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CST R9120-B 30x60 Media Pretreatment and Digestion Standard Development to Support Tank Closure Cesium Removal 1A (TCCR-1A) Operations

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Savannah River National Laboratory®

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

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EXECUTIVE SUMMARY

In support of continued operations of Savannah River Remediation's (SRR) ion exchange process to remove radioactive cesium from Savannah River Site (SRS) dissolved saltcake, referred to as the Tank Closure Cesium Removal 1A process (TCCR-1A; containing the second set of at-tank ion exchange columns), SRNL was tasked with: 1) validating the field protocol planned for pretreating the crystalline silicotitanate (CST) ion exchange media to be used in the columns, 2) preparing CST media for use in in-tank batch contact testing, and 3) developing a digestion standard to verify complete CST dissolution prior to characterization following each in-tank batch contact test. A procedure (SRNL L29 Manual, ITS-0229) was developed previously in support of the TCCR Demonstration (which contained the first set of ion exchange columns) based on evaluations of a different CST production lot with a larger particle size range to document the protocol for pretreating CST utilizing conditions similar to what will be performed in the field. Analysis of a sample of the new CST lot pretreated following this procedure confirmed similar conversion to the Na^+ media form as was observed for a separate sample treated with a larger reagent volume. The results indicate that the current field protocol (3.7 mL 3 M NaOH per g as-received CST) is adequate for conversion of the new CST media to the Na^+ ionic form with no modifications. It was observed during pretreatment that the conditions used for water upflow elutriation do not remove all fine particles (based on visual observations and subsequent sieving; "fine particles" does not necessarily refer to respirable fines in this case). Subsequent analyses of selected CST lots were conducted to determine the weight percent of fine particles for each CST sub-sample. This analysis revealed that the Na-form of the new CST media pretreated following the procedure (which includes upflow fines elutriation) contains a larger weight percentage (8 wt. %) of particles passing through a U. S. Standard #60 screen (250 µm screen opening) than the as-received, H-form material (5 wt. %). Portions of the batch of ion exchange media pretreated according to the developed protocol were also used to develop a digestion standard. Results from digestion and analysis of this standard were used to establish a set of statistical control limits for the measured Ti, Zr, and Nb concentrations in digested CST material. The upper and lower confidence limits for each element based on 99.7% confidence are provided in Table ES-1. These confidence intervals are larger than those determined for the TCCR Demonstration CST but %RSD values for the replicate data were still below 10%. An aliquot of this standard CST material will be digested and analyzed alongside each in-tank batch contact equilibrium CST sample (prepared from the same pretreatment batch) contacted with the TCCR-1A dissolved saltcake, and the measured concentrations of Ti, Zr, and Nb will be compared against the established control limits to confirm that complete CST digestion occurred.

Table ES-1. Statistical Analysis and Confidence Limits for the TCCR-1A CST Digestion Standard

Element	Within-Day %RSD	Day-to-Day %RSD	CST Avg µg/g (centerline)[a]	Total %RSD for CST	99.7% LCL µg/g[a]	99.7% UCL µg/g[a]
Ti	6.92	2.73	158400	7.44	123025	193775
Zr	7.22	1.56	105640	7.38	82240	129040
Nb	6.70	2.70	129800	7.23	101660	157940

[a] based on reference-state, hydrated CST mass (no water correction)

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LIST OF ABBREVIATIONS

ARD	Analytical Research and Development
BV	bed volume
cdf	cumulative distribution function
CST	crystalline silicotitanate
EDS	Energy Dispersive Spectroscopy
ELN	electronic laboratory notebook
ICP-ES	Inductively Coupled Plasma – Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
ISS	Interim Safe Storage
ITS	Immobilization Technology Section
IX	ion exchange
JMP	John's Macintosh Project (statistical analysis software)
K_d	distribution coefficient
LCL	lower confidence limit
LW	LabWare (analytical software)
pdf	probability distribution function
PT1	Pretreatment #1
PT2	Pretreatment #2
RSD	relative standard deviation
SEM	scanning electron microscopy
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TA	Thermal Analysis
TCCR	Tank Closure Cesium Removal
TGA	Thermal Gravimetric Analysis
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
UOP	Honeywell UOP
UCL	upper confidence limit
ZAM	ZAM (Zheng, Anthony, and Miller) Isotherm Model

1.0 Introduction

Savannah River Remediation (SRR) recently deployed the first Tank Closure Cesium Removal (TCCR) Demonstration system at the Savannah River Site (SRS) to remove radioactive cesium from dissolved saltcake solutions. The system was deployed consists of salt retrieval, filtration, ion exchange (IX), ventilation, and Interim Safe Storage (ISS).[1] The TCCR IX columns utilize crystalline silicotitanate (CST) to remove cesium. The media is currently manufactured by Honeywell UOP and is known commercially as IONSIV[TM] R9120-B. Demonstration of the TCCR unit performance in 2019 and 2020 involved treatment of three batches of salt solution generated by dissolving saltcake in Tank 10H. Current plans are to transfer Tank 9H dissolved salt solution to Tank 10H and process the solution through the TCCR unit with new CST media (referred to as R9120-B 30x60) added to new IX columns. This TCCR processing campaign is referred to as TCCR-1A. The new CST media requires pretreatment to convert the material from hydrogen to sodium form using a field protocol developed previously and utilized for the TCCR Demonstration. Pretreatment of this new CST media was conducted on a small scale in the laboratory to validate the applicability of current procedures[2] to this media lot. A pretreated CST standard of R9120-B 30x60 CST was confirmed to be converted to the sodium form by analysis and the results were statistically analyzed. This standard CST media will be utilized to support TCCR-1A testing. During TCCR-1A processing, in-field batch contact 'teabags'[2] containing the pretreated CST will be prepared in the laboratory, transferred into the tank, and then transferred back to the laboratory for analysis. Samples of the standard CST from the same pretreated CST batch will be digested and analyzed alongside the in-field teabag samples to ensure that the results fall within the expected uncertainty determined based on the analytical data for multiple standard replicate samples.

2.0 Experimental Procedure

2.1 CST Sample Receipt, Handling and Vendor-Supplied Characterization Data

Samples were received from SRR of four different IONSIV[TM] R9120-B CST lots prepared by the supplier (Honeywell UOP of Des Plaines, IL, U.S.A.). The R9120-B CST materials were designated as "30x60" since the particle size range was smaller than previous production batches. "30x60" refers to the U.S. Standard sieve number range and corresponds to particles ranging from 250 (or 60 mesh) to 595 (or 30 mesh) µm based on sieving with wire mesh screens. Note: The specified size range was produced by the supplier by sieving the CST particles rather than grinding to produce a smaller size distribution. The ion exchange media was contained in multiple drums containing ~150 kg of CST each. The CST production lot numbers were 2102020753, 2102020755, 2102020756, and 2102020757. The CST was distributed between four drums for each lot, except for lot 2102020757, which was contained in two drums. Lot 2102020757 therefore represented ~14 wt. % of the total CST and the remaining lots each contributed 29 wt. %.

One CST drum from each lot was selected for sub-sampling following SRR Procedure 241-H-4635 entitled "CST Drum Sampling." Drum designations 11, 7, 1, and 5 were sampled from CST lots 2102020753, 2102020755, 2102020756, and 2102020757, respectively. Each plastic sub-sample bottle contained ~200 mL of CST (see Figure 2-1). According to Procedure 241-H-4635, the CST in each bottle was a composite of three 1/4 cup (2 oz) sub-samples (two surface and one sub-surface).[3] Each sub-sample was
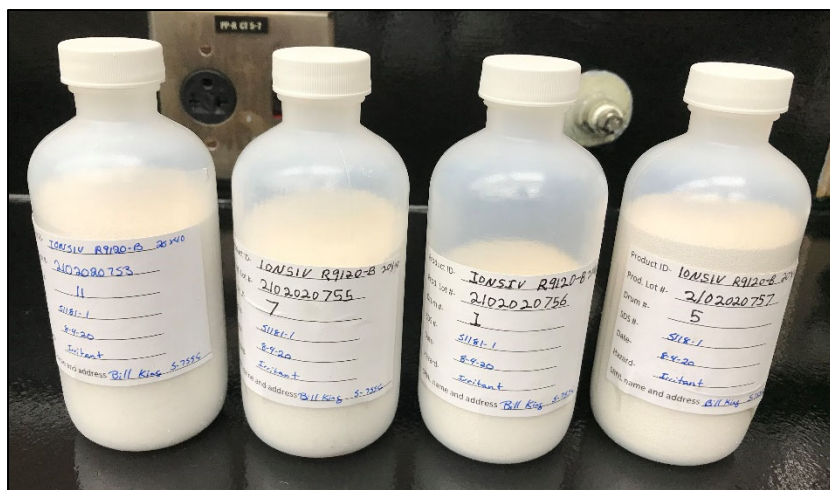
Figure 2-1. Sub-Samples of R9120-B 30x60 CST Lots Received at SRNL.

collected halfway between the center and the wall of the drum. The first sub-sample was collected from the surface at the 12 o'clock position and the second sub-sample was collected from the surface at the 8 o'clock position. The third sample was collected at the 4 o'clock position from 3 inches below the surface (after removing the material from the surface).

Performance and characterization data obtained from the supplier for the CST samples is provided in Tables 2-1 through 2-3. The cesium distribution coefficients were obtained at a temperature range of 20.5 to 25 °C. Lack of temperature control was observed initially during batch contacts and the temperature was ambient (20.5 °C) for the first 27 hours, before the samples were transferred to a second shaker oven at the target temperature of 25 °C to complete 96 hours of total contact. A simple simulant containing 5.1 M $NaNO_3$ and 0.6 M NaOH was contacted with the CST (0.1 g water-corrected CST mass and 10 mL of simulant). Initial cesium concentrations of 6.32 mg/L (Simulant #1) and 65.6 mg/L (Simulant #2) were tested for each CST lot. The CST lot with the highest overall average K_d in both simulants (Lot 2102020756) was selected for pretreatment and subsequent teabag preparation to provide the most conservative cesium loading data for Tank 9H supernate. Sieve data provided by the supplier for each CST lot is provided in Table 2-2. Modest differences in the particle size distribution between lots were observed with %RSD values ranging from approximately 5 to 80% for the various size ranges within the distribution. Most of the particles (~70 wt. % on average) fall within the range 400-595 μm (U. S. Standard sieve #30-#40). Approximately 22% on average of the particles are within the range 297-400 μm (U. S. Standard sieve #40-#50). The two ranges combined (297-595 μm or U. S. Standard sieve #30-#50) account for ~91 wt. % of the CST mass. On average, 5.8 wt. % of the material falls outside of the specified range of U. S. Standard sieve #30-#60. Elemental analysis results on an oxide basis for each CST lot as reported by the supplier are provided in Table 2-3. Similar results were observed for each lot as indicated by the low %RSD values (range: ~2-11%). It is assumed that the density and sieve data provided by the supplier are based on the as-prepared, hydrated CST mass.

All sub-sampling events for the CST samples involved the collection and compositing of multiple (ranging from 3 to 20) small aliquots with a spatula from different locations within the container with periodic sample mixing when practical.

Table 2-1. Cesium Distribution Coefficients (in simple NaNO₃/NaOH simulant), Moisture Content, and Density Data provided by UOP for the IONSIV™ R9120-B 30x60 CST Lots.

CST Lot #	Simulant 1 (6.32 mg Cs/L)		Simulant 2 (65.6 mg Cs/L)		Moisture wt. %[b]	Density (g/mL)
	$Cs^+ K_d$[a]	%RSD K_d	$Cs^+ K_d$[a]	%RSD K_d		
2102020753	738	2.8	766	0.2	19.9	1.08
2102020755	722	0.2	789	3.3	20.5	1.12
2102020756	733	1.1	809	1.3	21.5	1.10
2102020757	721	1.9	776	0.3	21.3	1.08
Average	735		778		20.8	1.10
Standard Dev.	20	---	31	---	0.74	0.02
%RSD	2.8%		3.9%		3.6%	1.6%

[a] dry CST basis, corrected for water content

[b] based on TGA mass loss from a 2 g sample at 400 ºC

Table 2-2. Sieve Data provided by UOP for the IONSIV™ R9120-B 30x60 CST Lots.

Screen Cut (U.S. Standard Sieve #)	Size Range (μm)	Lot 2102020753	Lot 2102020755	Lot 2102020756	Lot 2102020757	Average	%RSD
		Wt. %					
+30[a]	>595	2.3	4.3	4.1	2.8	3.4	29.0
30-40	595-400	74.1	68.6	69.8	65.8	69.6	5.0
40-50	400-297	21.6	17.8	19.8	26.8	21.5	17.9
50-60	297-250	1.5	4.8	3.2	3.2	3.2	42.4
-60[a]	<250	0.4	4.8	3.1	1.4	2.4	79.8

[a] "-" indicates particles passing and "+" indicates particles not passing the sieve number indicated

Table 2-3. Elemental Analysis Data provided by UOP for the IONSIV™ R9120-B 30x60 CST Lots.

Metal Oxide	Lot 2102020753	Lot 2102020755	Lot 2102020756	Lot 2102020757	Average	%RSD
	Wt. %					
Nb_2O_5	25.6	23.6	23.0	24.1	24.1	4.6
ZrO_2	17.5	20.4	19.7	18.8	19.1	6.6
Na_2O	3.1	3.1	2.5	2.6	2.8	11.3
TiO_2	35.2	34.4	36.3	36.0	35.5	2.4
SiO_2	18.6	17.9	18.3	18.6	18.4	1.8

2.2 <u>Calculation of Particle Size Statistics for the R9120-B 30x60 CST Lots Based on Sieve Data</u>

Computation of an average spherically-equivalent particle diameter for the CST beads in each CST Lot required generation of a cumulative distribution function based on the Rosin-Rammler fit for weight percent passing versus sieve size. The Rosin-Rammler equation is one of the most commonly used theoretical equations for fitting measured cumulative particle size distributions of crushed minerals and blastpiles.[4] Once the cumulative distribution function (cdf) was determined for each test sample, probability distribution functions (pdf) on a weight and number basis were computed. Given the pdf of the particle distribution on a number basis, the average spherically-equivalent diameter was computed based on distinct average diameter definitions over the sieve interval of interest. Nonlinear least squares optimization of the cost function computed from residuals of the sieve data and the Rosin-Rammler equation yielded characteristic size and uniformity coefficients, respectively. The Powder Technology Handbook[5] provides the definitions of the mean or average particle diameters. Additional details describing this calculational approach are provided in a separate report.[6]

2.3 <u>SRNL CST Dry Bulk Density Measurement</u>

The bulk dry density of as-received and pretreated CST samples from Lot 2102020756 were determined by transferring a known mass of CST into a graduated cylinder and recording the CST volume using the cylinder graduations after tapping the cylinder for several minutes to pack the CST bed. The inside diameter of the graduated cylinder was 1.0 inch. This diameter is considered sufficiently large relative to the CST particle size to minimize particle bridging effects across the cylinder which can impact the total measured volume. After recording the volume based on the cylinder graduations, the measured volume was checked by filling the cylinder with deionized water to the previously measured CST bed volume. The actual volume of the CST bed was calculated using the known density of water and the mass of the water required to give the same volume observed for the CST sample. This process was repeated twice with two separate as-received CST samples and the average bed density was calculated. This average density was used to determine the mass of CST corresponding to 29.4 mL (the specified volume of CST needed for the pretreatment task, as discussed in Section 2.5).

2.4 <u>NaOH Reagent Preparation and Analysis</u>

Two batches of 3 M NaOH solution were prepared to support the CST pretreatment tasks. In each case, 48.0 g of 50 wt. % NaOH solution was diluted to 200 mL in a volumetric flask using deionized water. The densities of the resulting solutions were generally consistent with the density expected for 3.0 M NaOH (1.12 g/mL). Sub-samples of each NaOH batch were analyzed by Inductively Couple Plasma – Emission Spectroscopy (ICP-ES) to determine the sodium concentration. An additional sample of 3 M NaOH solution was used to complete the extra caustic treatment conducted during CST Pretreatment #1. The density of this solution was confirmed to be similar to the densities of the two reagent batches prepared for this testing.

