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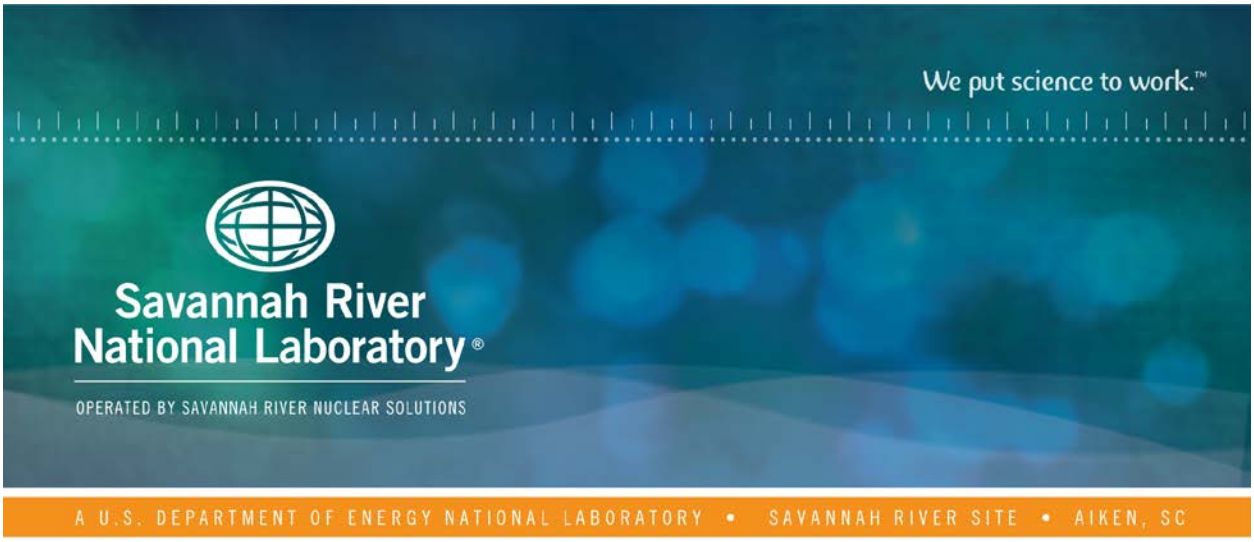

Characterization and CST Batch Contact Equilibrium Testing of Aged TCCR Tank 10H Batch 1A and 2 Process Supernate Samples

W. D. King, K. M. Taylor-Pashow, T. Hang, F. F. Fondeur

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EXECUTIVE SUMMARY

The Tank Closure Cesium Removal (TCCR) system uses ion exchange columns filled with Crystalline Silicotitanate (CST) media to process radioactive waste solutions for the removal of Cs-137. TCCR currently focuses on dissolving Savannah River Site (SRS) Tank 10H waste (primarily sodium saltcake solids) within the tank followed by at-tank ion exchange column treatment. Previous equilibrium batch contact tests conducted in the SRNL Shielded Cells laboratory and associated analyses indicated that CST cesium removal performance was lower than predicted by ZAM modeling for TCCR Tank 10H Production Supernate Batch 1A. An average cesium distribution coefficient of 1,948 mL/g which corresponds to 94.1% Cs^+ removal was observed for Batch 1A supernate at 38 °C in January of 2019 using laboratory pretreated IONSIV™ R9120-B[a] CST from Lot #209900034 (predominant TCCR CST batch) at a phase ratio of 122 mL/g. This cesium loading was approximately 32% lower than model predictions, presumably due to ion exchange competition or fouling associated with alkaline earth or transition metals present in the solutions at low levels. The current testing was designed to: 1) evaluate whether supernate compositional changes during storage would result in improved cesium removal performance with CST, and 2) assist in media selection and handling protocols for future TCCR columns by evaluating several CST manufacturer batches as well as samples of one CST batch which had been pretreated using two different methods (field and laboratory methods).

The Batch 1A supernate sample and a Tank 10H Batch 2 sample (second TCCR process batch) not previously evaluated by in-cell batch contact testing with CST were re-characterized after several months of storage in the Shielded Cells facility to identify any compositional changes that may have occurred during storage. No solids were visually observed in the waste samples. The data indicated that the carbonate anion concentration for the Batch 1A solution decreased by 32% during storage relative to the as-received sample. The average calcium concentration of the Batch 1A sample was observed to decrease while the calcium concentration of the Batch 2 sample was observed to increase, but the relative standard deviations of the duplicate measurements were high (55-120%) and the results were not conclusive. Only the initial Batch 1A sample contained measurable iron, while iron was below detectable levels during reanalysis of the aged sample. The Batch 2 supernate sample did not contain measurable iron during initial analysis or during reanalysis.

Cesium distribution coefficients (K_d), percent removal, and CST loading data for the TCCR production supernate batches (1A and 2) at 35.5 ºC are provided in Table ES-1. Average cesium distribution coefficients of 2,419 and 2,414 mL/g were observed with aged Tank 10H Batch 1A supernate with the R9120-B CST that had been pretreated using abbreviated field and exhaustive laboratory pretreatment methods, respectively. These results indicate that the pretreatment protocol does not impact the cesium removal performance in this waste supernate under these conditions. However, the pretreatment method was originally intended to alleviate bed fouling, not to equalize the cesium absorption results. The level of risk of bed fouling due to the modified pretreatment methods has not been investigated. These distribution coefficients are higher than were measured previously using the Batch 1A supernate and laboratory pretreated CST at a slightly higher temperature (38 ºC) and liquid-to-solid phase ratio. Relative to R9120-B CST, a lower average distribution coefficient was observed for the R9140-B CST batch (2,297 mL/g), while a higher average K_d value (2,605 mL/g) was observed with archived IE-911 CST media[b] with Batch 1A supernate. Similar trends, but lower distribution coefficients (K_d range: 2281-2444 mL/g), were

[a] IONSIV is a trademark of Honeywell UOP, Des Plaines, IL, U.S.A.; R9140-B, R0120-B, and IE-911 are engineered forms of CST.
[b] IE-911 refers to an archived sample of engineered CST that has had comparable preconditioning to the current R9140-B material.

observed with these CST batches and Batch 2 supernate, except that the R9140-B CST batch performed similarly to the R9120-B batches. Within the uncertainty of the analysis method (5%), the cesium distribution coefficients for the two supernate batches are statistically the same. The differing chemical compositions of the Batch 1A and Batch 2 samples (Batch 2 contained lower hydroxide and higher concentrations of other anions) is the likely cause of the apparent small CST performance differences between the tests.

The ZAM isotherm model evaluations of the batch contact equilibrium data are provided in Figures ES-1 and ES-2 for Tank 10H supernate Batches 1A and 2, respectively. Based on the modeling results, cesium loading on CST is still below the predicted values for both supernate samples. Previous testing with the engineered form of CST indicated that a dilution factor of 0.68 was required to account for CST mass contributions associated with the binder material. As shown in the figures, dilution factors of 0.578 and 0.568 were observed for the Tank 10H Batch 1A and 2 supernates, respectively. The dilution factors correspond to cesium loadings on the CST which are 15% (Batch 1A) and 17% (Batch 2) lower than expected. These results indicate that cesium loadings on the CST improved following supernate aging, since the cesium loadings were closer to the predicted values than was observed several months earlier (15% low versus 32% low for previous batch contact tests with Batch 1A supernate).

