.00	0.00			
248.9	0.00	0.00	12.00	0.00	0.00	0.578	0.00	0.00			
228.2	0.00	0.00	11.00	0.00	0.00	0.530	0.00	0.00			
209.3	0.00	0.00	10.09	0.00	0.00	0.486	0.00	0.00			
191.9	0.00	0.00	9.25	0.00	0.00	0.446	0.00	0.00			
176.0	0.00	0.00	8.48	0.00	0.00	0.409	0.00	0.00			
161.4	0.00	0.00	7.78	0.00	0.00	0.375	0.00	0.00			
148.0	0.00	0.00	7.13	0.00	0.00	0.344	0.00	0.00			
135.7	0.00	0.00	6.54	0.00	0.00	0.315	0.00	0.00			
124.5	0.00	0.00	6.00	0.00	0.00	0.2890	0.00	0.00			
114.1	0.00	0.00	5.50	0.00	0.00	0.2650	0.00	0.00			
104.7	0.00	0.00	5.04	0.00	0.00						
95.96	0.00	0.00	4.62	0.00	0.00						
88.00	0.00	0.00	4.24	0.00	0.00						
80.70	0.00	0.00	3.89	0.00	0.00						
74.00	0.00	0.00	3.57	0.00	0.00						

Summary	
Data	Value
MV(um):	520.7
MN(um):	448.0
MA(um):	492.5
CS:	1.22E-02
SD:	114.0
Mz:	510.8
σι:	119.4
Ski:	0.2657
Kg:	1.125

Percentiles	
%Tile	Size(um)
10.00	382.2
20.00	417.3
25.00	431.0
40.00	469.3
50.00	495.3
60.00	525.0
70.00	560.0
75.00	581.1
90.00	687.3
95.00	768.9

Peaks Summary		
Dia(um)	Vol%	Width
495.3	100	228.1

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WARNING: NONE

- Measurement Info -

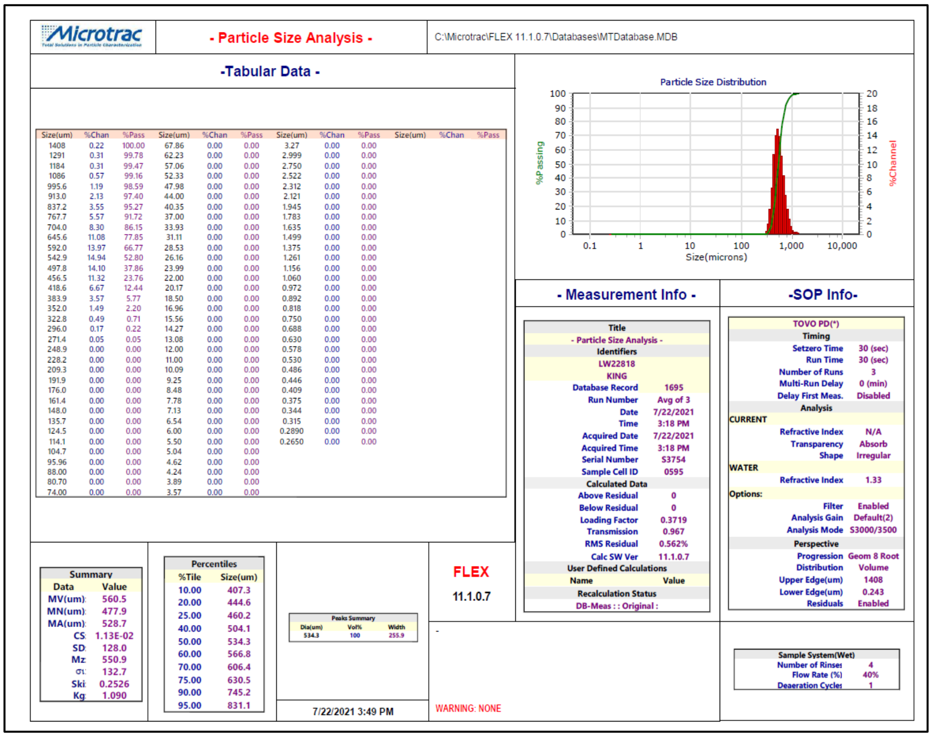
Title	
- Particle Size Analysis -	
Identifiers	
LW22817	
KING	
Database Record	1691
Run Number	Avg of 3
Date	7/22/2021
Time	3:12 PM
Acquired Date	7/22/2021
Acquired Time	3:12 PM
Serial Number	S3754
Sample Cell ID	0595
Calculated Data	
Above Residual	0
Below Residual	0
Loading Factor	0.2138
Transmission	0.982
RMS Residual	0.586%
Calc SW Ver	11.1.0.7
User Defined Calculations	
Name	Value
Recalculation Status	
DB-Meas : : Original :	