2.5 <u>CST Pretreatment</u>

Two CST sub-samples from Lot 2102020756 were pretreated separately using the protocol provided in SRNL Procedure ITS-0229.[2] In summary, this procedure specifies that 29.4 mL of CST be: 1) packed into a 1.9 cm ID column, 2) elutriated by upflow of deionized water through the bed at a flow rate of 28.7 mL/min, 3) pretreated by downward flow of two 63 mL portions of 3.0±0.16 M NaOH solution at a

flow rate of 26.8 mL/hour (0.45 mL/min), and 4) washed by downward flow with deionized water at a flow rate of 1.5 mL/min until the effluent pH was ≤11.5. For the caustic treatment step, the flow was stopped for ~5 minutes after the first 63 mL portion of solution was pumped into the system to simulate the exchange of totes in the field. The pH was monitored using pH-indicating paper during the dynamic pH transitions at the beginning of the NaOH addition and at the beginning of the water wash following caustic conditioning. The liquid flow rate was checked at various times during the pretreatment procedure using a graduated cylinder and a timer. Pump setting adjustments were made as needed to maintain the flow rate near the target value. The procedure also specifies that the CST be dried in an oven to constant mass at 35 °C and then allowed to stand at ambient temperature until the mass was constant. CST pretreated and handled in this way is referred to as "reference-state" CST. The mass of this material includes the mass of sorbed water. The water content of the pretreated reference-state sample should then be determined by Thermal Gravimetric Analysis (TGA) to correct the measured mass of the material for the mass of water. CST column effluent sub-samples collected periodically during the caustic pretreatment step were submitted for Inductively Couple Plasma – Mass Spectroscopy (ICP-MS) analysis to determine the concentrations of titanium, zirconium, and niobium. The metals are known to leach from CST during caustic conditioning.

During Pretreatment #1, equipment problems resulted in poor liquid flow control during the initial caustic pretreatment step (see further discussion in Section 3.0). As a result, the caustic contact time for the CST during the initial contact period was shorter than planned and the transition from water to caustic was more rapid than planned. The CST was subsequently exposed to a second caustic pretreatment step to ensure complete conversion to sodium form. After completion of this second caustic treatment, the total CST contact time and volume were greater than specified in the procedure. As a result, this CST sample was not used as a standard material for testing. Instead, this sample was used as a reference for comparison for the second CST pretreatment batch (Pretreatment #2) which was prepared using the field treatment method. The CST media from the first pretreatment is expected to be fully converted to the sodium form. A photograph of the equipment used for CST Pretreatment #2 is provided in Figure 2-2.

Sub-samples of the as-received and pretreated (Pretreatment #1 and #2) CST from Lot 2102020756 were submitted for acid (HF/HNO$_3$) digestion and ICP-MS analysis to determine the amounts of titanium, zirconium, and niobium in the samples. ICP-ES analysis was also utilized to determine the concentrations of sodium and minor metals. The acid digestion was conducted in the SRNL Shielded Cells for five CST samples. To evaluate variabilities in the digestion process, the five CST samples were digested on different days. Duplicate CST sub-samples from Pretreatment #2 were also submitted for Microtrac particle size analysis.
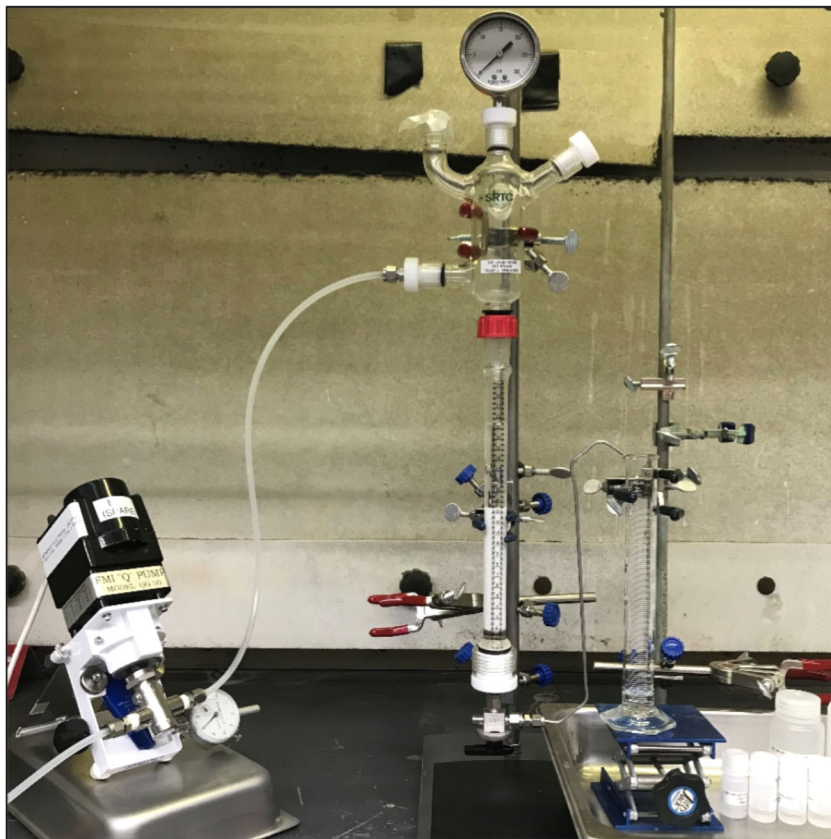
Figure 2-2. CST Pretreatment Equipment.

2.6 Statistical Analysis of the Digestion Data

JMP Pro Version 11.2.1[7] commercial software was used for calculations of the control limits described below in Section 3.5.

2.7 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. This work was performed following the applicable TTQAP.[8] The Task Technical Request (TTR) associated with this work[9] requested a functional classification of Safety Class (see Section 9.5 of the TTQAP entitled "Clarification of Safety Class Functional Classification"). To match the requested functional classification, this report and calculations within received a technical review by design verification (Manual E7 2.60, Section 5.3). Data are recorded in the electronic laboratory notebook (ELN) system as notebook/experiment number A2341-00117-16. The JMP Software used for statistical evaluations of the CST digestion data is classified as Level D.[10] However, the software was independently verified using an alternate software package previously as part of the design verification.[11]

3.0 Results and Discussion

3.1 Reagent and CST Characterization Prior to Pretreatment

Two batches of 3 M NaOH reagent were prepared for CST pretreatment. It was important to characterize these reagents since the testing was intended to confirm or refine the field pretreatment conditions. Characterization results for the reagents are provided in Table 3-1 where it is apparent that the densities and sodium concentrations for the solutions used for Pretreatment #1 and #2 were similar and were near the expected and target values. (Note: The designation LW refers to the assigned Labware analytical software number from the SRNL Analytical Research and Development division and the sample number is indicated after the designation (i.e. LWxxxxx).) An additional batch of 3 M NaOH solution was used in Pretreatment #1 that was not analyzed by ICP-ES, but the density was confirmed to be similar to (though slightly lower than) the other solutions. The sodium concentrations for the two analyzed solutions were each near 3.1 M, which is within the range specified in Procedure ITS-0229 (3.0±0.16 M NaOH). Extrapolated data from the CRC Handbook[12] indicates that 3.00 M NaOH solution should have a relative density of 1.119 g/mL. The measured density results agree with the CRC data to within 2%.

Table 3-1. 3 M NaOH Reagent Densities and Analysis Results.

CST Pretreatment #	Labware ID[a]	Density (g/mL)	Average Na$^+$ (M)	Na$^+$ M %RSD
1	LW18294, LW18295	1.115	3.06	0.50
1 (additional reagent)[b]	NA	1.110	NA	
2	LW18602, LW18603	1.113	3.10	0.10

[a] LW refers to the assigned Labware analytical software number

[b] contacted CST with additional caustic reagent from different preparation batch due to poor initial flow control in order to confirm complete conversion to sodium form

CST Lot 2102020756 was selected for use as a standard since it had the highest average cesium distribution coefficient (average of K_d's from both simulants). Sub-samples of this lot were evaluated to determine the density of a packed cylindrical (1-inch diameter) bed of the dry, as-received material. Results are provided in Table 3-2. The average measured bulk density was 1.141 g/mL. This result is 4.0% higher than the value reported by UOP for this CST lot of 1.097 g/mL. The SRNL results were calculated after calibrating the graduated cylinder volume using a known mass of water. Calculating the bed density based on the cylinder graduations gives a result more similar to the UOP data.

Table 3-2. SRNL Measured CST R9120-B 30x60 Lot 2102020756 Bulk Dry Bed Density.

Sample	CST Bulk Dry Bed Density (g/mL)*	Average*	%RSD
As-Received Replicate #1	1.156	1.141	1.9
As-Received Replicate #2	1.125		

* based on reference-state, hydrated CST mass (no water correction)

Duplicate sub-samples of as-received CST were characterized under nitrogen purge gas by Thermal Gravimetric Analysis (TGA) using a Model TA2050 analyzer from Thermal Analysis (TA) Instruments. During analysis, the temperature was increased at a rate of 5 °C/minute up to a temperature of 410 °C, at which point the temperature was held for 120 minutes. The sub-samples were then heated to 700 °C at a rate of 5 °C/minute. A water mass correction factor (F-factor) was calculated based on cumulative mass losses observed for the samples up to 410 °C. TGA data for one as-received CST replicate is provided in Figure 3-1. Results are summarized in Table 3-3. These F-factor results were utilized to convert measured as-received CST masses to a dry mass basis. The average moisture content of 21.5 wt. % was identical to the value reported by UOP, using a slightly lower temperature of 400 °C, for this CST lot (Table 2-1).
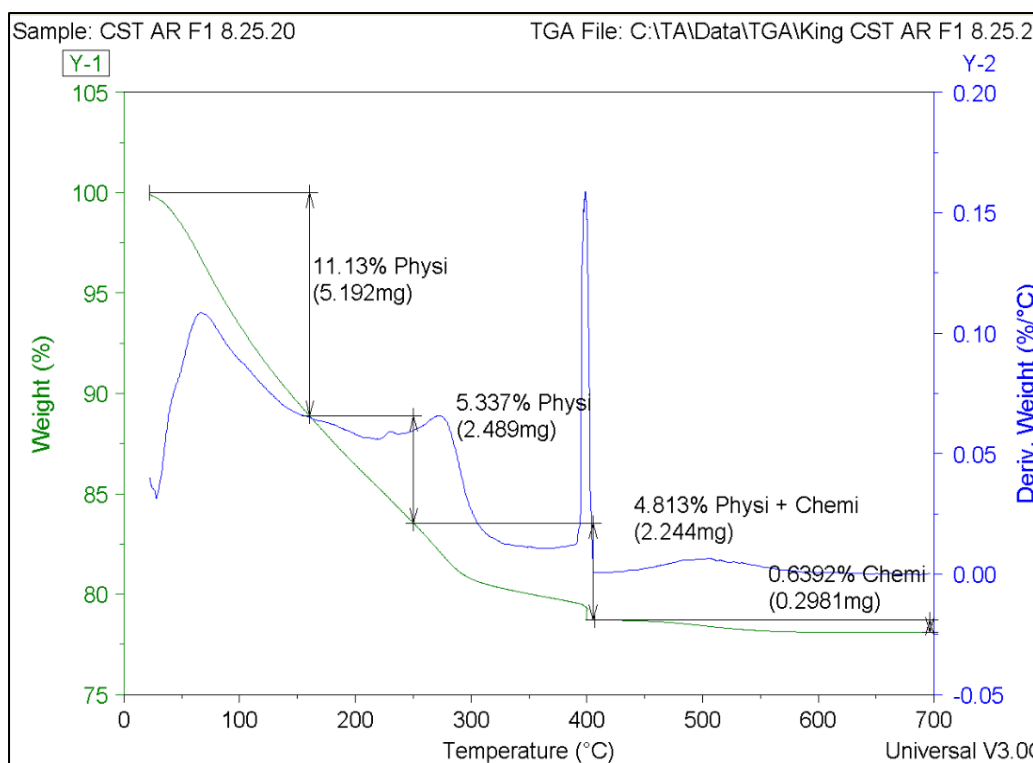
Figure 3-1. Thermal Gravimetric Analysis of As-Received CST from Lot 2102020756.

Table 3-3. **As-Received CST Lot 2102020756 Sub-Sample F-Factor Data.**

CST Sub-Sample	Cumulative Wt. % Mass Loss at 410 °C	F-Factor
As-Received F1	21.280	0.7872
As-Received F2	21.643	0.7836
Average	21.462	0.7854
%RSD	1.2	---

A sub-sample of as-received CST from Lot 21020202756 was submitted for acid digestion followed by ICP-MS and ICP-ES analysis. Results are provided in Table 3-4. ICP-MS and ICP-ES results agreed well for Ti and Zr. On a wt. % oxide and dry (corrected for water content) CST basis, the concentrations in Table 3-4 correspond to 33.6% TiO_2, 18.6% ZrO_2, and 24.4% Nb_2O_5 (based on ICP-MS), and 3.4% Na_2O (based on ICP-ES). These results are very similar to those reported by UOP (Table 2-3) for this CST lot. In addition, the Na:Ti molar ratio of 0.26 is similar to the ratio observed previously for the R9120-B CST media used in the TCCR Demonstration, which ranged from 0.21-0.23.[11]

Table 3-4. **Digestion and Analysis of As-Received CST from Lot 2102020756.**

Labware ID	Units	ICP-MS			ICP-ES						
		Ti	Zr	Nb	Ti	Zr	Na	Mg	Al	Ca	Fe
LW18446	μg/g	158000	108000	134000	153000	104000	20100	72.4	2160	<318	179
	wt. %	15.8	10.8	13.4	15.3	10.4	2.0	0.007	0.2	<0.03	0.02

* reference state, hydrated CST mass basis

3.2 R9120-B 30x60 CST Lot Sieve Data Analysis

The sieve data provided by UOP for the R9120-B 30x60 CST production samples (hydrogen-form material) from each lot was analyzed to calculate average particle diameter data for each lot. A log-normal distribution fit to the sieve data for Lot 2102020756, the lot pretreated for use as a standard for TCCR-1A testing, is provided in Figure 3-2. The log-normal distribution provides an adequate fit to this data when data uncertainty is considered. The particle size distribution profiles for the other lots were similar in appearance. The calculated mean diameter results on a number and volume basis for each of the four CST lots are provided in Table 3-5. The average number- and volume-based mean particle diameters were 432 and 457 μm, respectively, for the four CST lots. The mean diameter values were nearly the same from a statistical perspective for the four lots (range slightly greater than 1 standard deviation). The number- and volume-based mean particle diameters calculated for the TCCR Demonstration R9120-B CST (Lot #2099000034) were 497 and 572 μm, respectively.[6]

Table 3-5. **Calculated Particle Size Analysis Results for CST Lots.**

CST Lot	Diameter (μm)	
	Number Mean	Volume Mean
2102020753	440.4	460.7
2102020755	430.2	457.4
2102020756	433.5	459.1
2102020757	424.2	450.4
Average	432.1	456.9
Standard Deviation	6.8	4.5
%RSD	1.6	1.0
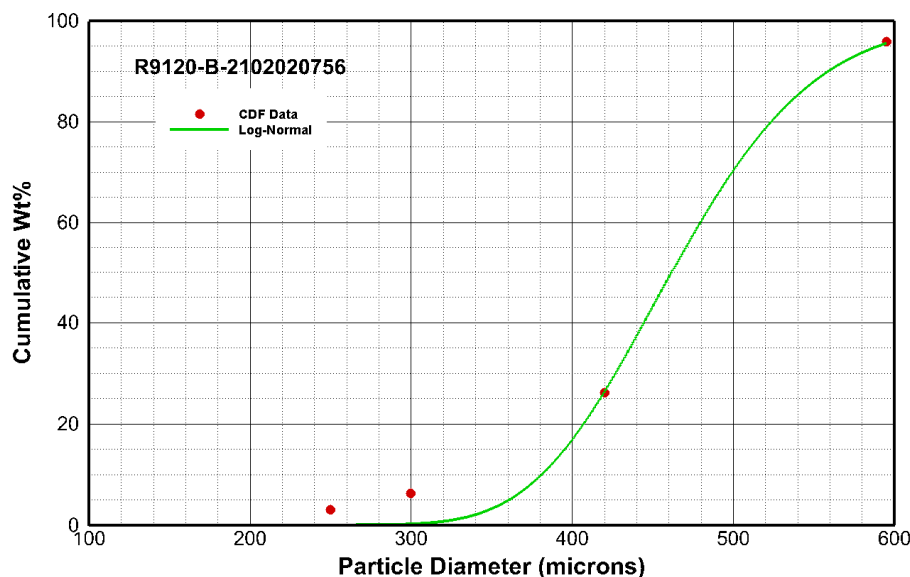
Figure 3-2. SRNL Calculated Cumulative Weight Percent Particle Size Distribution Based on UOP-Provided Sieve Data for R9120-B 30x60 CST Lot 2102020756.