Table ES-1. Average Cesium Equilibrium Distribution Coefficients (K_d), % Removal, and Loading for Various CST Batches and Aged TCCR Tank 10H Process Supernates (Batches 1A and 2) at 35.5 °C.

Tank 10H Supernate	CST Batch/Sample[a]	Average Cs^+ K_d (mL/g)[c]	Cs^+ K_d %RSD	Cs^+ % Removal	mmol Cs^+/g CST[c,d]
Batch 1A	FP R9120-B[b]	2419	6.9	96.0	1.08E-03
	LP R9120-B[b]	2414	4.3	96.0	1.09E-03
	VP IE-911	2605	1.7	96.4	1.06E-03
	VP R9140-B	2297	2.4	95.9	1.06E-03
Batch 2	FP R9120-B[b]	2301	5.9	95.8	1.12E-03
	LP R9120-B[b]	2281	0.7	95.8	1.13E-03
	VP IE-911	2444	2.9	96.2	1.10E-03
	VP R9140-B	2307	0.7	95.9	1.10E-03

[a] FP = field-pretreated, LP = laboratory-pretreated, VP = vendor pretreated
[b] Lot #209900034 (predominant TCCR column CST batch)
[c] dry engineered CST mass basis (mass at 400 °C)
[d] cesium loading corresponds to total of all isotopes

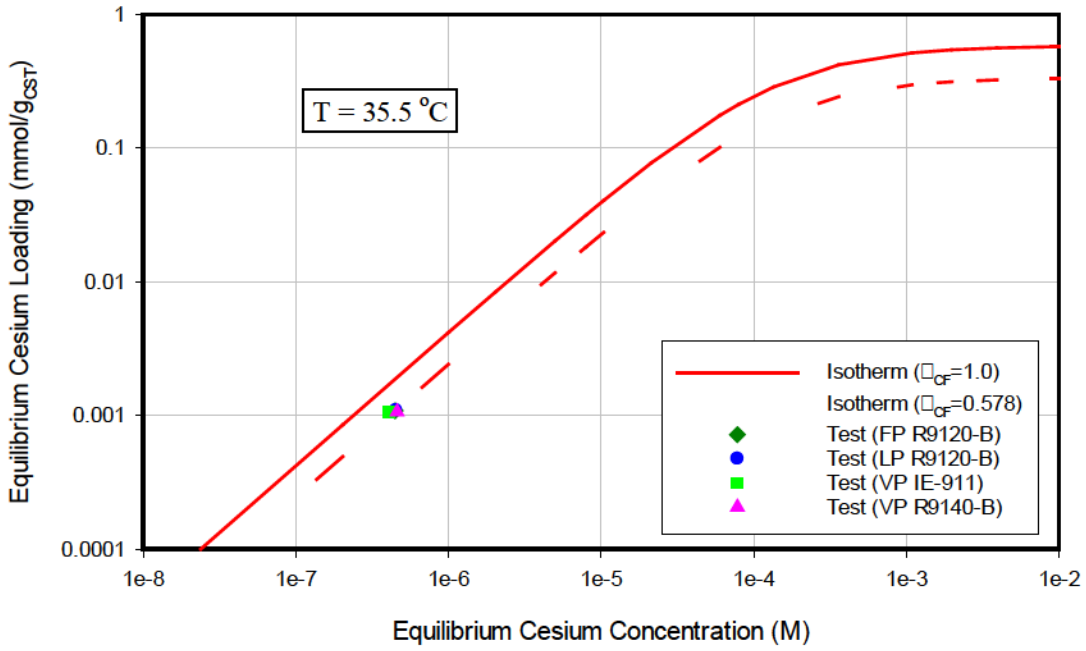

Figure ES-1. ZAM Model Prediction of Total Cesium Loading versus Batch Contact Results for TCCR Tank 10H Process Supernate Batch 1A.

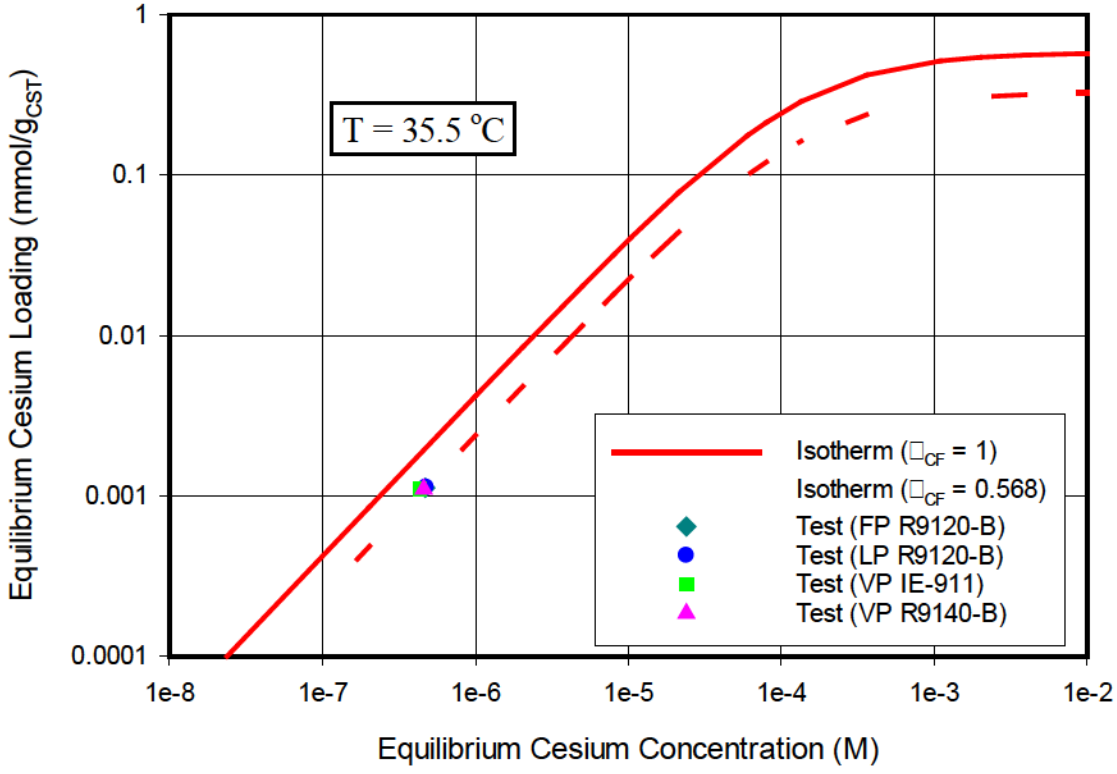

Figure ES-2. ZAM Model Prediction of Total Cesium Loading versus Batch Contact Results for TCCR Tank 10H Process Supernate Batch 2.