-SOP Info-

TOVO PD(*)	
Timing	
Setzero Time	30 (sec)
Run Time	30 (sec)
Number of Runs	3
Multi-Run Delay	0 (min)
Delay First Meas.	Disabled
Analysis	
CURRENT	
Refractive Index	N/A
Transparency	Absorb
Shape	Irregular
WATER	
Refractive Index	1.33
Options:	
Filter	Enabled
Analysis Gain	Default(2)
Analysis Mode	S3000/3500
Perspective	
Progression	Geom 8 Root
Distribution	Volume
Upper Edge(um)	1408
Lower Edge(um)	0.243
Residuals	Enabled

Sample System(Wet)	
Number of Rinses	4
Flow Rate (%)	40%
Deaeration Cycles	1

Figure 3-5. Microtrac Particle Size Distribution Data for the CST Stored in 3 M NaOH for ~2.5 years (Replicate #1).



- Particle Size Analysis -

C:\Microtrac\FLEX 11.1.0.7\Databases\MTDatabase.MDB

-Tabular Data -

Size(um)	%Chan	%Pass	Size(um)	%Chan	%Pass	Size(um)	%Chan	%Pass	Size(um)	%Chan	%Pass
1408	0.22	100.00	67.86	0.00	0.00	3.27	0.00	0.00			
1291	0.31	99.78	62.23	0.00	0.00	2.999	0.00	0.00			
1184	0.31	99.47	57.06	0.00	0.00	2.750	0.00	0.00			
1086	0.57	99.16	52.33	0.00	0.00	2.522	0.00	0.00			
995.6	1.19	98.59	47.98	0.00	0.00	2.312	0.00	0.00			
913.0	2.13	97.40	44.00	0.00	0.00	2.121	0.00	0.00			
837.2	3.55	95.27	40.35	0.00	0.00	1.945	0.00	0.00			
767.7	5.57	91.72	37.00	0.00	0.00	1.783	0.00	0.00			
704.0	8.30	86.15	33.93	0.00	0.00	1.635	0.00	0.00			
645.6	11.08	77.85	31.11	0.00	0.00	1.499	0.00	0.00			
592.0	13.97	66.77	28.53	0.00	0.00	1.375	0.00	0.00			
542.9	14.94	52.80	26.16	0.00	0.00	1.261	0.00	0.00			
497.8	14.10	37.86	23.99	0.00	0.00	1.156	0.00	0.00			
456.5	11.32	23.76	22.00	0.00	0.00	1.060	0.00	0.00			
418.6	6.67	12.44	20.17	0.00	0.00	0.972	0.00	0.00			
383.9	3.57	5.77	18.50	0.00	0.00	0.892	0.00	0.00			
352.0	1.49	2.20	16.96	0.00	0.00	0.818	0.00	0.00			
322.8	0.49	0.71	15.56	0.00	0.00	0.750	0.00	0.00			
296.0	0.17	0.22	14.27	0.00	0.00	0.688	0.00	0.00			
271.4	0.05	0.05	13.08	0.00	0.00	0.630	0.00	0.00			
248.9	0.00	0.00	12.00	0.00	0.00	0.578	0.00	0.00			
228.2	0.00	0.00	11.00	0.00	0.00	0.530	0.00	0.00			
209.3	0.00	0.00	10.09	0.00	0.00	0.486	0.00	0.00			
191.9	0.00	0.00	9.25	0.00	0.00	0.446	0.00	0.00			
176.0	0.00	0.00	8.48	0.00	0.00	0.409	0.00	0.00			
161.4	0.00	0.00	7.78	0.00	0.00	0.375	0.00	0.00			
148.0	0.00	0.00	7.13	0.00	0.00	0.344	0.00	0.00			
135.7	0.00	0.00	6.54	0.00	0.00	0.315	0.00	0.00			
124.5	0.00	0.00	6.00	0.00	0.00	0.2890	0.00	0.00			
114.1	0.00	0.00	5.50	0.00	0.00	0.2650	0.00	0.00			
104.7	0.00	0.00	5.04	0.00	0.00						
95.96	0.00	0.00	4.62	0.00	0.00						
88.00	0.00	0.00	4.24	0.00	0.00						
80.70	0.00	0.00	3.89	0.00	0.00						
74.00	0.00	0.00	3.57	0.00	0.00						

Summary	
Data	Value
MV(um):	560.5
MN(um):	477.9
MA(um):	528.7
CS:	1.13E-02
SD:	128.0
Mz:	550.9
σι:	132.7
Ski:	0.2526
Kg:	1.090