3.3 <u>CST Pretreatment Details</u>

Two sub-samples of CST from Lot 2102020756 were pretreated. Flow control issues were experienced during Pretreatment #1 and extra NaOH was contacted with this sample to ensure complete conversion to the sodium ionic form. Pretreatment #2 was conducted with good flow control following Procedure ITS-0229 and the CST from this preparation is considered the standard material for future testing and teabag preparation.

3.3.1 Pretreatment #1

An approximately 33.5 g sub-sample (hydrated, as-received mass) of CST Lot 2102020756 (corresponds to 29.4 mL based on measured density of 1.141 g/mL) was gradually poured into the pretreatment column (Figure 2-2) after removing the column head and partially filling the column with deionized water. The height of the water in the column was maintained approximately 1-3 cm above the CST bed as a well-defined, packed cylinder (~11.6 cm tall) of ion exchange beads formed within the column. All column pumping operations throughout pretreatment were conducted with a vented, unpressurized head. The column head was reattached, and water was pumped from the bottom of the column to remove fines by elutriation at a flow rate of ~28.8 mL/min (58.8 BV/hr; BV = volume of fluid equivalent to packed CST bed volume). Elutriation resulted in the fluidization of nearly all the CST bed (except the bottom centimeter) and the suspension and transfer of fine particles from the bed through the upper liquid-filled portion of the column and out of the column head into a collection vessel. During upflow elutriation, numerous air bubbles were immediately observed to form in the bed. The bubbles began to coalesce into larger bubbles and an air pocket formed in the bed and gradually ascended the column (Figure 3-3) with much of the CST bed above it. Below this pocket, CST beads were observed settling back down into a continuous, packed, cylindrically shaped bed. Above the air pocket, bed movement and agitation were observed as the bubbles coalesced and

gradually released from the top of the slurry. This process continued until all the bubbles were removed. (Note: Similar bubble formation and release were observed during laboratory pretreatment of R9120-B CST for the TCCR demonstration, but this observation was not reported.[11]) Once the CST bed was packed, water upflow resulted in the expansion of the bed by ~1-2 cm (Figure 3-4). Upflow elutriation was continued until the solution exiting the column was nearly clear. At this point, it was apparent that there was a population of fine particles that had migrated to the top of the bed without exiting the column resulting in bed classification (see Figure 3-5). A total water volume of 613 mL was collected during water upflow elutriation. The pH of the water collected during elutriation was 4.0, which is consistent with hydrogen-form CST. The fine particles isolated during elutriation settled over a period of a couple of days to give a clear solution.

After completion of water elutriation, 63.0 mL (70.25 g) of 3 M NaOH solution were transferred into the column in a downward flow direction. Although the target flow rate was 0.45 mL/min, issues with the downstream effluent collection lines resulted in variability in the liquid level height in the column headspace and this resulted in poor overall flow control in the column. As a result, this portion of 3 M NaOH passed through the column in 26 minutes (average flow rate: 2.4 mL/min). During the processing of the first portion of caustic through the column the pH remained between 4.5 and 5.0. The flow was stopped for approximately five minutes and then a second 63.8 mL (71.1 g) portion of 3 M NaOH was pumped through the column with similar flow control problems such that this portion of 3 M NaOH passed through the column in 30 minutes (average flow rate: 2.1 mL/min). Near the beginning of processing the second portion of caustic solution through the column, the pH increased rapidly to >11. The pump was stopped and the CST bed was left in 3 M NaOH solution for 17 hours.

At this time, since the caustic flow rate had not been controlled, an additional portion of 3 M NaOH was pumped through the column to ensure complete conversion to sodium-form CST. Prior to adding the additional NaOH, the flexible polymer effluent collection line was removed from the column and a 1/8th inch inside diameter section of stainless steel tubing was attached and shaped into a leg which would not allow the column to drain below the top of the packed CST bed. Two additional portions of NaOH solution (63.3 mL and 70.3 g each) from a different reagent preparation batch were then pumped through the column. The initial flow rate was 0.29 mL/min and the flow rate was adjusted during the first couple of hours through small pump setting adjustments to 0.48 mL/min with a 5 minute break between the processing of the two solutions (per procedure). Flow control was quite good after dial setting adjustments were completed due to the effluent line modification. Reddish-brown color was observed in the leachate during caustic processing (Figure 3-6), as has been observed previously.[13] At the conclusion of processing the caustic through the column, the CST bed remained in caustic solution for 72 hours per procedure. A total of 273.5 mL of effluent solution was collected from the column during the entire caustic treatment process.

After 3 days, the caustic solution was displaced from the column and the CST was washed with water by pumping 1.57 L of deionized water through the column at a flow rate of 1.41 mL/min (2.9 BV/hr) until the effluent solution pH decreased to 11.4. No changes in the height of the CST bed were observed throughout the pretreatment process once downflow processing was initiated and bed packing was complete. The column was then disassembled and the CST was quantitatively removed and transferred into a pre-weighed beaker (Figure 3-7). During isolation of the CST from the column it was observed that some fine CST particles still appeared to be present in the sample. The CST was dried in an oven at 35 °C over several days

to a constant mass and then allowed to equilibrate with the air until the mass was constant. The CST sample was then transferred to a polymer bottle for storage. The fine particles isolated during elutriation were also dried to a constant weight as described above for the CST beads.

Liquid volumes and flowrates measured during Pretreatment #1 are summarized in Table 3-6.

Table 3-6. **CST Lot 2102020756 Pretreatment** <u>**Liquid**</u> **Masses, Volumes, and Flowrates.**

CST Pretreatment	Water Upflow Elutriation Volume (mL)	Water Upflow Elutriation Flow Rate (mL/min)	3 M NaOH Volume (mL)	3 M NaOH Flow Rate (mL/min)	Water Wash Volume (mL)	Water Wash Flow Rate (mL/min)
1	613	28.8	126[a]	2.1-2.4[b]	1,572	1.4
			126[a]	0.29-0.48[b]		
2	605	27.7	126[c]	0.48	1,705	1.5

[a] The CST was contacted with four ~63 mL portions of 3 M NaOH with 5 minutes of no fluid flow between the 1st and 2nd and the 3rd and 4th portions of reagent and 17 hours without flow between the 2nd and 3rd portions of reagent. The CST was then allowed to soak for 72 hours in 3 M NaOH.
[b] variable, uncontrolled flow rate
[c] sample contacted with two 63 mL portions of 3 M NaOH with 5 minutes without flow in between followed by a 72-hour soak
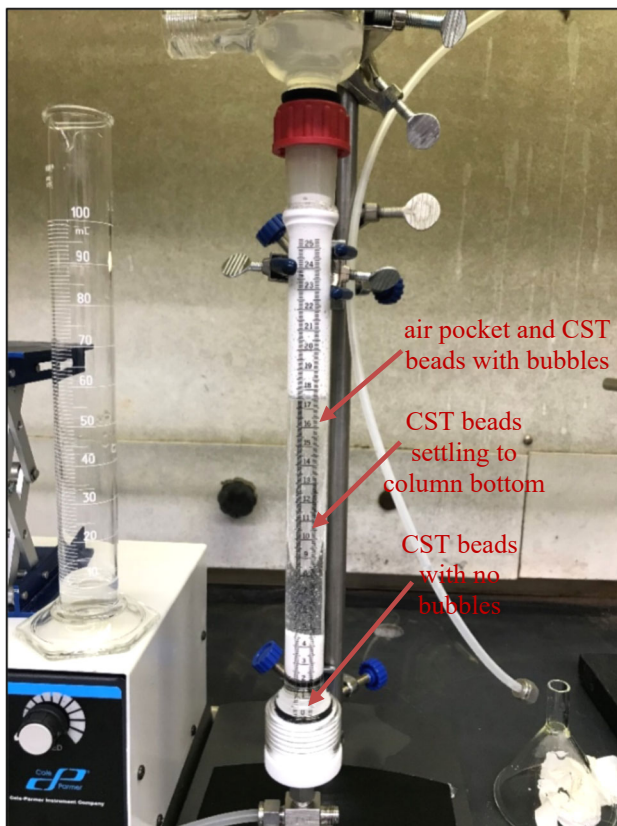
Figure 3-3. **Photograph of CST During Upflow Elutriation Before Air Bubble Removal.**
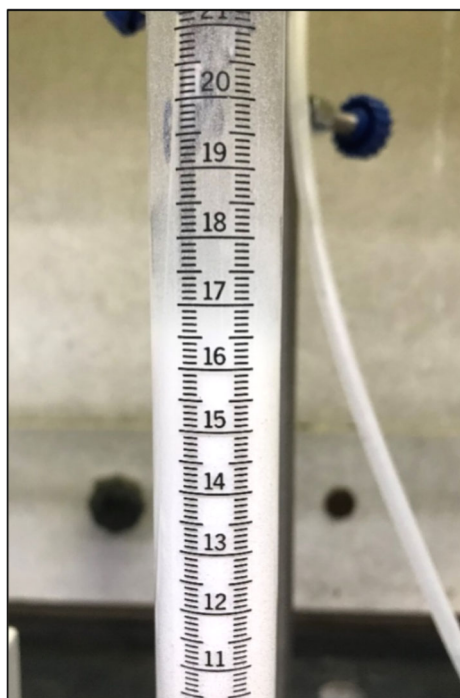
Figure 3-4. Photograph of CST During Upflow Elutriation After Bubble Removal.
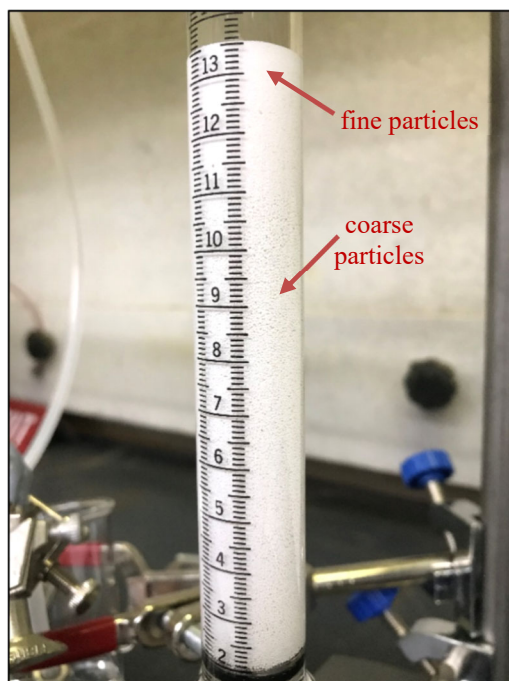
Figure 3-5. Photograph Showing CST Bed Classification Following Elutriation.
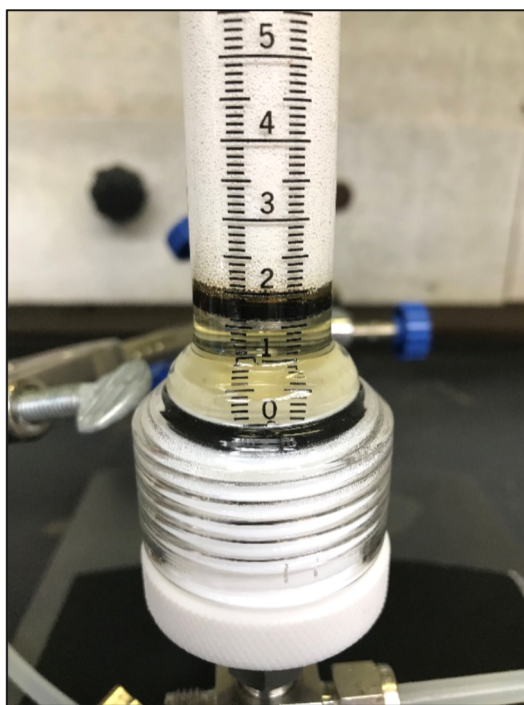
Figure 3-6. Photograph Showing Color Leaching from CST During Pretreatment Caustic Conditioning Step.

Figure 3-7. Disassembled Column and Isolated Fines and CST Following Pretreatment.

3.3.2 Pretreatment #2

A second approximately 33.5 g sub-sample (hydrated, as-received mass) of CST Lot 2102020756 was gradually poured into the re-assembled and water-refilled pretreatment column in a manner very similar to Pretreatment #1 to prepare a standard CST sample for testing following Procedure ITS-0229. Flow control was acceptable throughout this pretreatment procedure (56.5 BV/hr for elutriation, 0.98 BV/hr for caustic treatment, and 3.1 BV/hr for water wash) and this CST sample is considered the standard material for future testing and teabag preparation. Observations for this pretreatment were very similar to those described above for Pretreatment #1. In this case the pH was observed to increase to >11 at the very end of processing the first portion of caustic solution through the column, as was observed previously for the TCCR Demonstration CST.[11] Fine particles were isolated during water upflow elutriation (Figure 3-8). For this sample it was also observed during final sample isolation that additional small fine particles were present in the sample. These particles appeared to behave more like a powder than well-formed beads. They were observed to settle to the bottom of the beaker containing the dry CST beads (Figure 3-9) and adhere to the glass funnel (Figure 3-10) used for sample transfer to the bottle. ~5 mL sub-samples of the effluent solution were collected periodically from the column during the processing of caustic solution and during the beginning portion of the water wash. ICP-MS analysis results for these solutions are provided in Table 3-7. For all solutions, the highest metal concentration observed was for niobium. Note: Silicon (another primary CST component) was not analyzed. The final sample analyzed, which was collected following the 72-hour caustic soak and after pumping water into the column, had the highest niobium concentration of 214 mg/L. Based on the data trends, metal leaching was not complete from the CST at the conclusion of the caustic treatment.
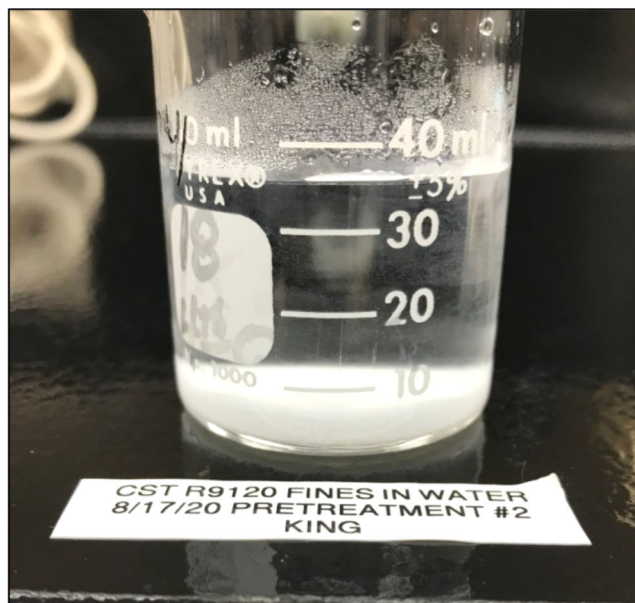
Figure 3-8. **CST Fines After Isolation and Settling in Water for Pretreatment #2.**
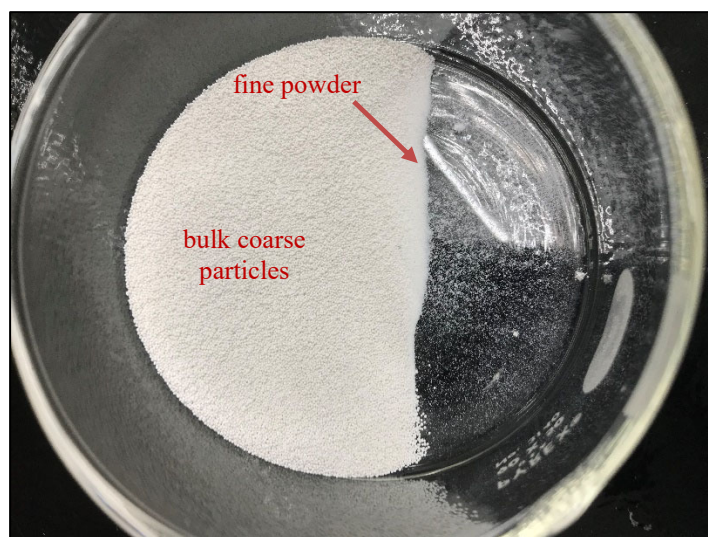
Figure 3-9. Photograph of Oven- and Air-Dried CST from Pretreatment #2.
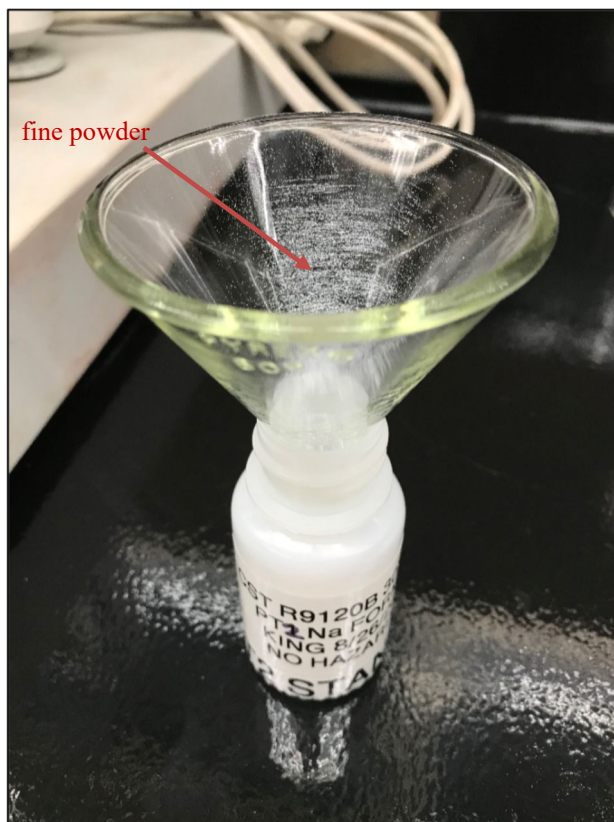
Figure 3-10. **Final Isolated Dry CST from Pretreatment #2.**

Table 3-7. CST Lot 2102020756 Pretreatment #2 Effluent Sample Analysis Results.