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LIST OF ABBREVIATIONS

CST	crystalline silicotitanate
DOE	Department of Energy
dpm	disintegrations per minute
ELN	Electronic Laboratory Notebook
g	gram
ICP-ES	Inductively Coupled Plasma - Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma - Mass Spectroscopy
K_d	Distribution Coefficient
mL	milliliter
PVDF	polyvinyldifluoride
rpm	revolutions per minute
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TCCR	Tank Closure Cesium Removal
TGA	Thermal Gravimetric Analysis
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
ZAM	ZAM (Zheng, Anthony, and Miller) Isotherm Model

1.0 Introduction

Near the beginning of calendar year 2019, Savannah River Remediation (SRR) deployed the Tank Closure Cesium Removal (TCCR) system using an ion exchange process to remove radioactive cesium from waste supernate. In TCCR, radioactive salt solution is filtered and then passed through ion exchange columns containing crystalline silicotitanate (CST) media, commercially known as UOP IONSIV™ R9120-B[a] (formerly called IE-911), to remove cesium. TCCR currently focuses on dissolving Savannah River Site (SRS) Tank 10H waste (primarily sodium saltcake solids) within the tank followed by at-tank ion exchange column treatment. Four TCCR columns were prepared, loaded with CST, and installed at SRS. Measurements of the projected maximum cesium loading on CST media from this waste supernate were conducted prior to TCCR processing using a "teabag" approach which involved contacting a small amount of CST solids (~0.1 g) with the large volume of Tank 10H radioactive waste supernate over a 10-day period. Cesium loading on the CST media within the teabags was 63-65% lower than ZAM (Zheng, Anthony, and Miller) isotherm model predictions for the waste compositions tested [1, 2]. To explore the difference, traditional CST batch contact tests were conducted at the Savannah River National Laboratory (SRNL) under controlled conditions using Tank 10H waste supernate samples (Batches 1 and 1A) in the first half of calendar year 2019 [3]. In these tests, the cesium loading was approximately 32% lower than model predictions. After several months of aging, the Tank 10H supernate samples were recharacterized and sub-samples were used to conduct additional batch contact tests using various CST media batches. The cesium equilibrium loading data from these tests are compared to the previous results and ZAM model predictions. In addition, the spent CST samples from the batch contact tests were analyzed to gain further insight into the impacts of alkaline earth and transition metals on cesium removal performance.

1.1 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Manual E7, Procedure 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. The work was performed following the applicable TTQAP, Technical Task and Quality Assurance Plan [4]. The Technical Task Request (TTR) associated with this work [5] indicates that portions of this work are Safety Significant, but that the testing reported herein and the supporting modeling are for Production Support rather than technical baseline and are not Safety Significant (see section entitled "Clarification of Safety Significant Tasks"). The software packages used as part of this work scope must comply with 1Q, QAP 20-1 Software Quality Assurance, E7, Section 5.0 and Software Engineering and Control, Applicable provisions of Section 5.4, Procedure 2.31, E7 Manual. Data are recorded in the Electronic Laboratory Notebook (ELN) system as notebook/experiment number A2341-00117-12 and E7518-00211-44.

The ZAM software is currently classified as Level D software [6] and ZAM calculations meet the Production Support needs specified for this task in the TTR. The functional requirements placed on ZAM were verified and validated [7].

[a] IONSIV is a trademark of Honeywell UOP, Des Plaines, IL, U.S.A.

2.0 Experimental Methods and Modeling Approach

2.1 CST Media Pretreatment

Two samples of the predominant TCCR column CST media from production batch IONSIV R9120-B, Lot #2099000034 (Mat. #8103701-556, Sub-sample from CUA #125953-A) which had been pretreated in two separate ways as described in previous reports [8, 9] were used for equilibrium testing. The pretreatment methods varied in both the total volume of 3 M NaOH used and the contact time, with the field pretreatment method utilizing much less caustic solution but more time than the laboratory method. The IE-911 and R9140-B CST batches were pretreated by the vendor prior to shipment and were used as-received. The R9140-B batch is a recently prepared CST batch while the IE-911 CST media has been stored at SRS for nearly two decades. Recent batch contact testing with the IE-911 CST batch and SRS Average simulant confirmed that the cesium removal performance of this batch had not changed significantly during storage [10].

2.2 CST Water Content Determination

Thermal Gravimetric Analysis (TGA) was conducted on each CST batch in duplicate to determine the water content. The thermal analysis involved heating sub-samples of CST 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. Mass loss profiles versus temperature during thermal analysis are provided in the Appendix. The total mass loss was determined as the sum of several successive mass losses believed to be associated with both physisorbed and chemisorbed water loss. Mass loss data for each CST sample up to 400 ºC is summarized and average F-factor (water content correction) values are provided in Table 2-1.

2.3 Tank 10H Supernate Sample Characterization

Two Tank 10H dissolved salt samples were characterized and used for cesium batch contact equilibrium testing. TCCR Tank 10H Batch 1A surface samples HTF-10-18-118 and -119 were received at SRNL in December of 2018 and were subsequently composited for analysis [1, 12]. Tank 10H TCCR Batch 2 surface sample HTF-10-19-43 was originally received at SRNL in April of 2019 [2]. In August of 2019, additional sub-samples were obtained from the archived solutions from these tank sampling events and were prepared for analysis. Samples were then filtered and diluted in either 3 M HNO_3 (ICP-ES analysis) or deionized water (IC Anion, Total Inorganic Carbon, and Free Hydroxide analysis) and submitted for analysis. Dilution factors for all samples ranged from 4-6.

2.4 CST Batch Contact Testing

Duplicate 10 mL sub-samples of the Tank 10H Batch 1A surface composite and Batch 2 surface samples were filtered (0.45 µm PVDF) and used for equilibrium batch contact testing with 0.12 g samples (~0.1 g after water content correction) of CST media. A ThermoScientific Incubator Shaker unit with a temperature controlled air atmosphere and an orbital agitation motion was installed in the Shielded Cells and the equilibrium tests were completed using an agitation rate of 150 rpm. The supernate and CST test samples were placed in 60 mL polyethylene bottles, transferred to the shaker oven, and continuously agitated for 6 contact days at 35.5 °C. The TTQAP [4] specified a target temperature for batch contact testing of 34 °C, but the ambient cell temperature at the time of testing was too high to achieve the target temperature. The oven display temperature was manually monitored and recorded periodically throughout testing and was checked with a calibrated thermocouple at test completion and confirmed to be within 1 °C of the

displayed value. The display temperature did not vary from 35.5 °C throughout testing. At test completion, individual samples were removed from the shaker, filtered through 0.45-µm syringe filters, and submitted for Cs-137 (gamma) analysis with no dilution. To prepare "blanks" for comparison, separate filtered sub-samples of each Tank 10H batch contact feed solution were also placed in 60 mL bottles, agitated in the shaker oven alongside the batch contact test samples (no CST contact), filtered again, and submitted for analysis. CST and Tank 10H supernate masses for individual samples during equilibrium batch contact testing are provided in Table 2-2.

Table 2-1. CST F-factor (Dry Mass Correction Factor) Data.

CST Batch/Sample[a]	Sample	Mass Loss at 410 °C
FP R9120-B	A	17.848
	B	17.976
Average Mass Loss		17.912
Mass Loss %RSD		0.5%
F-factor		0.821
LP R9120-B	A	18.530
	B	18.572
Average Mass Loss		18.551
Mass Loss %RSD		0.2%
F-factor		0.814
VP IE-911	A	16.167
	B	16.079
Average Mass Loss		16.123
Mass Loss %RSD		0.4%
F-factor		0.839
VP R9140-B	A	16.194
	B	16.122
Average Mass Loss		16.158
Mass Loss %RSD		0.3%
F-factor		0.838

[a] FP = field-pretreated, LP = laboratory-pretreated Lot 209900034, VP = vendor pretreated

Table 2-2. CST and Tank 10H Supernate Masses Used for Cesium Equilibrium Batch Equilibrium Testing at 35.5 °C.