Percentiles	
%Tile	Size(um)
10.00	407.3
20.00	444.6
25.00	460.2
40.00	504.1
50.00	534.3
60.00	566.8
70.00	606.4
75.00	630.5
90.00	745.2
95.00	831.1

Peaks Summary		
Dia(um)	Vol%	Width
534.3	100	255.9

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WARNING: NONE

- Measurement Info -

Title	
- Particle Size Analysis -	
Identifiers	
LW22818	
KING	
Database Record	1695
Run Number	Avg of 3
Date	7/22/2021
Time	3:18 PM
Acquired Date	7/22/2021
Acquired Time	3:18 PM
Serial Number	S3754
Sample Cell ID	0595
Calculated Data	
Above Residual	0
Below Residual	0
Loading Factor	0.3719
Transmission	0.967
RMS Residual	0.562%
Calc SW Ver	11.1.0.7
User Defined Calculations	
Name	Value
Recalculation Status	
DB-Meas : : Original :	

-SOP Info-

TOVO PD(*)	
Timing	
Setzero Time	30 (sec)
Run Time	30 (sec)
Number of Runs	3
Multi-Run Delay	0 (min)
Delay First Meas.	Disabled
Analysis	
CURRENT	
Refractive Index	N/A
Transparency	Absorb
Shape	Irregular
WATER	
Refractive Index	1.33
Options:	
Filter	Enabled
Analysis Gain	Default(2)
Analysis Mode	S3000/3500
Perspective	
Progression	Geom 8 Root
Distribution	Volume
Upper Edge(um)	1408
Lower Edge(um)	0.243
Residuals	Enabled

Sample System(Wet)	
Number of Rinses	4
Flow Rate (%)	40%
Deaeration Cycles	1

Figure 3-6. Microtrac Particle Size Distribution Data for the CST Stored in 3 M NaOH for ~2.5 years (Replicate #2).

Table 3-2. Metals Analysis Results for Filtrate Following CST Contact with 3 M NaOH After ~2.5 Years.

Analytical Sample ID	mg/L			
	Si	Ti	Nb	Zr
LW22819	149	<0.67	<5.27	2.39

4.0 Conclusions

Smaller CST particle diameters isolated by sieving from pretreated media samples may load slightly higher amounts of cesium, though the differences are within analytical uncertainty. No visual indications of CST particle attrition or agglomeration were observed for samples stored in caustic solutions (NaOH and waste simulant) for 2.5 years. Particle size analysis indicated a slight decrease may have occurred in the average particle diameter following contact with 3 M NaOH relative to the original pretreated CST. A small increase in the number of particles below 322 µm was also observed relative to the original pretreated CST. However, these small changes could be due to sub-sampling differences or analytical uncertainty. It does not appear that small particles are formed to a significant degree during CST caustic contact or that small particles which do form load significantly more cesium than the bulk material. Minimal other negative consequences were associated with extended caustic or simulant contact, except for the tendency for more concentrated salt solutions to form some crystals over time.

5.0 Recommendations, Path Forward or Future Work

Since the entire pretreated CST particle size distribution (unsieved material) is being used for TCCR in-tank batch contacts, impacts from the slightly higher (though within uncertainty) loadings observed for the smaller CST particles are captured by this testing. Therefore, no future work or recommendations addressing this issue are required.

6.0 References

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[i] King, W. D., Taylor, S., Aleman, S. E., “CST 9120-B 30x60 Media Pretreatment and Digestion Standard Development to Support Tank Closure Cesium Removal 1A (TCCR 1A) Operations”, SRNL-STI-2020-00435, Rev. 0, January 2021.

[ii] Mathurin, L. E., Taylor-Pashow, K. M. L, “Structural Stability of Crystalline Siliotitatanate Dispersed in Caustic Solutions for Extended Periods”, SRNL-STI-2019-00463, Rev. 0, August 2019.

[iii] Taylor-Pashow, K. M. L., King, W. D., Hang, T., Fondeur, F. F., “Characterization and CST Batch Contact Equilibrium Testing of Tank 9H Process Supernate Samples in Support of TCCR”, SRNL-STI-2020-00128, Rev. 0, April 2020.

[iv] King, W. D., Hamm, L. L., Coleman, C. J., Fondeur, F. F., Reboul, S. H., “Crystalline Silicotitanate (CST) Ion Exchange Media Performance Evaluations in SRS Average Supernate Simulant and Tank 10H Waste Solution to Support TCCR”, SRNL-STI-2018-00277, Rev. 0, June 2018.

[v] King, W. D., Hamm, L. L., Fondeur, F. F., “CST Ion Exchange Media Pretreatment and Batch Contact Test Results with Tank 10H Supernate to Support TCCR”, SRNL-L3100-2017-00149, Rev. 0, December 2017.

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