Labware ID[a]	Solution BV Processed Since Initial Caustic Contact	Liquid Entering Column	mg/L		
			Ti	Zr	Nb
LW18453	1.0	3 M NaOH	<1.0E-02	<4.0E-02	5.17E-01
LW18454	1.9		8.78E+00	1.04E+00	1.27E+02
LW18455	2.4		1.23E+01	1.65E+00	1.31E+02
LW18456	2.8		1.09E+01	1.92E+00	1.38E+02
LW18457	3.3		1.09E+01	2.10E+00	1.14E+02
LW18458	3.6	Deionized Water[b]	1.15E+01	3.56E+00	1.28E+02
LW18459	6.8		7.56E+00	1.06E+00	2.14E+02

[a] LW refers to the assigned Labware analytical software number.

[b] Deionized water sub-samples were collected following the 72-hour caustic soak.

3.4 Pretreated CST Characterization

Sub-samples of pretreated (#1 and #2) CST samples from Lot 2102020756 were evaluated to determine the density of a packed cylindrical (1-inch diameter) bed of the reference-state, hydrated material. Results are provided in Table 3-8. The measured density was 1.25 g/mL for a Pretreatment #1 sub-sample and the density was 1.23 g/mL for a Pretreatment #2 sub-sample. The results were calculated after calibrating the graduated cylinder volume using a known mass of water, as described above. The densities of the pretreated CST samples were similar to each other and were higher than the density of the as-received material. This was expected, since the as-received materials are in the hydrogen ionic form and the pretreated materials have been converted to the sodium form. CST conversion to the sodium form should result in a mass increase since sodium ions are heavier than hydrogen ions as indicated by the atomic masses of each element. These bulk densities are slightly higher (2-3%) than the values measured for sodium-form R9120-B CST used for the TCCR Demonstration of 1.21 g/mL.[6] A bulk measured density of 1.23 g/mL was reported for sodium-form IE-911 CST.[14]

Table 3-8. SRNL Measured Bulk Dry Bed Density for Pretreated R9120-B 30x60 Lot 2102020756.

Sample	CST Bulk Dry Density (g/mL)*
Pretreatment #1	1.250
Pretreatment #2	1.232

* based on reference-state CST mass (no water correction)

Replicate samples of sodium-form CST from Pretreatment #2 were submitted for Microtrac particle size analysis. The results are provided in Figures 3-11 and 3-12 and Table 3-9. Significant differences were observed for the two replicate samples due to the presence of a population of smaller particles below 250 μm in replicate B (Figure 3-12) that were absent in replicate A (Figure 3-11). On a volume-weighted basis, the mean particle diameters for the two samples were similar (477 μm for replicate A vs 443 μm for replicate B). These results are similar to the volume-based diameter determined from the sieve data for this lot of 459 μm. However, on a number basis the mean diameters were dramatically different (407 μm for replicate A vs 208 μm for replicate B). (Note: The number-based mean diameter is the mean calculated from the number distribution of particle diameters of each size, assuming a spherical particle shape. The volume-based mean diameter is the mean calculated from the distribution of particle volumes which is a cubic function of the particle diameter, assuming a spherical particle shape. The area-based mean diameter is the mean calculated from the distribution of particle area which is a square function of the particle diameter, assuming a spherical particle shape.) The population of small particles significantly shifted the number-based mean toward a smaller value for replicate B. For replicate A, no particles were observed below 228 μm. In contrast, smaller particles (~4.3% of the total particles observed) were observed in the range from 80 to 209 μm for replicate B. Visual observations during sample handling discussed in Section 3.2 explain this variability. No particles were observed by Microtrac for either sample below 80 μm. The primary peaks in the distributions are very similar for the two samples and are centered at 457 μm. Inspection of the particle size analyzer channel data (not shown) indicates that 14.2 and 11.5% of the particles (on a number basis), for replicates A and B respectively, are in the diameter range >592 μm. The channel data indicates that 0.12 and 4.8% of the particles (on a number basis) for replicates A and B

respectively, are in the diameter range <249 µm. It should be emphasized that the Microtrac particle size analysis algorithm converts all of the diameter data to a spherically equivalent diameter, so the data does not correlate directly to the sieve mesh dimension criteria used for CST specifications (U. S. Standard #30-#60 which corresponds to a sieve opening range of 250 to 595 µm). For comparison, the volume-based mean particle diameter for IE-911 CST was reported to be 325 µm based on Microtrac analysis, although both materials were sieved to produce a 30-60 mesh size range.[15]
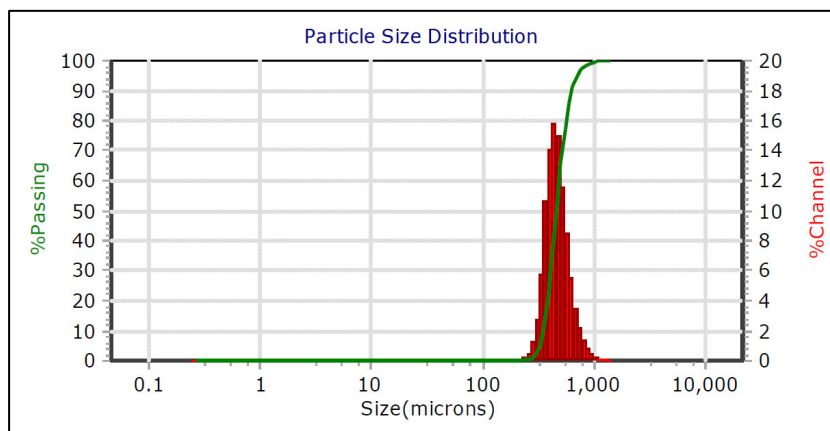
Figure 3-11. Microtrac Particle Size Analysis Result for R9120-B 30x60 CST Lot 2102020756 in Water Following Pretreatment #2 (replicate A, LW18604).
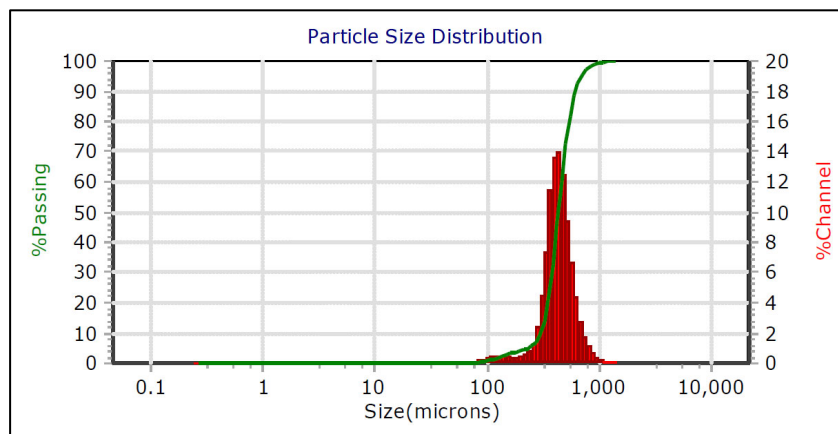
Figure 3-12. Microtrac Particle Size Analysis Result for R9120-B 30x60 CST Lot 2102020756 in Water Following Pretreatment #2 (replicate B, LW18605).

Table 3-9. Microtrac Particle Size Distribution Data for Pretreatment #2 CST in Water

Sample ID	LW18604 CST PT2 A*	LW18605 CST PT2 B*
Mean Volume Diameter (μm)	477.1	443.3
Mean Number Diameter (μm)	406.9	207.7
Mean Area Diameter (μm)	450.3	387.4
Percentile %	μm	
10	350.1	301.1
20	380.9	348.4
25	393.8	363.8
40	430.3	403.2
50	454.5	429.1
60	480.8	456.6
70	512.8	489.1
75	532.8	508.8
90	630.9	608.2
95	709.9	690.0

* LW refers to the assigned Labware analytical software number.

Duplicate sub-samples of pretreated CST (Pretreatment #1 and #2) were characterized under nitrogen purge gas by TGA using a Model TA2050 analyzer from TA Instruments following the same methodology used for the as-received sample (Section 3-1). Water mass correction factors (F-factor) were calculated based on cumulative mass losses observed for the samples up to 410 °C. TGA data for one replicate CST sub-sample from Pretreatment #2 is provided in Figure 3-13. Results are summarized in Table 3-10. These F-factors are in the typical range observed for reference-state, hydrated CST. A slightly lower F-factor (larger water content) of 0.79 was observed for the as-received, hydrogen form of Lot 2102020756 (Table 3-3). Although the F-factor values for the two CST media forms were similar, the drying method used for the as-received material was unknown and the Na- and H-forms of the media may have different waters of hydration.
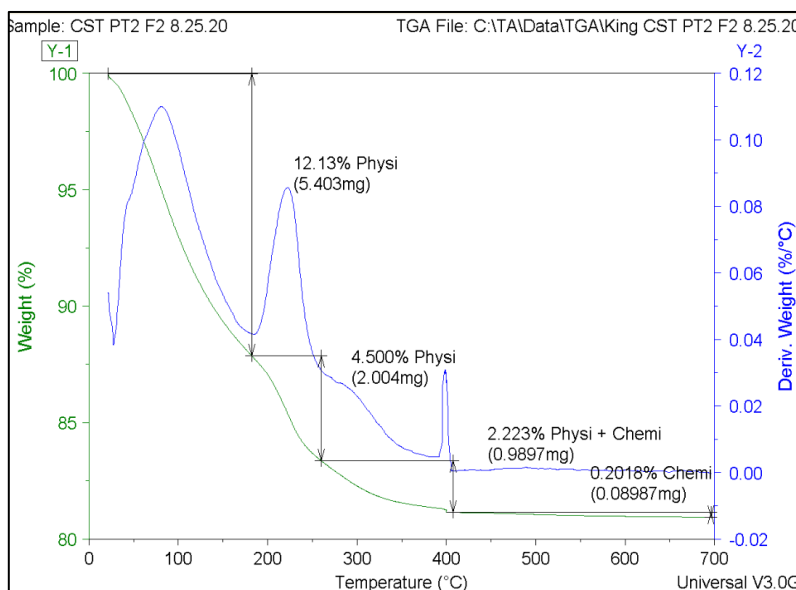
Figure 3-13. Thermal Gravimetric Analysis of Pretreated CST from Lot 2102020756 (sub-sample from Pretreatment #2).

Table 3-10. CST Lot 2102020756 Sub-Sample F-Factor Data.

CST Sub-Sample	Cumulative Wt. % Mass Loss at 410 °C	F-Factor
Pretreatment #1 F1	19.433	0.8057
Pretreatment #1 F2	19.373	0.8063
Average	19.403	0.8060
%RSD	0.2	---
Pretreatment #2 F1	19.010	0.8099
Pretreatment #2 F2	18.853	0.8115
Average	18.932	0.8107
%RSD	0.6	---

CST masses and volumes measured prior to and after Pretreatment #1 and #2 are provided in Table 3-11. After correction for water content, the CST sample masses were observed to increase by 9.9 and 10.3 wt. % after pretreatment, respectively, for Pretreatment #1 and #2. For comparison, a CST mass increase of 10.8% was observed previously with the R9120-B CST used for the TCCR Demonstration.[13] If the observed CST mass increase during pretreatment is associated with an increase in the fraction of sites occupied by Na^+ ions, then the observed CST mass increases would correspond to the absorption of 4.1 and 4.3 mmol of Na^+/g of dry (corrected for sorbed water) Na-form CST, respectively, for Pretreatment #1 and #2. This sodium loading is 85-89% of the reported ion exchange capacity of powder-form CST of 4.8 milliequivalents/g of Na-form CST.[16] For comparison, mass-based sodium loading values calculated for previous pretreatments of R9120-B CST were 4.3-4.4 mmol Na^+/g dry CST.[11] The difference between the measured values and the literature value could be explained by a mixed Na-/H-form of as-received CST media, by a binder content for the engineered CST media ranging from 11-15 wt. % assuming H-form CST, or some combination of these two cases. In addition, it does not appear that the value reported in the literature was corrected for water content. The data indicates that the as-received R9120-B 30x60 CST media from Lot 2102020756 was primarily in the H^+ ionic form. In addition, the fact that a similar mass increase was observed for Pretreatment #2 relative to what was observed for Pretreatment #1 (despite the fact that twice as much NaOH solution was used in Pretreatment #1) indicates that the abbreviated field pretreatment is adequate for complete CST conversion to the sodium ionic form. As indicated in Table 3-11, <100 mg of fines were isolated during each pretreatment.

Table 3-11. CST Lot 2102020756 Pretreatment Media Masses and Volumes.

CST Pretreatment	Initial As-Received CST Mass (g)[a]	Initial As-Received CST Dry Mass (g)[b]	As-Received CST Volume (mL)	Pretreated CST Mass (g)[a]	Pretreated CST Dry Mass (g)[b]	% Dry Mass Increase	CST Fines Mass (g)[a]
1	33.5451	26.3463	29.4	35.9203	28.9518	9.89	0.074
2	33.5454	26.3466	29.4	35.8448	29.0594	10.30	0.011

[a] reference-state, hydrated mass
[b] after correction for water content using F-factor

A single CST sub-sample from Pretreatment #1 was submitted for acid digestion and analysis to determine the concentrations of Ti, Zr, Nb, Na and minor metals in the solid. Five replicate sub-samples of CST from Pretreatment #2 were analyzed to establish control limits to confirm that complete CST digestion occurred based on statistical analysis of the ICP-MS Ti, Zr, and Nb data. Two samples (A and B) from Pretreatment #2 were also analyzed by ICP-ES to compare the sodium content to samples of as-received and Pretreatment #1 CST. The analytical results are provided in Table 3-12 and the averages and standard deviations for the five replicates are provided in Table 3-13. Titanium and zirconium results were consistent between the two methods. In general, the concentrations of each of the metals were similar to previous analytical results with the TCCR Demonstration CST. Average results reported previously were 15.60 wt. % Ti, 10.10 wt. % Zr, and 12.32 wt. % Nb.[11] Although the %RSD values for the three elements were below 7.5%, they were larger than the values reported for the TCCR Demonstration CST (3.87% for Ti, 2.60% for Zr, and 2.66% for Nb).