TCCR Tank 10H Supernate Sample	CST Batch[a]	CST (g)[b]	Tank 10H (g)	Tank 10H (mL)[c]
Batch 1A Sample A	FP R9120-B Lot 209900034	0.1222	11.652	10.01
Batch 1A Sample B		0.1225	11.646	10.01
Batch 1A Sample A	LP R9120-B Lot 209900034	0.1221	11.655	10.01
Batch 1A Sample B		0.1221	11.652	10.01
Batch 1A Sample A	VP IE-911	0.1221	11.647	10.01
Batch 1A Sample B		0.1222	11.654	10.01
Batch 1A Sample A	VP R9140-B	0.1223	11.653	10.01
Batch 1A Sample B		0.1222	11.658	10.02
Batch 2 Sample A	FP R9120-B Lot 209900034	0.1222	11.603	10.01
Batch 2 Sample B		0.1223	11.608	10.02
Batch 2 Sample A	LP R9120-B Lot 209900034	0.1221	11.595	10.00
Batch 2 Sample B		0.1223	11.558	9.97
Batch 2 Sample A	VP IE-911	0.1224	11.596	10.01
Batch 2 Sample B		0.1223	11.612	10.02
Batch 2 Sample A	VP R9140-B	0.1223	11.601	10.01
Batch 2 Sample B		0.1223	11.594	10.00

[a] FP = field-pretreated, LP = laboratory-pretreated, VP = vendor pretreated
[b] hydrated CST reference state masses; multiply by appropriate F-factors to correct to dry state mass basis
[c] supernate volumes calculated based on measured masses and previously reported densities: 1.164 g/mL for Batch 1A [1] and 1.159 g/mL for Batch 2 [2]

2.5 Spent CST Digestion

After the completion of batch contact testing and the collection of sub-samples for analysis, the remaining CST media and a small amount of residual Tank 10H solution were stored at test temperature (35.5 ºC) without agitation. The solids were then washed and air dried as specified in SRNL Manual L29 Procedure ITS-0230. The ~0.1 g CST samples were then dissolved/digested in a hot HF-HNO_3 acid mixture in a sealed Teflon digestion vessel following established procedures and analyzed by ICP-ES and gamma spectroscopy. Blank samples from the field-pretreated R9120-B CST batch which were not exposed to supernate were also digested in the cells and analyzed alongside the batch contact samples. The field-pretreated R9120-B CST blank samples were also submitted for ICP-MS analysis in addition to the ICP-ES and gamma analyses to confirm the digestion was complete by comparing the Ti, Zr, and Nb concentrations to the control limits previously established for this standard [9]. In addition, blank unused samples of IE-911 and R9140-B were submitted for digestion and ICP-ES analysis. The digestion of these blank samples was performed in a non-radiological lab.

2.6 ZAM Isotherm Model Calculations

The ZAM Isotherm Model code is purchased commercial software developed at Texas A&M University by Rayford G. Anthony, Zhixin Zheng, and James E. Miller and designed to simulate ion-exchange equilibria of electrolytic solutions and CST solids. The ZAM code is a product of several years of development and research in Professor R. G. Anthony's Kinetics, Catalysis and Reaction Engineering Laboratory in the Department of Chemical Engineering Texas A&M University. A description of the current ZAM model is available [11].

R9120-B, R9140-B, and IE-911 are engineered forms of crystalline silicotitanate ion exchange media that are composed of submicron-sized CST "powder" bound into engineered beads with a binding agent. ZAM only calculates the CST media performance in its powdered form. Therefore, to adjust for the engineered CST media, a fixed amount of engineered-form media must be mathematically converted into its powdered form (i.e., to maintain the actual amount of exchange sites present in each batch contact sample) by multiplying the CST dry mass by a binder mass dilution factor (DF). Once the media is put into its equivalent powdered-form dry mass basis, ZAM calculations are performed. Upon completion of the ZAM batch contact calculations, the resulting cesium loadings and distribution coefficient (K_d) values are then converted back to an engineered-form basis. All ZAM calculations were made using software version-4. Although version-5 was developed to improve the calculated competition between $SrOH^+$ and Cs^+, the outcome is identical to version-4 in SRS tank waste compositions and version-4 converges better than the later version-5.

3.0 Results and Discussion

3.1 Tank 10H Supernate Characterization

Reanalysis results for the Tank 10H Batches 1A and 2 supernate samples are provided in Table 3-1 along with comparisons to previous analysis results [1,3,12]. Analysis results for most species agreed within 20% relative to previous analyses. The potassium concentration for the Batch 2 sample was nearly twice as high in the recent analysis relative to the previous result. The average calcium concentration observed for the Batch 1A sample was observed to decrease relative to previous results while the calcium concentration of the Batch 2 sample was observed to increase. However, as indicated in Table 3-1, the relative standard deviations of the duplicate measurements were high (55-120%) and the results were therefore inconclusive with regards to changes in the calcium concentration. Only the initial Batch 1A sample contained measurable iron (2.8 mg/L), while iron was below detectable levels (<1.5 mg/L) during reanalysis of this sample. The Batch 2 sample did not contain measurable iron during initial analysis or during reanalysis. The carbonate anion concentration for the Batch 1A solution was observed to decrease by 32% during storage relative to the as-received sample. The impact of this change on cesium loading is expected to be small since the decrease in the carbonate concentration is small. Initial Cs-137 concentrations for both Tank 10H samples were similar (within 6%) to results reported previously (Table 3-1). It is important to note that the TCCR Tank 10H supernate samples were recently formed by tank water additions and salt dissolution and had not aged in the tanks as is typical of many waste supernates.

3.2 CST Batch Contact Test Results

Based on the gamma scan results and the original total Cs^+ analysis reported previously [1, 3], cesium distribution coefficients (K_d; Equation 1), % removal (Equation 2), and loading (mmol Cs^+/g CST; Equation 3) values were calculated for each test sample. Results are provided in Table 3-2. Cesium loading results were very consistent between replicate samples for both Tank 10H

surface samples (0.7-6.9% RSD for the K_d values of all samples). Average cesium distribution coefficients of 2,419 and 2,414 mL/g were observed with aged Tank 10H Batch 1A supernate with the R9120-B CST pretreated using abbreviated field and exhaustive laboratory pretreatment methods, respectively. These results indicate that the pretreatment protocol does not impact the cesium removal performance in this waste supernate. These distribution coefficients are slightly (~24%) higher than were reported previously (1,948 mg/g) using the Batch 1A supernate and laboratory-pretreated CST at a slightly higher temperature (38 ºC) and liquid-to-solid phase ratio. Lower distribution coefficients were observed for the R9140-B CST batch (2,297 mL/g) while higher K_d values were observed with archived IE-911 CST media (2,605 mL/g) with Batch 1A supernate. Similar trends but lower distribution coefficients were observed with these CST batches and Batch 2 supernate (K_d range: 2281-2444 mL/g) except that the R9140-B CST batch performed similarly to the R9120-B batches. Within the uncertainty of the analysis method (5%), the cesium distribution coefficients for the two supernate batches are statistically the same. The differing chemical compositions of the Batch 1A and Batch 2 samples (Batch 2 contained lower hydroxide and higher concentrations of other anions) is the likely cause of the apparent small CST performance differences between the tests.

$$K_d = \left[\left(\frac{C_i}{C_f}\right) - 1\right]\left[\frac{V}{MF}\right] \qquad \text{(Equation 1)}$$

$$\%\ Cs^+\ \text{Removal} = [(C_i - C_f)/C_i][100] \qquad \text{(Equation 2)}$$

$$Q = (C_i - C_f)(V)/(MF) \qquad \text{(Equation 3)}$$

where,

K_d - distribution coefficient, (mL/g) on a dry mass basis (mass at 400 °C)

C_i - initial liquid-phase Cs^+ concentration, [M]

C_f - final (i.e., equilibrium) liquid-phase Cs^+ concentration, [M]

V - liquid-phase volume, (mL)

M - CST in hydrated reference state mass, (g)

F - mass correction factor for CST water content, and

Q - total Cs^+ loading.

Note: Since cesium K_d and percent removal calculations involve cesium concentration ratios, these values can be calculated using Cs-137 concentration data only or total cesium concentrations. In contrast, total cesium loading calculations require the determination of the sum of all cesium isotopes.

Overall, the results indicate modest improvement in CST performance with supernate aging. Approximately 20% more CST was used for each batch contact test on average relative to previous testing and the final cesium concentrations for the samples were ~34% lower than were observed previously. This difference appears to be statistically significant given the 5% uncertainty reported

for Cs-137 analysis. However, there was also a slight temperature difference between the tests (35.5 versus 38 °C for previous testing). Since lower temperatures should result in greater cesium loading on the CST, it is possible that the observed loading differences are the result of the small temperature difference which may not be accurately accounted for by ZAM. The supernate analysis results do not clearly identify any compositional changes that may have led to these improvements.

Table 3-1. Characterization Data for As-Received and Aged TCCR Tank 10H Process Supernate Batches 1A and 2.

Component	Batch 1A[a,c] August 2019	Batch 1A[a] December 2018	Ratio aged: as-received	Batch 2[b,c] August 2019	Batch 2[b] April 2019	Ratio aged: as-received
	mg/L		Ratio	mg/L		Ratio
Na^+	87493	87082	1.00	81267	81912	0.99
K^+	77.0	86.3	0.89	71.9	37.7	1.9
Al (as AlO_4^-)	1075	1138	0.94	1051	1054	1.0
Ca	1.5[d]	2.9	0.53	3.8[d]	0.89	4.3
Cr	9.5	9.5	1.00	9.0	9.8	0.92
Fe	<1.5	2.8	---	<1.4	<0.28	---
	Molarity		Ratio	Molarity		Ratio
Free OH^-	1.83	1.82	1.0	0.60	0.66	0.91
NO_3^-	0.90	0.73	1.2	1.30	1.19	1.1
CO_3^{2-}	0.22[e]	0.32	0.68	0.45	0.43	1.0
SO_4^{2-}	0.19	0.17	1.1	0.29	0.28	1.0
NO_2^-	0.090	0.076	1.2	0.073	0.069	1.0
PO_4^{3-}	<0.006	<0.0003	---	<0.006	<0.001	---
Total Cs^+ (ICP-MS)	---	1.13E-5[f]	---	---	1.17E-5[f]	---
	dpm/mL		Ratio	dpm/mL		Ratio
Cs-137	4.73E+07	4.87E+07	0.97	4.81E+07	5.10E+07	0.94

[a] composite of samples HTF-10-18-118 and -119; previous characterization reported in references [1] and [12]
[b] sample HTF-10-19-43; previous characterization reported in reference [2]
[c] average of duplicate results, % RSD ≤6% unless otherwise indicated
[d] %RSD 119% for Batch 1B and 55% for Batch 2
[e] %RSD 21%
[f] as reported previously [1,2]; total cesium not reanalyzed

Table 3-2. Cesium Equilibrium Distribution Coefficients, % Removal, and Loading for Various CST Batches and Aged TCCR Tank 10H Process Supernates (Batches 1A and 2) at 35.5 °C.

CST Batch[a]	TCCR Tank 10H Supernate Sample	Final Cs-137 (dpm/mL)	Initial Cs-137 (dpm/mL)	Cs^+ K_d (mL/g)[b]	Cs^+ % Removal	mmol Cs^+/g CST[b,c]
FP R9120-B	Batch 1A Sample A	1.79E+06	4.73E+07	2537	96.2	1.08E-03
	Batch 1A Sample B	1.96E+06		2302	95.9	1.08E-03
			Average	2419	96.0	1.08E-03
			%RSD	6.9	---	---
LP R9120-B	Batch 1A Sample A	1.84E+06	4.73E+07	2488	96.1	1.09E-03
	Batch 1A Sample B	1.95E+06		2341	95.9	1.09E-03
			Average	2414	96.0	1.09E-03
			%RSD	4.3	---	---
VP IE-911	Batch 1A Sample A	1.69E+06	4.73E+07	2637	96.4	1.06E-03
	Batch 1A Sample B	1.73E+06		2573	96.3	1.06E-03
			Average	2605	96.4	1.06E-03
			%RSD	1.7	---	---
VP R9140-B	Batch 1A Sample A	1.96E+06	4.73E+07	2259	95.9	1.06E-03
	Batch 1A Sample B	1.90E+06		2336	96.0	1.06E-03
			Average	2297	95.9	1.06E-03
			%RSD	2.4	---	---
FP R9120-B	Batch 2 Sample A	1.92E+06	4.81E+07	2398	96.0	1.12E-03
	Batch 2 Sample B	2.08E+06		2205	95.7	1.12E-03
			Average	2301	95.8	1.12E-03
			%RSD	5.9	---	---
LP R9120-B	Batch 2 Sample A	2.02E+06	4.81E+07	2292	95.8	1.13E-03
	Batch 2 Sample B	2.03E+06		2269	95.8	1.13E-03
			Average	2281	95.8	1.13E-03
			%RSD	0.7	---	---
VP IE-911	Batch 2 Sample A	1.88E+06	4.81E+07	2393	96.1	1.10E-03
	Batch 2 Sample B	1.81E+06		2495	96.2	1.10E-03
			Average	2444	96.2	1.10E-03
			%RSD	2.9	---	---
VP R9140-B	Batch 2 Sample A	1.96E+06	4.81E+07	2295	95.9	1.10E-03
	Batch 2 Sample B	1.94E+06		2319	96.0	1.10E-03
			Average	2307	95.9	1.10E-03
			%RSD	0.7	---	---

[a] FP = field-pretreated, LP = laboratory-pretreated Lot #209900034, VP = vendor pretreated
[b] dry CST mass basis
[c] cesium loading corresponds to total of all isotopes based on previous analyses [1] and [2]

3.3 Batch Contact CST Sample Digestion Data

Net metal loadings on the CST samples at the completion of batch contact testing are provided in Table 3-3 for Batch 1A supernate and Table 3-4 for Batch 2 supernate. Results presented in the tables are measured concentrations of each of the elements minus the amount measured in the blank sample for the same material (i.e., CST batch). Data for the standards (blanks) is provided in Appendix B, along with Ti and Zr weight percent data for all samples. Results are also summarized for the blank CST and samples (uncorrected for blanks) contacted with both supernates in Figures 3-1 through 3-3 for calcium, magnesium, and iron, respectively. The blanks contained measurable amounts of all of these metals except cesium at varying levels. Given that the R9120-B blanks contained no Cs, the cesium on the batch contact residuals can be assumed to represent Cs sorbed during batch contact rather than contaminant cesium from the Shielded Cells. Cesium from the wash samples was not included in the total cesium reported for the CST as has been done during previous teabag analyses since this amount is usually less than 5% of the total. The cesium loading results determined by CST digestion agree within 10% with the loading results based on the liquid phase analysis, with two digestion data points exceeding and the remaining six results being lower than was observed with the liquid. Given the 5% uncertainty associated with Cs-137 gamma analysis, many of the liquid- and solid-based cesium loading results are not statistically different. In general, the IE-911 contained less of the trace metals (Ca, Mg, Fe) than the R9120-B material. Presumably, alkaline earth and transition metals sorb to the CST media during synthesis or subsequent handling. In general, no major differences were observed for samples contacted with Batch 1A or 2 supernates. Compared to the blank samples, the IE-911 and R9140-B appeared to uptake higher amounts of iron during the batch contact testing than the R9120-B CST samples.