The sodium concentrations in the CST sub-samples from Pretreatment #1 and #2 were similar indicating that the field pretreatment method utilized for Pretreatment #2 was sufficient to completely convert the CST to the sodium ionic form. Based on the data in Tables 3-4 and 3-12, the sodium loading values resulting from pretreatment increased by 3.3 and 3.0 mmol Na^+/g dry CST, respectively, for the sub-samples from Pretreatment #1 and #2 relative to the as-received media. These loading values are lower than the values calculated based on mass increases (Table 3-11). The sodium loading values based on the data in Table 3-12 correspond to 69.2 and 63.3% of the theoretical maximum loading for powder-form CST of 4.8 mmol/g. These percentages are similar in magnitude to dilution/correction factors frequently used in ZAM cesium isotherm calculations to correct for mass contributions from the inert binder in engineered forms of CST. The Na:Ti molar ratios for the CST from Pretreatment #1 and #2 were 1.16 and 1.09, respectively, which is similar to the ratios observed previously for the R9120-B CST media used in the TCCR Demonstration, which ranged from 1.03 to 1.09.[11] These values are consistent with Na:Ti ratio of 1.07 for crystalline silicotitanate based on the published empirical formula, $Na_3Si_2(Nb_{0.3}Ti_{0.7})_4O_{13}(OH)\cdot4H_2O$.[17]

Additional statistical analysis of the CST compositional data is discussed in Section 3.5.

Table 3-12. Digested CST Lot 2102020756 From Pretreatment #1 and #2 Analysis Results.

CST Sample	Labware ID	µg/g*									
		ICP-MS			ICP-ES						
		Ti	Zr	Nb	Ti	Zr	Na	Mg	Al	Ca	Fe
PT1	LW18447	148000	102000	124000	148000	100000	82200	68.9	1610	<383	<103
PT2 A	LW18448	142000	94200	117000	142000	93500	74200	<81.0	<1947	246	<254
PT2 B	LW18449	153000	102000	125000	154000	102000	80500	<82.5	<1969	257	<259
PT2 C	LW18450	166000	111000	136000							
PT2 D	LW18451	162000	108000	133000	---	---	---	---	---	---	---
PT2 E	LW18452	169000	113000	138000							

* reference-state, hydrated CST mass basis

Table 3-13. Averages and Standard Deviations from ICP-MS Analysis of Digested CST from Pretreatment #2.

Statistic	µg/g*					
	ICP-MS			ICP-ES		
	Ti	Zr	Nb	Ti	Zr	Na
Average	158400	105640	129800	148000	97750	77350
Standard Deviation	10968	7625	8701	8485	6010	4455
%RSD	6.9	7.2	6.7	5.7	6.1	5.8
Wt. %	15.8	10.6	13.0	14.8	9.8	7.7

* reference-state, hydrated CST mass basis

3.5 Statistical Analysis of the Digestion Standards Data

Data obtained from the ICP-MS analysis of the five sample digestions of the CST standard described in Section 3.3 were used to develop a set of reference values and control limits for the concentrations of Ti, Zr, and Nb in future CST digestions. These data are provided in Table A-1 in Appendix A; JMP Pro Version 11.2.1 was used to conduct these evaluations.

The mean values for Ti, Zr, and Nb in Table 3-13 are consistent with prior analysis of CST. A summary of this data is provided in Table 3-14, along with current data for comparison. Differences between the elemental analysis data for the R-9120-B and IE-911 CST are near the %RSD values observed for the current R-9120-B data set (Table 3-13) and are not considered to be statistically significant.

Table 3-14. Comparison of CST Component Concentrations

	Ti (wt%)	Zr (wt%)	Nb (wt%)
ICP-MS of Standards (data from Table 3-13)	15.8	10.6	13.0
ICP-ES for Standards (data from Table 3-13)	14.8	9.8	--
TCCR Demonstration CST[11]	15.6	10.1	12.3
Walker ICP-ES (averages for IE-911)[18]	16.28	9.82	12.78

The five CST digestions were performed on different days to capture variability that is likely to be experienced in future digestions of the pretreated CST. The ICP-MS analysis of the standards was conducted on the same day, leading to the within-day variation of the ICP-MS method. Table 3-15 provides descriptive statistics for these measurements.

Table 3-15. Summary Statistics for ICP-MS Measurement of 5 Standard CST Digestions.

Type of Data	Value
Number of Observations	5
Mean µg/g (Ti Result)	158400
Mean µg/g (Zr Result)	105640
Mean µg/g (Nb Result)	129800
Standard Deviation µg/g (Ti Result)	10968
Standard Deviation µg/g (Zr Result)	7625
Standard Deviation µg/g (Nb Result)	8701
% Relative Standard Deviation (Ti Result)	6.924
% Relative Standard Deviation (Zr Result)	7.218
% Relative Standard Deviation (Nb Result)	6.703

While the summary statistics seen in Table 3-15 provide estimates of the within-day variation in the ICP-MS data, estimates of day-to-day variation of the ICP-MS method in the measurement of Ti, Zr, and Nb are needed to construct limits for Statistical Process Control (SPC) charts. Historical measurements of the laboratory standards utilized as part of routine ICP-MS analysis were used to address this issue. These data are provided in

Table A-2 of Appendix A. Measurements of Cs, Nb, Ti, and Zr are provided in this table, and results of the statistical analysis are displayed in Exhibit A-1 of Appendix A. This exhibit provides an analysis of variance of a random effects model for each element across the originating file. Included in the exhibit is an estimate of the variance of the percent difference between measurement and reference values across the originating files, which is assumed to represent a day-to-day relative standard deviation (%RSD) for each of the elements: 1.40% for Cs, 2.73% for Ti, 1.56% for Zr, and 2.70% for Nb.

The results in Table 3-15 and Exhibit A-1 are utilized to establish the centerline and 3-sigma limits (99.7%) for the SPC chart for each element. The centerline is the mean value from the table. The estimate of "sigma" (i.e., the total %RSD) underlying each of these charts is determined as the square root of the sum of the day-to-day variance and the within-day variance for each element. These variances are expressed as %RSD in Table 3-16 with the Lower Confidence Limit (LCL) and the Upper Confidence Limit (UCL) determined as 3 times sigma (99.7%) below and above the centerline, respectively.

Table 3-16. Determining Parameters for SPC Charts.

Element	Within-Day %RSD	Day-to-Day %RSD	CST Avg µg/g (centerline)	Total %RSD for CST*	99.7% LCL µg/g	99.7% UCL µg/g
Ti	6.92	2.73	158400	7.44	123025	193775
Zr	7.22	1.56	105640	7.38	82240	129040
Nb	6.70	2.70	129800	7.23	101660	157940

$$* \ Total\,\%RSD = \sqrt{(Within-Day\,\%RSD)^2 + (Day-to-Day\,\%RSD)^2}$$

For each in-tank batch contact test sample, an aliquot of the CST digestion standard will be processed alongside and Ti, Zr, and Nb concentrations as measured by ICP-MS will be compared against the control limits (LCL to UCL range) established here to confirm complete digestion of the sample.

3.6 Isolation and Characterization of CST Fine Particles in the As-Received CST Lots

Based on observations regarding the amount of fine particles in the CST sub-samples following pretreatment (see Section 3.3), the fine particles from two as-received (hydrogen form) R9120-B 30x60 CST lot sub-samples (Lots 2102020753 and 2102020756) were isolated from the bulk samples using wire mesh screens with 250 and 125 µm openings (separation between parallel wires within the screen). The screen with 250 µm openings was a #60 U. S. Standard (ASTM E-11) wire mesh sieve. The screen with 125 µm openings was a DIN 4188 sieve which corresponds to a #120 U. S. Standard ASTM E-11 sieve. The entire remaining samples were sieved to eliminate any additional sub-sampling biases. The masses of fine particles isolated from each lot are provided in Table 3-17. Photographs of the sub-samples from Lots 2102020753 and 2102020756 after sieving are provided in Figures 3-14 and 3-15, respectively. Optical micrographs of small particles isolated from Lot 2102020753 are provided in Figures 3-16 and 3-17. A greater fraction of the particles from the sample passing through the 125 µm screen (Figure 3-17) was irregular in shape, which may be an indication that some of these particles formed by attrition of larger particles. Both as-received samples from Lots 2102020753 and 2102020756 contained greater weight percentages of particles below 250 µm than reported by UOP (Table 2-2). Lot 2102020753 was reported to have 0.4 wt. % below 250 µm and Lot 2102020756 was reported to have 3.1 wt. % below 250 µm. The increase in small particles may have resulted from particle attrition during shipping or from sub-sampling differences. Since these sub-samples were primarily collected from the tops of the shipment drums, it was expected that the size

distributions would be depleted rather than enriched in fines. During handling of pretreated CST, fine particles were observed to migrate toward the bottom of a sample. However, during sieving of multiple sub-samples it was observed that fine particles were concentrated at various locations throughout the container.

The pretreated samples from CST Lot 2102020756 (PT1 and PT2) were also sieved to determine the weight percent of particles passing through #60 and #120 (U. S. Standard) screens. The results are provided in Table 3-17. Photographs of the sub-samples from the PT1 samples after sieving are provided in Figure 3-18. These results revealed that caustic pretreatment and subsequent water washing results in significant CST particle attrition. Presumably, osmotic shock effects associated with ionic strength changes occurring in the column during transitions from water to 3 M NaOH and then back to water promote particle attrition. Previous reports have indicated that caustic exposure of CST particles may promote particle attrition and exfoliation.[17] Subsequent evaluations revealed that the particle attrition was a consequence of the fact that the analysis method exposed the samples to both elevated temperature and vacuum.[19] Exposure of CST to only heat or only vacuum did not lead to cracking or exfoliation. For the PT1 sub-sample, which was pretreated with a higher flow rate than the target value during the transition from water to 3 M NaOH, the weight percent of particles below 250 μm of 16.8% was significantly larger than the as-received sample (4.8%) and the weight percent of particles below 125 μm was 2.9%. This result indicates that caustic treatment and subsequent water washing resulted in a shift in the distribution toward smaller particle sizes. Note that for the TCCR field pretreatment process, these fine particles would be generated after up-flow water elutriation to remove CST fines. The amount of fine particles in the PT1 sample is likely higher than would be observed in the TCCR columns due to: 1) the unexpected fast flow rate during the initial caustic exposure of this sample, and 2) the fact that the PT1 sample was exposed to two ionic strength transitions rather than the single ionic strength transition experienced in the TCCR columns prior to waste treatment. The spent CST in the TCCR columns will, however, be exposed to a second ionic strength transition at the conclusion of TCCR processing. In addition, the impact of continued caustic exposure during processing and preliminary column storage could create more fine particles in the TCCR columns. This data explains the observation of fine particles during the isolation of the PT1 sample following pretreatment (see Section 3.3). Note: SRNL is currently evaluating the impacts of soaking CST in 3 M NaOH for extended time periods. This testing includes exposure to rapid ionic strength transitions.

Fine particles were also observed for the PT2 sample following pretreatment. However, good flow control near the target values was achieved during the pretreatment of this sample. The data indicates that a shift in the particle size distribution was also observed for this sample relative to the as-received material, but the shift was reduced relative to the PT1 sample. Only 7.9 wt. % of the particles in the PT2 sample were below 250 μm, versus 4.8 wt. % in the original as-received sample and 16.8 wt. % in the PT1 sample. Presumably, this is because the ionic strength transitions during pretreatment for the PT2 sample were more gradual than those for the PT1 sample. This observation indicates that good flow control and slow ionic strength transitions are important during CST pretreatment to avoid particle attrition. The particle size shift observed for the PT2 sample, which was pretreated with the TCCR target flow rates, was smaller than was observed for the PT1 sample and the particle size shifts that occur in the TCCR columns may not significantly alter the cesium removal or hydraulic performance of the CST media.

To compare the fraction of fine particles observed for the R9120-B 30x60 CST lots versus historical samples, sub-samples of the TCCR Demonstration R9120-B and archived IE-911 CST were sieved using the same

method. The R9120-B CST sample was the remaining field-pretreated material which had been used for teabag preparation in previous testing. The IE-911 CST was vendor-pretreated, sodium form media collected from drum #36232-1-5 following the guidelines of SRR Procedure 241-H-4635 (used to collect R9120-B 30x60 sub-samples from shipment drums). The sieve data for each of these samples is provided in Table 3-17, where it is apparent that both sub-samples contained relatively few fine particles (≤0.26 wt. %) below 250 µm. This data indicates that the recently received R9120-B 30x60 CST lots contain significantly more fine particles than historical batches.

Table 3-17. Fine Particle Mass and Wt. % Data for Various CST Lots and Samples.

Vendor Product Designation	CST Lot	Media Form (H/Na)	Initial Mass (g)[a]	-60 to +120 (g)[a,b]	-60 to +120 (wt. %)[b]	-120 (g)[a,b]	-120 (wt. %)[b]	Total -60 (wt. %)[b]
R9120-B 30x60 (TCCR-1A)	2102020753	H	205.7	3.5986	1.7	0.0346	0.02	1.8
	2102020756	H	162.4	7.1413	4.4	0.7116	0.44	4.8
	2102020756 (PT1[c])		35.4308	4.9271	13.9	1.0368	2.9	16.8
	2102020756 (PT2[c])		34.3368	2.4699	7.2	0.2565	0.75	7.9
R9120-B (TCCR Demonstration CST)	2099000034	Na	16.6670	0.0261	0.16	0.0049	0.03	0.19
IE-911 (archived)	2081000056		244.4	0.6077	0.25	0.0345	0.01	0.26

[a] reference-state or as-received hydrated masses

[b] U. S. Standard Sieve # equivalent; "-" indicates particles passing and "+" indicates particles not passing the sieve number indicated

[c] PT = pretreated
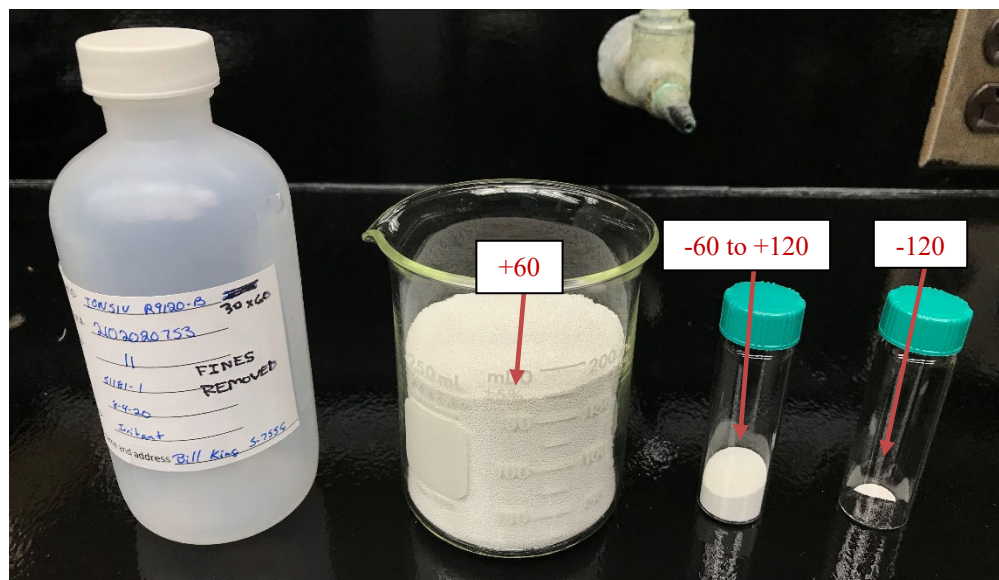
Figure 3-14. As-received CST Lot 2102020753 Following Separation of Small Particles by Sieving (U. S. Standard Sieve # equivalent indicated).
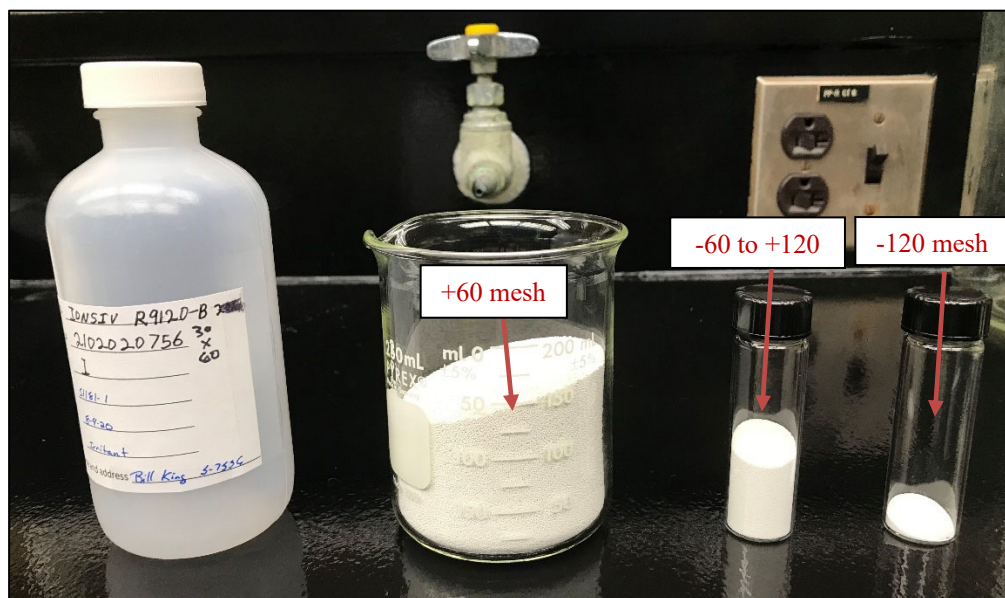
Figure 3-15. As-received CST Lot 2102020756 Following Separation of Small Particles by Sieving (U. S. Standard Sieve # equivalent indicated).