Table 3-3. Comparison of Cesium Loading for Tank 10H Batch 1A Batch Contact Equilibrium Samples (Post Contact) With That of Other Elements on the CST (Corrected for the F-Factor).

CST[a]	FP R9120-B	LP R9120-B	VP IE-911	VP R9140-B
Element	Net Loading (Average) mmol/g (%RSD[b])			
Cs[c]	1.0E-03 (5.6%)	1.2E-03 (2.7%)	1.0E-03 (1.8%)	9.8E-04 (0.0%)
Al	-6.1E-02 (2.0%)	-4.2E-02 (19%)	2.1E-02 (4.9%)	1.0E-01 (21%)
Ca	4.5E-03 (0.0%)	1.2E-02 (10%)	1.1E-03 (8.9%)	8.9E-03 (18%)
Fe	1.9E-03 (13%)	3.1E-03 (25%)	6.9E-03 (17%)	1.6E-02 (93%)
Mg	-3.1E-03 (23%)	2.3E-03 (28%)	-1.8E-03 (24%)	7.6E-04 (33%)
Na	1.2E-01 (7.3%)	9.0E-01 (9.2%)	-3.9E-01 (5.7%)	-1.5E-01 (25%)

[a] FP = field-pretreated, LP = laboratory-pretreated Lot 209900034, VP = vendor pretreated
[b] %RSD values based on original measured values before blank subtraction.
[c]Based on ^{137}Cs gamma measurements corrected for the isotopic ratio measured in the Tank 10 Batch 1A samples of 16.7% [1].

Table 3-4. Comparison of Cesium Loading for Tank 10H Batch 2 Batch Contact Equilibrium Samples (Post Contact) With That of Other Elements on the CST (Corrected for the F-Factor).

CST[a]	FP R9120-B	LP R9120-B	VP IE-911	VP R9140-B
Element	Net Loading (Average) mmol/g (%RSD[b])			
Cs[c]	1.1E-03 (5.1%)	1.1E-03 (2.1%)	9.8E-04 (0.2%)	1.0E-03 (1.9%)
Al	9.0E-04 (15%)	1.9E-02 (34%)	3.5E-02 (6.5%)	1.2E-01 (64%)
Ca	7.4E-03 (0.6%)	2.1E-02 (33%)	5.9E-03 (7.4%)	-7.4E-04 (5.2%)
Fe	8.9E-04 (28%)	5.6E-03 (28%)	5.9E-03 (11%)	1.7E-02 (65%)
Mg	-7.8E-04 (12%)	9.7E-03 (43%)	-1.7E-03 (21%)	-7.1E-04 (8.7%)
Na	2.4E-01 (11%)	-4.3E-02 (17%)	-4.4E-01 (2.5%)	-6.4E-01 (0.4%)

[a] FP = field-pretreated, LP = laboratory-pretreated Lot 209900034, VP = vendor pretreated
[b] %RSD values based on original measured values before blank subtraction.
[c]Based on ^{137}Cs gamma measurements corrected for the isotopic ratio measured in the Tank 10 Batch 2 samples of 16.8% [2].

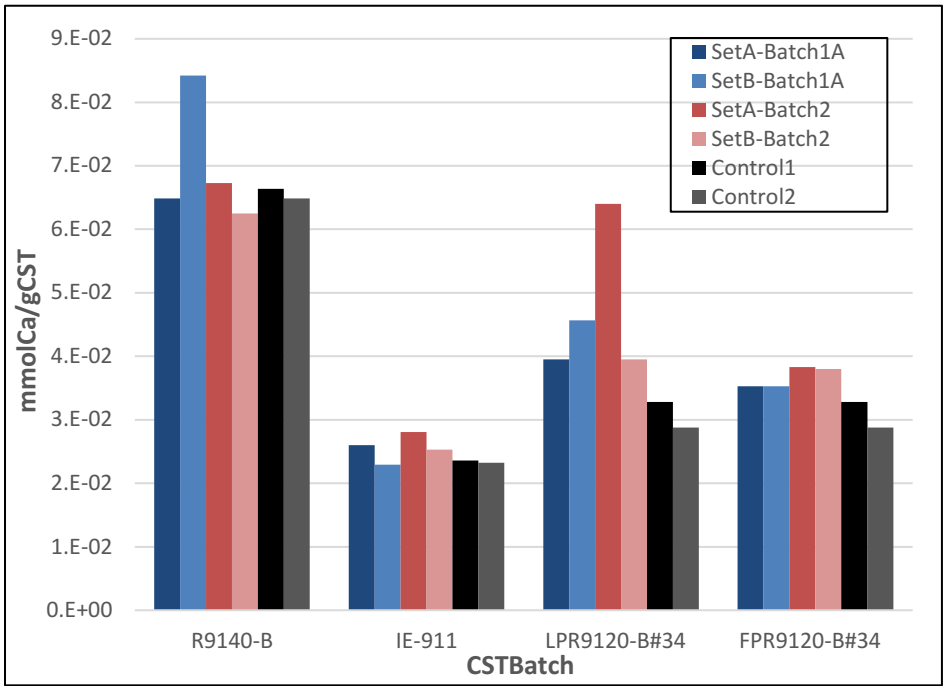

Figure 3-1. Comparison of Total Calcium Loading on the CST Batches for each Sample used for Equilibrium Testing with Tank 10H Supernate (corrected for the F-Factor).

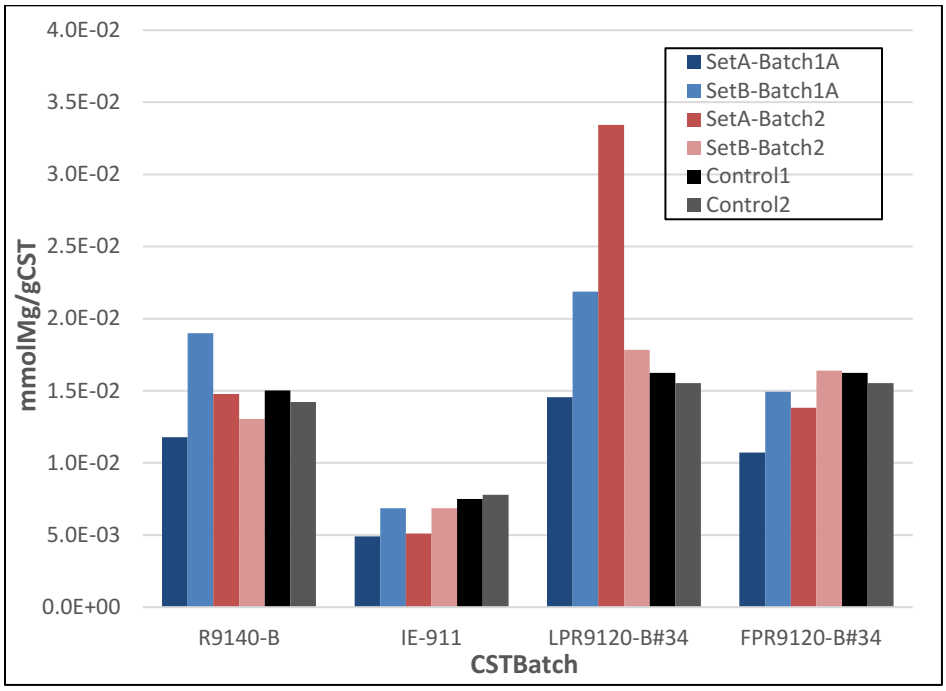

Figure 3-2. Comparison of Total Magnesium Loading on the CST Batches for each Sample used for Equilibrium Testing with Tank 10H Supernate (corrected for the F-Factor).

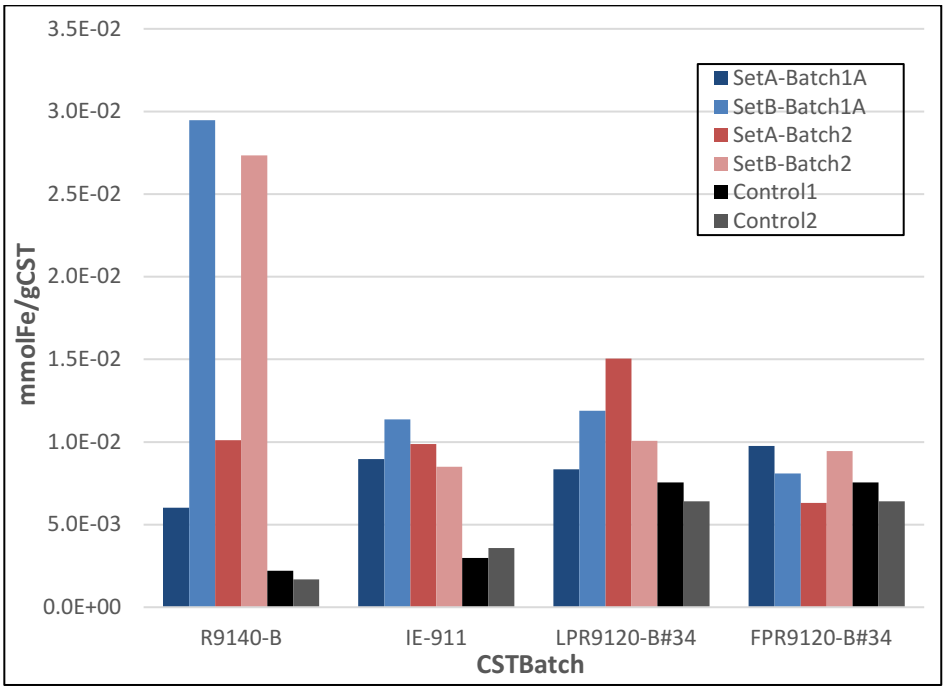

Figure 3-3. Comparison of Total Iron Loading on the CST Batches for each Sample used for Equilibrium Testing with Tank 10H Supernate (corrected for the F-Factor).

3.4 ZAM Isotherm Modeling of the Batch Contact Data

The ZAM model evalutions of the batch contact equilibrium data are provided in Figures 3-4 and 3-5 for Tank 10H supernate Batches 1A and 2, respectively. Two isotherms are presented in the figures with different dilution factors (DF) applied. A DF of 1 corresponds to no CST mass correction for binder dilution. A DF near 0.6 indicates that the measured CST mass was reduced by this factor to correct for binder dilution or poor performance resulting from some other mechanism (such as competitive ion exchange from species not considered in the model or from some other process influencing cesium removal performance such as media fouling). Based on the modeling results, cesium loading on the CST batches is still below the predicted values for both supernate samples. Previous testing with the engineered form of CST indicated that a DF of 0.68 was required to account for CST mass contributions associated with the binder material. As shown in the figures, the dilution factors need a further correction to 0.578 and 0.568 to match the observed values for the Tank 10H Batch 1A and 2 supernates, respectively. The results correspond to cesium loadings on the CST which are 15% (Batch 1A) and 17% (Batch 2) lower than expected, assuming a DF of 0.68. So based on analysis results that are statistically different, but with experimental conditions that are not identical, the modeling analysis indicates that cesium loadings on the CST may be improving with time, since the cesium loadings were closer to the predicted values than was observed several months earlier (currently 15% low versus 32% low for previous batch contact tests with Batch 1A supernate). It is unknown why this appears to have occurred or why the results are lower than predicted. The mechanisms discussed above (ion exchange competition not included in the model or media fouling phenomena) or model weaknesses such as inaccurate temperature dependence or inaccurate prediction with low ionic strength solutions may be the source of these inconsistencies between the model and the data.

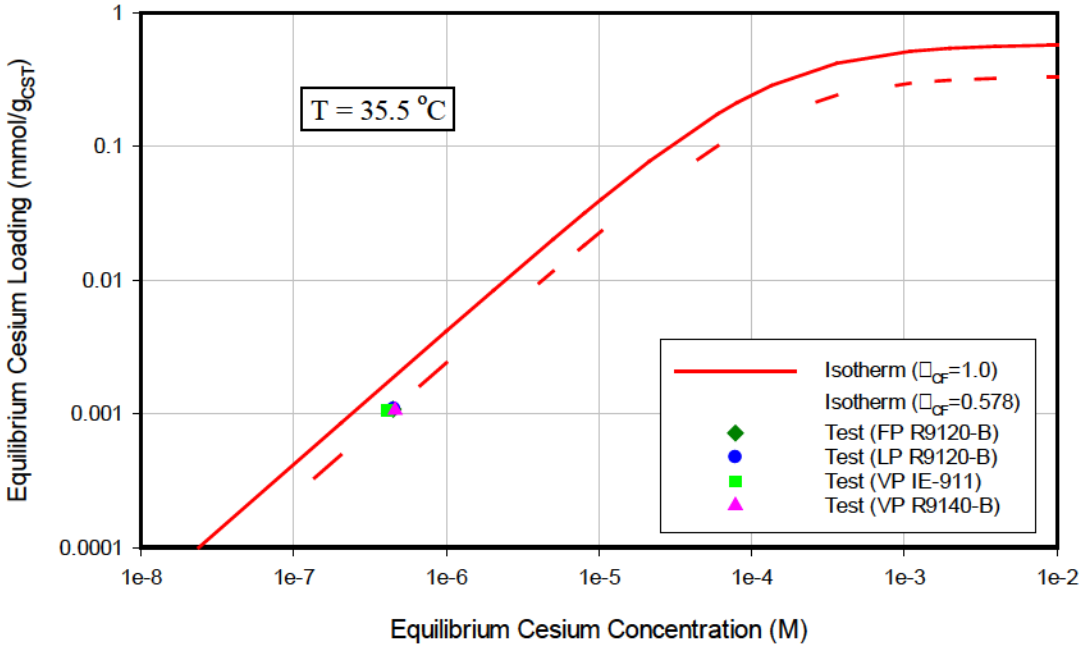

Figure 3-4. ZAM Model Prediction versus Batch Contact Results for TCCR Tank 10H Process Supernate Batch 1A.