Figure 3-16. CST Lot 2102020753 Optical Micrograph of -60 to +120 (U. S. Standard equivalent) Particles.
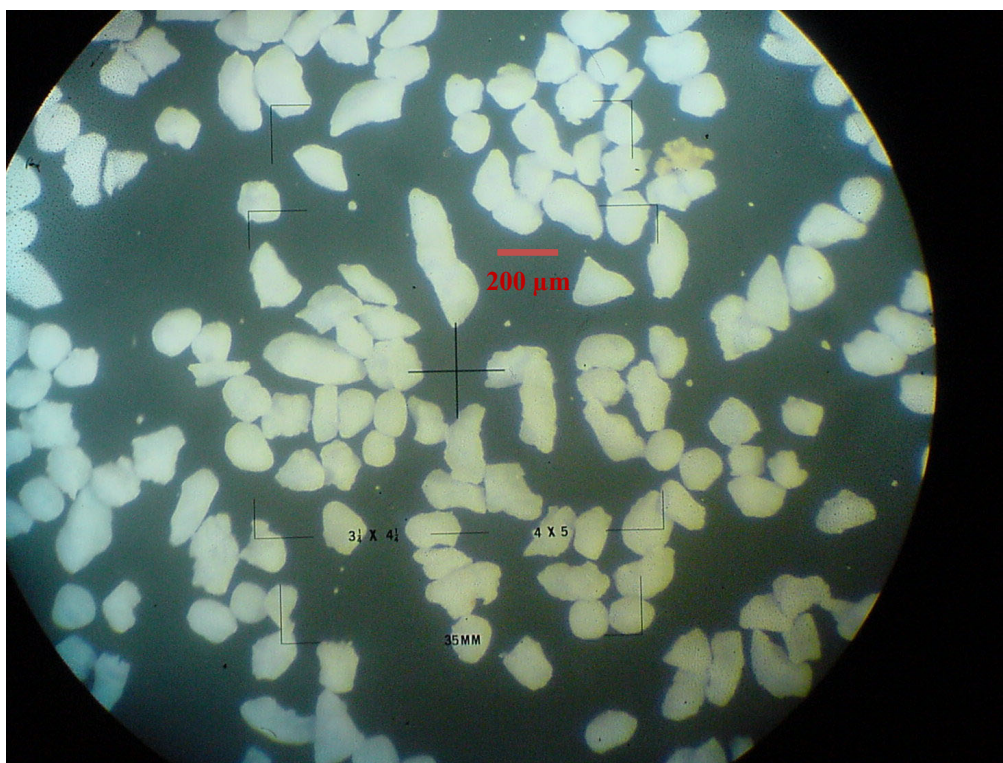
Figure 3-17. CST Lot 2102020753 Optical Micrograph of -120 (U. S. Standard Sieve # equivalent) Particles.
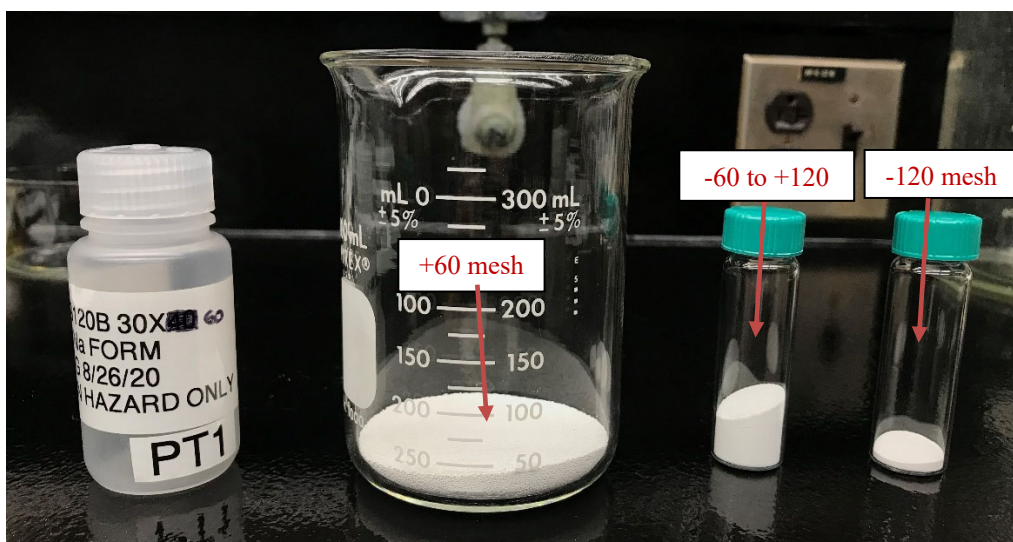
Figure 3-18. PT1 Pretreated CST Lot 2102020756 Following Separation of Small Particles by Sieving (U. S. Standard Sieve # equivalent indicated).

Sub-samples of the sieved CST media from the PT1 sample (Lot 2102020756) were submitted for Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) elemental analysis to determine whether the composition of the fine particles differed from the bulk material. Micrographs of the particles analyzed are provided in Figures 3-19 to 3-20 for the bulk and fine particles, respectively. Elemental analysis data for each spot identified in the figures is provided in Tables 3-18 to 3-19 for the bulk and fine particles, respectively. Additional analysis was subsequently conducted for the smallest of the fine particles. Micrographs of the smallest fine particles are provided in Figure 3-21 and elemental analysis data for each spot is provided in Table 3-20. Statistical summaries of the results from all three analyses are provided in Table 3-21. Elemental analysis results were very similar for the larger particles (Figure 3-19) and the initial fine particles (Figure 3-20) analyzed. As shown in Table 3-21, the average atomic percentages of O, Na, Si, Ti, Nb, and Zr (known CST components) in these two types of samples were near 62.5%, 2%, 7%, 10.5%, 4%, and 4.5%, respectively. Summary statistics for the smallest of the fine particles based on the data in Table 3-20 are also provided in Table 3-21 where it is apparent that no significant changes in the elemental composition were observed relative to the bulk and fine particles.
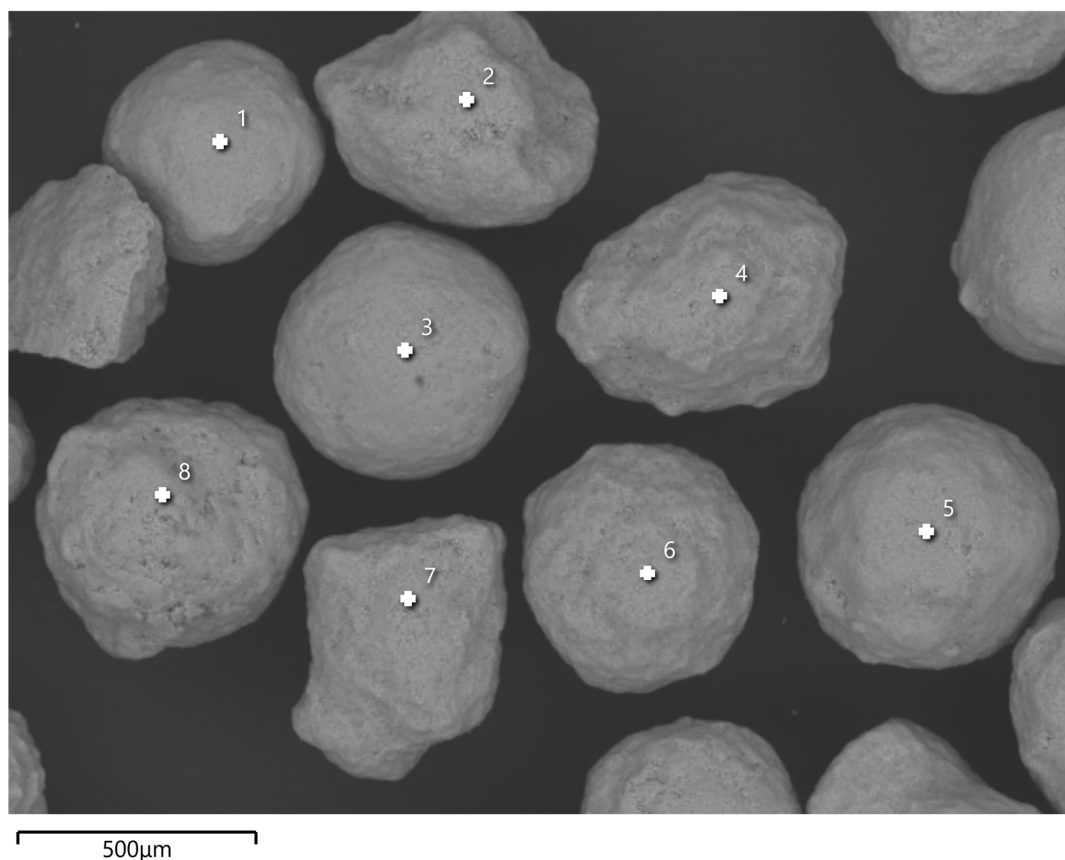
Figure 3-19. SEM Analysis of PT1 Pretreated CST Lot 2102020756 <u>Bulk</u> Particles (number labels indicate spots selected for elemental analysis).

Table 3-18. Atomic Percentages for Elements Observed at Each Spot Indicated in Figure 3-19 for the <u>Bulk</u> Particles from PT1 Pretreated CST Lot 2102020756.

Spectrum Label	1	2	3	4	5	6	7	8
Element	Atomic Percent							
C[a]	5.7	6.0	5.2	8.3	6.8	7.5	7.7	7.5
O	66.4	64.3	64.5	69.1	66.1	53.2	66.1	64.0
Na	2.1	2.1	1.9	2.0	1.9	1.7	2.3	1.3
Al	---	---	---	---	---	0.33	0.18	0.41
Si	7.1	7.7	7.4	6.2	7.1	9.4	6.7	7.4
Ti	10.7	11.1	12.0	8.4	10.0	17.4	9.2	11.3
Zr	3.5	4.1	4.3	2.6	3.8	4.6	3.8	3.7
Nb	4.4	4.8	4.8	3.5	4.4	6.0	4.2	4.4
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[a] carbon data is associated with the sample holder matrix

Figure 3-20. SEM Analysis of PT1 Pretreated CST Lot 2102020756 <u>Fine</u> Particles (number labels indicate spots selected for elemental analysis).

Table 3-19. Atomic Percentages for Elements Observed at Each Spot Indicated in Figure 3-20 for the <u>Fine</u> Particles from PT1 Pretreated CST Lot 2102020756.

Spectrum Label	1	2	3	4	5	6	7	8	9	10	11
Element	Atomic Percent										
C[a]	8.1	7.3	8.3	14.4	10.1	6.8	9.9	9.9	15.2	14.8	9.6
O	65.6	65.7	62.4	57.7	63.9	58.2	57.5	66.2	62.5	63.4	63.9
Na	2.2	2.4	2.3	2.2	2.0	1.9	1.7	2.0	2.0	2.4	2.5
Al	0.17	---	---	---	0.15	---	0.18	---	---	---	0.28
Si	7.2	6.8	7.4	6.9	6.8	8.4	8.0	6.6	6.0	5.7	7.0
Ti	10.0	9.6	11.0	10.4	9.2	14.6	13.4	8.8	8.0	7.5	9.4
Zr	2.8	3.8	3.8	4.0	3.7	4.5	4.0	2.6	2.8	3.1	3.3
Nb	4.1	4.4	4.8	4.4	4.2	5.6	5.3	3.8	3.6	3.2	4.1
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[a] carbon data is associated with the sample holder matrix
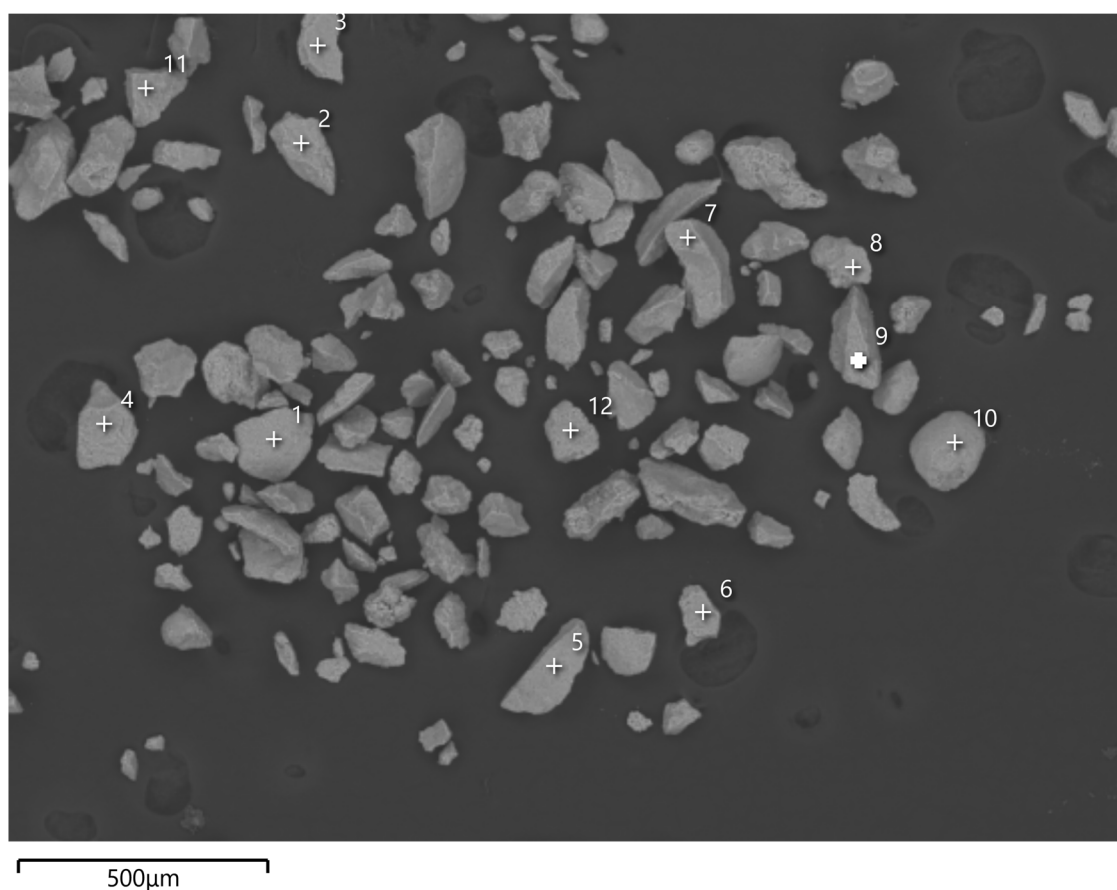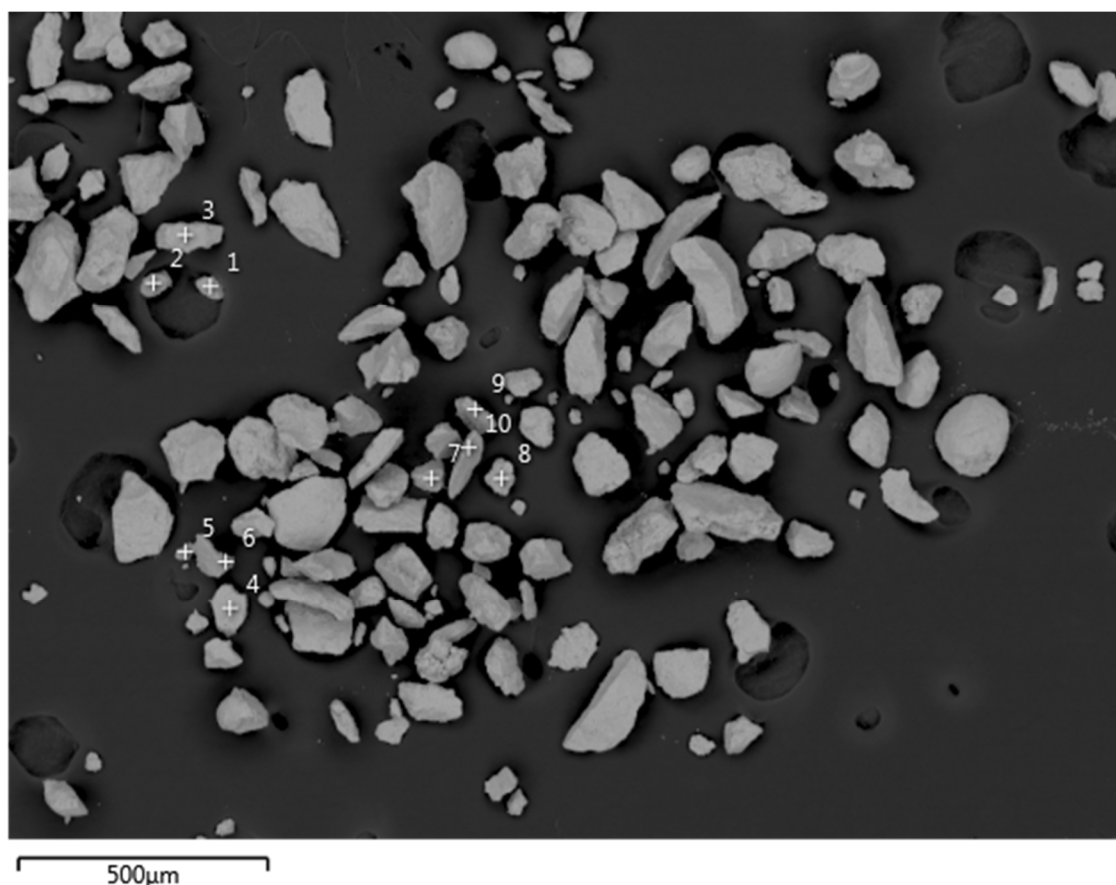

Figure 3-21. SEM Analysis of PT1 Pretreated CST Lot 2102020756 <u>Smallest Fine</u> Particles (number labels indicate spots selected for elemental analysis).

Table 3-20. Atomic Percentages for Elements Observed at Each Spot Indicated in Figure 3-21 for the <u>Smallest Fine</u> Particles from PT1 Pretreated CST Lot 2102020756.

Spectrum Label	1	2	3	4	5	6	7	8	9	10
Element	Atomic Percent									
C[a]	22.4	21.4	5.6	3.8	7.6	7.6	3.6	3.8	5.5	22.2
O	53.6	57.7	67.6	63.3	58.3	66.6	66.4	54.7	69.7	58.8
Na	1.6	1.6	1.9	2.4	1.4	1.2	3.8	1.6	1.4	1.2
Al	---	---	---	---	0.56	0.13	---	0.19	---	---
Si	6.0	5.3	6.9	8.4	8.6	6.7	7.1	9.2	6.4	4.8
Ti	8.7	7.8	9.9	12.2	12.9	9.7	10.2	17.8	9.0	7.0
Zr	3.8	3.0	3.7	4.8	5.1	3.9	3.8	5.6	3.7	2.8
Nb	3.9	3.2	4.5	5.1	5.5	4.1	5.3	7.0	4.3	3.2
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[a] carbon data is associated with the sample holder matrix

Table 3-21. Atomic Percentage Statistics Summary for Elements Observed for each Sample of PT1 Pretreated CST Lot 2102020756.

Element	C[a]	O	Na	Al	Si	Ti	Zr	Nb
Atomic % Statistics for <u>Bulk</u> Particles in Table 3-18								
Maximum	8.3	69.1	2.3	0.41	9.4	17.4	4.6	6.0
Minimum	5.2	53.2	1.3	0.18	6.2	8.4	2.6	3.5
Average	6.8	64.2	1.9	---	7.4	11.3	3.8	4.6
Standard Deviation	1.1	4.7	0.29	---	0.95	2.7	0.59	0.72
Atomic % Statistics for <u>Fine</u> Particles in Table 3-19								
Maximum	15.2	66.2	2.5	0.28	8.4	14.6	4.5	5.6
Minimum	6.8	57.5	1.7	0.15	5.7	7.5	2.6	3.2
Average	10.4	62.5	2.1	---	7.0	10.2	3.5	4.3
Standard Deviation	3.0	3.2	0.25	---	0.80	2.2	0.62	0.70
Atomic % Statistics for <u>Smallest Fine</u> Particles in Table 3-20								
Maximum	22.4	69.7	3.8	0.56	9.2	17.8	5.6	7.0
Minimum	3.6	53.6	1.2	0.13	4.8	7.0	2.8	3.2
Average	10.4	61.7	1.8	---	6.9	10.5	4.0	4.6
Standard Deviation	8.2	5.7	0.77	---	1.4	3.1	0.90	1.1

[a] carbon data is associated with the sample holder matrix

4.0 Conclusions

The field protocol utilized for the TCCR Demonstration has been validated regarding conversion of CST to the sodium form for use in TCCR-1A with R9120-B 30x60 media. No changes to the volume of caustic used for CST pretreatment per CST mass in the TCCR unit are recommended. A ratio of 3.7 mL of 3 M NaOH per g of as-received CST (corresponds to 4.3 mL of NaOH per mL of CST) was adequate for essentially complete CST conversion to sodium form. It was discovered that the up-flow elutriation step does not remove all the fine particulates. A digestion standard sample has been prepared from the pretreated CST and a set of statistical control limits for future in-field teabag sample (Ti, Zr, and Nb ICP-MS data) has been developed based on statistical evaluations of analysis data from five replicate samples. The

confidence intervals for the R9120-B 30x60 media are larger than those determined for the TCCR Demonstration CST. Teabag samples will be prepared from this standard material.

Various CST samples (vendor-pretreated, laboratory-pretreated, and as-received) and lots were sieved to determine the weight percentage of particles passing through #60 and #120 U. S. Standard equivalent screens (with openings of 250 and 125 μm, respectively). Comparison of results revealed that the as-received, H-form R9120-B 30x60 CST contains a significantly higher weight percentage of small particles (passing through a #60 U. S. Standard equivalent screen) than as-received, vendor-pretreated, Na-form IE-911 CST. In addition, pretreated, Na-form R9120-B 30x60 CST contains a larger weight percentage (8-17 wt. %) of particles passing through a #60 (U. S. Standard equivalent) screen than the as-received, H-form material (5 wt. %). More rapid exposure of CST to caustic solution during pretreatment using a higher liquid flow rate resulted in a much larger shift toward smaller particle sizes in the distribution. This observation indicates that good flow control and slow ionic strength transitions are important during CST pretreatment to avoid particle attrition. EDS elemental analysis of larger CST particles and fine particles removed by sieving revealed that the elemental composition of the fine particles is very similar to the bulk material.

The mean particle diameter of the R-9120-B 30x60 CST is smaller than the R9120-B CST used for the TCCR Demonstration, but not as small as the mean particle diameter reported for IE-911 CST. Compositionally, each of the CST lots evaluated (IE-911, R9120-B, and R9120-B 30x60) are very similar and would be expected to perform similarly. A direct comparison of the cesium ion exchange performance of the IE-911 and R9120-B 30x60 CST media lots has not been conducted. The ZAM isotherm model could be used to evaluate the cesium K_d data reported by the supplier and determine the binder dilution factor for the R9120-B 30x60 for comparison to the other CST lots.

5.0 Future Work

SRR should evaluate the impact of the presence of a significantly greater percentage of fine particles in the R9120-B 30x60 CST following pretreatment than was specified for this material. The upper and lower compositional confidence limits provided for the standard CST sample following digestion should be used for evaluation of the teabag field batch contact CST sample data and data for the associated control samples analyzed alongside the teabag samples. Teabag and control samples should be prepared using the standard CST from Pretreatment #2. ZAM modeling should be utilized to determine the binder dilution factor for R9120-B 30x60 CST prior to conducting modeling predictions of full-scale TCCR-1A column performance.

Given that significant numbers of fine particles exist in the pretreated CST samples, it is recommended that cesium loading batch contact experiments be conducted with simulant on an isolated portion of these particles for comparison to the bulk material to evaluate the cesium removal performance of the fine particles. This testing should also provide the ZAM dilution factor for modeling performance evaluations.

Based on the fact that the CST particle size appears to have shifted due to caustic exposure during pretreatment, it is recommended that additional evaluations of the impacts of CST caustic exposure be conducted. A ground CST sample has been stored in caustic solution at SRNL for several years. Examination and analysis of this material may provide insight on the stability of CST in caustic solution.

6.0 References

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Appendix A

Table A-1. ICP-MS Analytical Data for Samples of the CST Digestion Standard.

Sample	µg/g		
	Ti	Zr	Nb
Sample 18448 (PT2 A)	142000	94200	117000
Sample 18449 (PT2 B)	153000	102000	125000
Sample 18450 (PT2 C)	166000	111000	136000
Sample 18451 (PT2 D)	162000	108000	133000
Sample 18452 (PT2 E)	169000	113000	138000

Table A-2. Historical Measurements of ICP-MS Opening and Closing Standards.

Upload Date	Analysis Date	Originating File	Opening (O)/ Closing (C)	Mass	Analyte	Measurement (µg/g)	Reference Value (µg/g)
7/10/2020 6:55	7/1/2020	200604-3 Fnl Rpt.xlsm	O	m/z = 47	Ti	0.7536	0.744
7/10/2020 6:55	7/1/2020	200604-3 Fnl Rpt.xlsm	O	m/z = 90	Zr	5.1026	5.145
7/10/2020 6:55	7/1/2020	200604-3 Fnl Rpt.xlsm	O	m/z = 93	Nb	9.9136	10
7/10/2020 6:55	7/1/2020	200604-3 Fnl Rpt.xlsm	O	m/z = 133	Cs	9.9851	10
7/10/2020 6:55	7/1/2020	200604-3 Fnl Rpt.xlsm	C	m/z = 47	Ti	0.7253	0.744
7/10/2020 6:55	7/1/2020	200604-3 Fnl Rpt.xlsm	C	m/z = 90	Zr	5.0456	5.145
7/10/2020 6:55	7/1/2020	200604-3 Fnl Rpt.xlsm	C	m/z = 93	Nb	9.7824	10
7/10/2020 6:55	7/1/2020	200604-3 Fnl Rpt.xlsm	C	m/z = 133	Cs	9.9795	10
7/14/2020 14:40	7/13/2020	Nash 12569-12572 Fnl Rpt.xlsx	O	m/z = 47	Ti	0.7710	0.744
7/14/2020 14:40	7/13/2020	Nash 12569-12572 Fnl Rpt.xlsx	O	m/z = 90	Zr	4.9938	5.145
7/14/2020 14:40	7/13/2020	Nash 12569-12572 Fnl Rpt.xlsx	O	m/z = 93	Nb	10.3444	10
7/14/2020 14:40	7/13/2020	Nash 12569-12572 Fnl Rpt.xlsx	O	m/z = 133	Cs	10.0880	10
7/14/2020 14:40	7/13/2020	Nash 12569-12572 Fnl Rpt.xlsx	C	m/z = 47	Ti	0.7518	0.744
7/14/2020 14:40	7/13/2020	Nash 12569-12572 Fnl Rpt.xlsx	C	m/z = 90	Zr	5.0249	5.145
7/14/2020 14:40	7/13/2020	Nash 12569-12572 Fnl Rpt.xlsx	C	m/z = 93	Nb	9.9641	10
7/14/2020 14:40	7/13/2020	Nash 12569-12572 Fnl Rpt.xlsx	C	m/z = 133	Cs	10.1587	10
7/18/2020 20:02	7/15/2020	200617-1 Fnl Rpt.xlsx	O	m/z = 47	Ti	0.7295	0.744
7/18/2020 20:02	7/15/2020	200617-1 Fnl Rpt.xlsx	O	m/z = 90	Zr	4.9290	5.145
7/18/2020 20:02	7/15/2020	200617-1 Fnl Rpt.xlsx	O	m/z = 93	Nb	9.7527	10
7/18/2020 20:02	7/15/2020	200617-1 Fnl Rpt.xlsx	O	m/z = 133	Cs	10.0219	10
7/18/2020 20:02	7/15/2020	200617-1 Fnl Rpt.xlsx	C	m/z = 47	Ti	0.7268	0.744

Upload Date	Analysis Date	Originating File	Opening (O)/ Closing (C)	Mass	Analyte	Measurement (µg/g)	Reference Value (µg/g)
7/18/2020 20:02	7/15/2020	200617-1 Fnl Rpt.xlsx	C	m/z = 90	Zr	4.9662	5.145
7/18/2020 20:02	7/15/2020	200617-1 Fnl Rpt.xlsx	C	m/z = 93	Nb	10.4223	10
7/18/2020 20:02	7/15/2020	200617-1 Fnl Rpt.xlsx	C	m/z = 133	Cs	10.2200	10
7/22/2020 10:31	7/21/2020	200628-1200628-1 Fnl Rpt.xlsm	O	m/z = 47	Ti	0.7440	0.744
7/22/2020 10:31	7/21/2020	200628-1200628-1 Fnl Rpt.xlsm	O	m/z = 90	Zr	4.9757	5.145
7/22/2020 10:31	7/21/2020	200628-1200628-1 Fnl Rpt.xlsm	O	m/z = 93	Nb	10.1505	10
7/22/2020 10:31	7/21/2020	200628-1200628-1 Fnl Rpt.xlsm	O	m/z = 133	Cs	10.0016	10
7/22/2020 10:31	7/21/2020	200628-1200628-1 Fnl Rpt.xlsm	C	m/z = 47	Ti	0.7542	0.744
7/22/2020 10:31	7/21/2020	200628-1200628-1 Fnl Rpt.xlsm	C	m/z = 90	Zr	5.0253	5.145
7/22/2020 10:31	7/21/2020	200628-1200628-1 Fnl Rpt.xlsm	C	m/z = 93	Nb	10.2661	10
7/22/2020 10:31	7/21/2020	200628-1200628-1 Fnl Rpt.xlsm	C	m/z = 133	Cs	10.1157	10
7/27/2020 8:40	7/24/2020	200617-2 Fnl Rpt.xlsm	O	m/z = 47	Ti	0.7365	0.744
7/27/2020 8:40	7/24/2020	200617-2 Fnl Rpt.xlsm	O	m/z = 90	Zr	4.9052	5.145
7/27/2020 8:40	7/24/2020	200617-2 Fnl Rpt.xlsm	O	m/z = 93	Nb	9.7447	10
7/27/2020 8:40	7/24/2020	200617-2 Fnl Rpt.xlsm	O	m/z = 133	Cs	10.0779	10
7/27/2020 8:40	7/24/2020	200617-2 Fnl Rpt.xlsm	C	m/z = 47	Ti	0.7431	0.744
7/27/2020 8:40	7/24/2020	200617-2 Fnl Rpt.xlsm	C	m/z = 90	Zr	5.0007	5.145
7/27/2020 8:40	7/24/2020	200617-2 Fnl Rpt.xlsm	C	m/z = 93	Nb	10.2056	10
7/27/2020 8:40	7/24/2020	200617-2 Fnl Rpt.xlsm	C	m/z = 133	Cs	10.3482	10
7/30/2020 9:56	7/27/2020	200623-3 Final Report.xlsx	O	m/z = 47	Ti	0.7447	0.744
7/30/2020 9:56	7/27/2020	200623-3 Final Report.xlsx	O	m/z = 90	Zr	4.9386	5.145

Upload Date	Analysis Date	Originating File	Opening (O)/ Closing (C)	Mass	Analyte	Measurement (µg/g)	Reference Value (µg/g)
7/30/2020 9:56	7/27/2020	200623-3 Final Report.xlsx	O	m/z = 93	Nb	10.0721	10
7/30/2020 9:56	7/27/2020	200623-3 Final Report.xlsx	O	m/z = 133	Cs	10.0500	10
7/30/2020 9:56	7/27/2020	200623-3 Final Report.xlsx	C	m/z = 47	Ti	0.7369	0.744
7/30/2020 9:56	7/27/2020	200623-3 Final Report.xlsx	C	m/z = 90	Zr	4.8803	5.145
7/30/2020 9:56	7/27/2020	200623-3 Final Report.xlsx	C	m/z = 93	Nb	9.9619	10
7/30/2020 9:56	7/27/2020	200623-3 Final Report.xlsx	C	m/z = 133	Cs	9.9839	10
8/13/2020 15:39	8/6/2020	200721-1 Fnl Rpt.xlsm	O	m/z = 47	Ti	0.7218	0.744
8/13/2020 15:39	8/6/2020	200721-1 Fnl Rpt.xlsm	O	m/z = 90	Zr	5.0267	5.145
8/13/2020 15:39	8/6/2020	200721-1 Fnl Rpt.xlsm	O	m/z = 93	Nb	9.9878	10
8/13/2020 15:39	8/6/2020	200721-1 Fnl Rpt.xlsm	O	m/z = 133	Cs	10.1864	10
8/13/2020 15:39	8/6/2020	200721-1 Fnl Rpt.xlsm	C	m/z = 47	Ti	0.7090	0.744
8/13/2020 15:39	8/6/2020	200721-1 Fnl Rpt.xlsm	C	m/z = 90	Zr	4.9514	5.145
8/13/2020 15:39	8/6/2020	200721-1 Fnl Rpt.xlsm	C	m/z = 93	Nb	9.8330	10
8/13/2020 15:39	8/6/2020	200721-1 Fnl Rpt.xlsm	C	m/z = 133	Cs	10.2252	10
8/20/2020 9:54	8/18/2020	200810-4 Fnl Rpt.xlsm	O	m/z = 47	Ti	0.7430	0.744
8/20/2020 9:54	8/18/2020	200810-4 Fnl Rpt.xlsm	O	m/z = 90	Zr	4.9729	5.145
8/20/2020 9:54	8/18/2020	200810-4 Fnl Rpt.xlsm	O	m/z = 93	Nb	9.7899	10
8/20/2020 9:54	8/18/2020	200810-4 Fnl Rpt.xlsm	O	m/z = 133	Cs	10.2398	10
8/20/2020 9:54	8/18/2020	200810-4 Fnl Rpt.xlsm	C	m/z = 47	Ti	0.7364	0.744
8/20/2020 9:54	8/18/2020	200810-4 Fnl Rpt.xlsm	C	m/z = 90	Zr	4.9123	5.145
8/20/2020 9:54	8/18/2020	200810-4 Fnl Rpt.xlsm	C	m/z = 93	Nb	9.7570	10
8/20/2020 9:54	8/18/2020	200810-4 Fnl Rpt.xlsm	C	m/z = 133	Cs	10.1898	10
8/20/2020 9:59	8/19/2020	200810-4 18360 Fnl Rpt.xlsm	O	m/z = 47	Ti	0.7365	0.744
8/20/2020 9:59	8/19/2020	200810-4 18360 Fnl Rpt.xlsm	O	m/z = 90	Zr	4.8972	5.145

Upload Date	Analysis Date	Originating File	Opening (O)/ Closing (C)	Mass	Analyte	Measurement (µg/g)	Reference Value (µg/g)
8/20/2020 9:59	8/19/2020	200810-4 18360 Fnl Rpt.xlsm	O	m/z = 93	Nb	9.6159	10
8/20/2020 9:59	8/19/2020	200810-4 18360 Fnl Rpt.xlsm	O	m/z = 133	Cs	9.8855	10
8/20/2020 9:59	8/19/2020	200810-4 18360 Fnl Rpt.xlsm	C	m/z = 47	Ti	0.7503	0.744
8/20/2020 9:59	8/19/2020	200810-4 18360 Fnl Rpt.xlsm	C	m/z = 90	Zr	4.9484	5.145
8/20/2020 9:59	8/19/2020	200810-4 18360 Fnl Rpt.xlsm	C	m/z = 93	Nb	9.6925	10
8/20/2020 9:59	8/19/2020	200810-4 18360 Fnl Rpt.xlsm	C	m/z = 133	Cs	9.9553	10
8/27/2020 10:09	8/24/2020	200806-1 Fnl Rpt.xlsm	O	m/z = 47	Ti	0.7420	0.744
8/27/2020 10:09	8/24/2020	200806-1 Fnl Rpt.xlsm	O	m/z = 90	Zr	4.8501	5.145
8/27/2020 10:09	8/24/2020	200806-1 Fnl Rpt.xlsm	O	m/z = 93	Nb	9.7684	10
8/27/2020 10:09	8/24/2020	200806-1 Fnl Rpt.xlsm	O	m/z = 133	Cs	9.8489	10
8/27/2020 10:09	8/24/2020	200806-1 Fnl Rpt.xlsm	C	m/z = 47	Ti	0.7327	0.744
8/27/2020 10:09	8/24/2020	200806-1 Fnl Rpt.xlsm	C	m/z = 90	Zr	4.8591	5.145
8/27/2020 10:09	8/24/2020	200806-1 Fnl Rpt.xlsm	C	m/z = 93	Nb	9.7647	10
8/27/2020 10:09	8/24/2020	200806-1 Fnl Rpt.xlsm	C	m/z = 133	Cs	9.9688	10
9/4/2020 18:40	9/2/2020	King 200820-5 Fnl Rpt.xlsx	O	m/z = 47	Ti	0.7752	0.744
9/4/2020 18:40	9/2/2020	King 200820-5 Fnl Rpt.xlsx	O	m/z = 90	Zr	5.2221	5.145
9/4/2020 18:40	9/2/2020	King 200820-5 Fnl Rpt.xlsx	O	m/z = 93	Nb	10.9281	10
9/4/2020 18:40	9/2/2020	King 200820-5 Fnl Rpt.xlsx	O	m/z = 133	Cs	10.5142	10
9/4/2020 18:40	9/2/2020	King 200820-5 Fnl Rpt.xlsx	C	m/z = 47	Ti	0.8453[a]	0.744
9/4/2020 18:40	9/2/2020	King 200820-5 Fnl Rpt.xlsx	C	m/z = 90	Zr	5.1768	5.145
9/4/2020 18:40	9/2/2020	King 200820-5 Fnl Rpt.xlsx	C	m/z = 93	Nb	11.0209	10

[a] This data point was excluded from the control limit calculations as an outlier.

Upload Date	Analysis Date	Originating File	Opening (O)/ Closing (C)	Mass	Analyte	Measurement (μg/g)	Reference Value (μg/g)
9/4/2020 18:40	9/2/2020	King 200820-5 Fnl Rpt.xlsx	C	m/z = 133	Cs	10.6148	10
9/10/2020 11:15	9/4/2020	Daniel 18482-18489 Fnl Rpt.xlsx	O	m/z = 47	Ti	0.7409	0.744
9/10/2020 11:15	9/4/2020	Daniel 18482-18489 Fnl Rpt.xlsx	O	m/z = 90	Zr	4.9674	5.145
9/10/2020 11:15	9/4/2020	Daniel 18482-18489 Fnl Rpt.xlsx	O	m/z = 93	Nb	9.9704	10
9/10/2020 11:15	9/4/2020	Daniel 18482-18489 Fnl Rpt.xlsx	O	m/z = 133	Cs	10.0398	10
9/10/2020 11:15	9/4/2020	Daniel 18482-18489 Fnl Rpt.xlsx	C	m/z = 47	Ti	0.7379	0.744
9/10/2020 11:15	9/4/2020	Daniel 18482-18489 Fnl Rpt.xlsx	C	m/z = 90	Zr	4.9890	5.145
9/10/2020 11:15	9/4/2020	Daniel 18482-18489 Fnl Rpt.xlsx	C	m/z = 93	Nb	9.8712	10
9/10/2020 11:15	9/4/2020	Daniel 18482-18489 Fnl Rpt.xlsx	C	m/z = 133	Cs	10.2001	10
9/15/2020 12:47	9/14/2020	200821-6 Fnl Rpt.xlsm	O	m/z = 47	Ti	0.7527	0.744
9/15/2020 12:47	9/14/2020	200821-6 Fnl Rpt.xlsm	O	m/z = 90	Zr	5.0221	5.145
9/15/2020 12:47	9/14/2020	200821-6 Fnl Rpt.xlsm	O	m/z = 93	Nb	10.3870	10
9/15/2020 12:47	9/14/2020	200821-6 Fnl Rpt.xlsm	O	m/z = 133	Cs	10.2075	10
9/15/2020 12:47	9/14/2020	200821-6 Fnl Rpt.xlsm	C	m/z = 47	Ti	0.7555	0.744
9/15/2020 12:47	9/14/2020	200821-6 Fnl Rpt.xlsm	C	m/z = 90	Zr	4.9950	5.145
9/15/2020 12:47	9/14/2020	200821-6 Fnl Rpt.xlsm	C	m/z = 93	Nb	10.3242	10
9/15/2020 12:47	9/14/2020	200821-6 Fnl Rpt.xlsm	C	m/z = 133	Cs	10.1220	10
9/16/2020 12:38	9/15/2020	200821-4 Fnl Rpt.xlsm	O	m/z = 47	Ti	0.7326	0.744
9/16/2020 12:38	9/15/2020	200821-4 Fnl Rpt.xlsm	O	m/z = 90	Zr	4.9458	5.145
9/16/2020 12:38	9/15/2020	200821-4 Fnl Rpt.xlsm	O	m/z = 93	Nb	10.4351	10
9/16/2020 12:38	9/15/2020	200821-4 Fnl Rpt.xlsm	O	m/z = 133	Cs	10.0393	10

Upload Date	Analysis Date	Originating File	Opening (O)/ Closing (C)	Mass	Analyte	Measurement (µg/g)	Reference Value (µg/g)
9/16/2020 12:38	9/15/2020	200821-4 Fnl Rpt.xlsm	C	m/z = 47	Ti	0.6801	0.744
9/16/2020 12:38	9/15/2020	200821-4 Fnl Rpt.xlsm	C	m/z = 90	Zr	4.8759	5.145
9/16/2020 12:38	9/15/2020	200821-4 Fnl Rpt.xlsm	C	m/z = 93	Nb	9.7670	10
9/16/2020 12:38	9/15/2020	200821-4 Fnl Rpt.xlsm	C	m/z = 133	Cs	10.0663	10
9/18/2020 17:12	9/16/2020	King 18448-18452 Fnl Rpt.xlsx	O	m/z = 47	Ti	0.7563	0.744
9/18/2020 17:12	9/16/2020	King 18448-18452 Fnl Rpt.xlsx	O	m/z = 90	Zr	4.9532	5.145
9/18/2020 17:12	9/16/2020	King 18448-18452 Fnl Rpt.xlsx	O	m/z = 93	Nb	9.9984	10
9/18/2020 17:12	9/16/2020	King 18448-18452 Fnl Rpt.xlsx	O	m/z = 133	Cs	10.1436	10
9/18/2020 17:12	9/16/2020	King 18448-18452 Fnl Rpt.xlsx	C	m/z = 47	Ti	0.7480	0.744
9/18/2020 17:12	9/16/2020	King 18448-18452 Fnl Rpt.xlsx	C	m/z = 90	Zr	4.9270	5.145
9/18/2020 17:12	9/16/2020	King 18448-18452 Fnl Rpt.xlsx	C	m/z = 93	Nb	9.8841	10
9/18/2020 17:12	9/16/2020	King 18448-18452 Fnl Rpt.xlsx	C	m/z = 133	Cs	9.9819	10
9/23/2020 12:52	9/18/2020	200720-3 Fnl Rpt.xlsm	O	m/z = 47	Ti	0.7969	0.744
9/23/2020 12:52	9/18/2020	200720-3 Fnl Rpt.xlsm	O	m/z = 90	Zr	5.0724	5.145
9/23/2020 12:52	9/18/2020	200720-3 Fnl Rpt.xlsm	O	m/z = 93	Nb	10.1299	10
9/23/2020 12:52	9/18/2020	200720-3 Fnl Rpt.xlsm	O	m/z = 133	Cs	10.1586	10
9/23/2020 12:52	9/18/2020	200720-3 Fnl Rpt.xlsm	C	m/z = 47	Ti	0.8101	0.744
9/23/2020 12:52	9/18/2020	200720-3 Fnl Rpt.xlsm	C	m/z = 90	Zr	5.1226	5.145
9/23/2020 12:52	9/18/2020	200720-3 Fnl Rpt.xlsm	C	m/z = 93	Nb	10.2492	10
9/23/2020 12:52	9/18/2020	200720-3 Fnl Rpt.xlsm	C	m/z = 133	Cs	10.0971	10

Exhibit A-1. Random Effects Analysis of ICP-MS Opening and Closing Standards

Response % Relative Difference mass=m/z = 133, Analyte=Cs
Whole Model

Summary of Fit

RSquare	0.837295
RSquare Adj	0.837295
Root Mean Square Error	0.851032
Mean of Response	1.161063
Observations (or Sum Wgts)	32

REML Variance Component Estimates

Random Effect	Var Ratio	Var Component	Std Error	95% Lower	95% Upper	Sqrt Variance Component	Pct of Total
Originating File	2.7215432	1.9710938	0.8615385	0.2825094	3.6596782	1.4039565	73.129
Residual		0.7242559	0.2560631	0.4017318	1.6775707	0.8510323	26.871
Total		2.6953497	0.8615385	1.569786	5.6738515	1.641752	100.000

-2 LogLikelihood = 109.38411621
Note: Total is the sum of the positive variance components.

Total including negative estimates = 2.6953497

Response % Relative Difference mass=m/z = 47, Analyte=Ti
Whole Model

Summary of Fit

RSquare	0.82768
RSquare Adj	0.82768
Root Mean Square Error	1.720394
Mean of Response	0.048994
Observations (or Sum Wgts)	31

REML Variance Component Estimates

Random Effect	Var Ratio	Var Component	Std Error	95% Lower	95% Upper	Sqrt Variance Component	Pct of Total
Originating File	2.5235277	7.469027	3.3672394	0.8693591	14.068695	2.7329521	71.619
Residual		2.9597563	1.0858739	1.6111778	7.1255518	1.7203942	28.381
Total		10.428783	3.3475642	6.0617988	22.035507	3.2293627	100.000

-2 LogLikelihood = 147.59980995
Note: Total is the sum of the positive variance components.

Total including negative estimates = 10.428783

Response % Relative Difference mass=m/z = 90, Analyte=Zr
Whole Model

Summary of Fit

RSquare	0.897785
RSquare Adj	0.897785
Root Mean Square Error	0.720472
Mean of Response	-3.13697
Observations (or Sum Wgts)	32

REML Variance Component Estimates

Random Effect	Var Ratio	Var Component	Std Error	95% Lower	95% Upper	Sqrt Variance Component	Pct of Total
Originating File	4.658539	2.4181509	0.9820507	0.4933668	4.3429349	1.5550405	82.328
Residual		0.5190792	0.1835222	0.287924	1.2023265	0.7204715	17.672
Total		2.9372301	0.9820507	1.6745671	6.4417956	1.7138349	100.000

  -2 LogLikelihood = 106.12027272
Note: Total is the sum of the positive variance components.

Total including negative estimates = 2.9372301

Response % Relative Difference mass=m/z = 93, Analyte=Nb
Whole Model

Summary of Fit

RSquare	0.76298
RSquare Adj	0.76298
Root Mean Square Error	2.072981
Mean of Response	0.548469
Observations (or Sum Wgts)	32

REML Variance Component Estimates

Random Effect	Var Ratio	Var Component	Std Error	95% Lower	95% Upper	Sqrt Variance Component	Pct of Total
Originating File	1.6969307	7.2921329	3.5299848	0.3734898	14.210776	2.700395	62.921
Residual		4.2972485	1.5193068	2.3836068	9.9535779	2.0729806	37.079
Total		11.589381	3.5299848	6.9005731	23.410563	3.404318	100.000

  -2 LogLikelihood = 158.84027425
Note: Total is the sum of the positive variance components.

Total including negative estimates = 11.589381

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