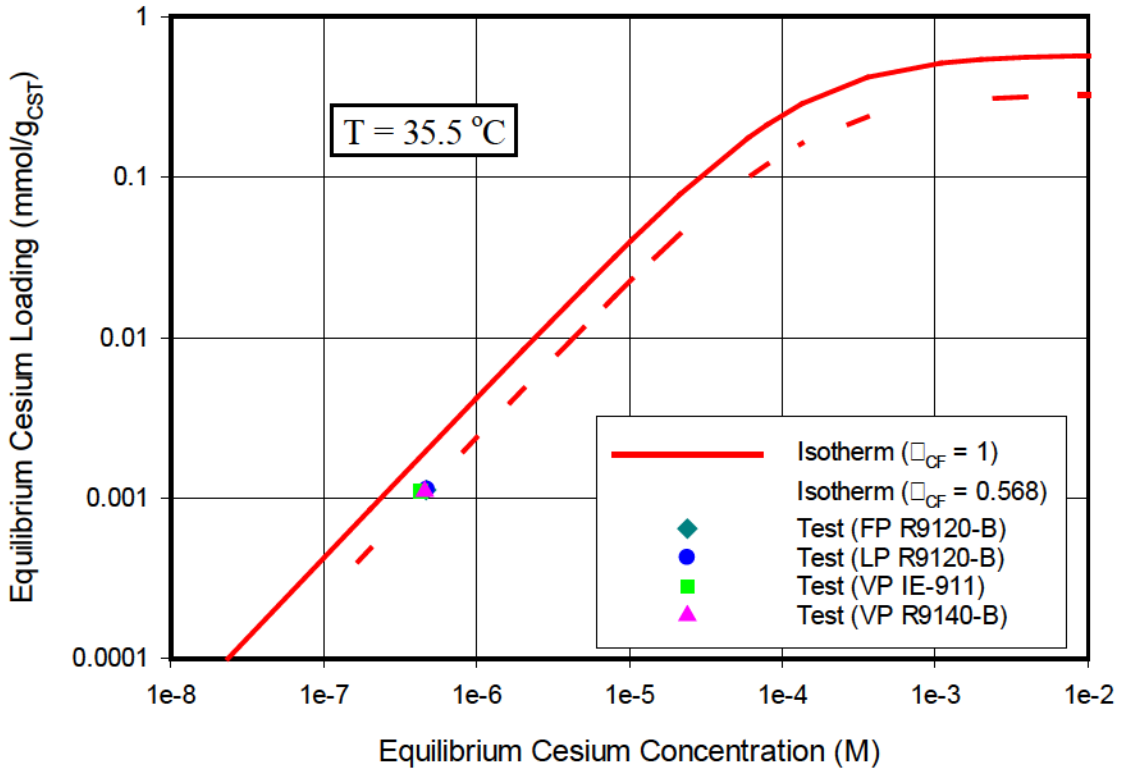

Figure 3-5. ZAM Model Prediction versus Batch Contact Results for TCCR Tank 10H Process Supernate Batch 2.

4.0 Conclusions

Previous equilibrium batch contact tests conducted in the SRNL Shielded Cells and associated analyses indicated that TCCR Tank 10H production supernate Batch 1A was a unique solution for which CST cesium removal performance was lower than predicted by ZAM modeling [3]. A small compositional change may have occurred for TCCR supernate process Batch 1A during SRNL storage primarily with regard to the decreased carbonate concentration; however, the %RSD was relatively large for that measurement making it difficult to conclusively say there was a change. The impact of this change on cesium loading is expected to be small since the decrease in the carbonate concentration is small. The soluble iron was also observed to decrease for the Batch 1A sample, although the previous result was near the analytical detection limit. Cesium distribution coefficients (K_d), percent removal, and CST loading data for the TCCR production supernate batches at 35.5 ºC with several CST media batches were determined after aging at ambient Shielded Cell temperature for several months. Average cesium distribution coefficients of 2,419 and 2,414 mL/g were observed with aged Tank 10H Batch 1A supernate with the major TCCR CST batch (R9120-B) using CST sub-samples which had been conditioned using abbreviated field and exhaustive laboratory pretreatment methods, respectively. These results indicate that the pretreatment protocol does not impact the cesium removal performance in this waste supernate, although the pretreatment protocol was developed to remove excess/alternate chemical phases to alleviate bed fouling and not to equalize cesium absorption. The effect of the altered pretreatment protocol on bed fouling was not investigated. These distribution coefficients are higher than were reported previously using the Batch 1A supernate and laboratory-pretreated CST at a slightly

higher temperature (38 ºC) and liquid-to-solid phase ratio indicating improved CST performance with supernate aging. Although improved performance was observed relative to previous testing, cesium loading performance was still 15-17% lower than has been historically observed with CST. The R9140-B CST batch performed comparably to or slightly worse than R9120-B CST batches, while moderately higher K_d values (relative to R9120-B) were observed with archived IE-911 CST media. This finding indicates that the equilibrium performance of the media has not changed appreciably from the original production batches, and that the lower than expected loading is attributed to poor agreement with ZAM possibly due to waste component interference or temperature effects.

5.0 Recommendations

Additional batch contact tests under identical experimental conditions after further supernate aging may provide further insight into this effect. Testing of the impact of the modified pretreatment protocol on the propensity to foul the bed is recommended.

6.0 References

1. K. M. L. Taylor-Pashow, T. Hang, C. A. Nash, "Summary of Expedited Results from Samples Supporting Tank Closure Cesium Removal (TCCR) Batch 1A and Modeling Results for Cs Loading on CST", SRNL-L3100-2019-00002, Rev. 2, February 19, 2019.
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12. K. M. L. Taylor-Pashow, C. A. Nash, "Summary of Analytical Results from Samples Supporting Tank Closure Cesium Removal (TCCR) Batch 1A", SRNL-L3100-2019-00009, Rev. 0, March 2019.

Appendix A. TGA Results

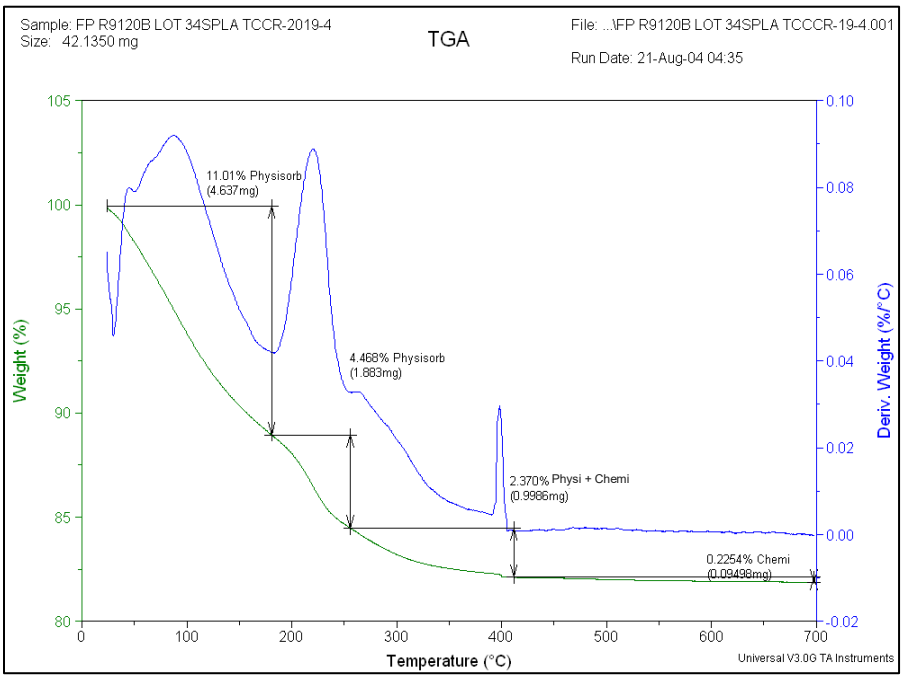

Figure A-1. TGA Mass Loss Profiles versus Time for Field-Pretreated CST Batch R9120-B Lot #2099000034 Sample A.

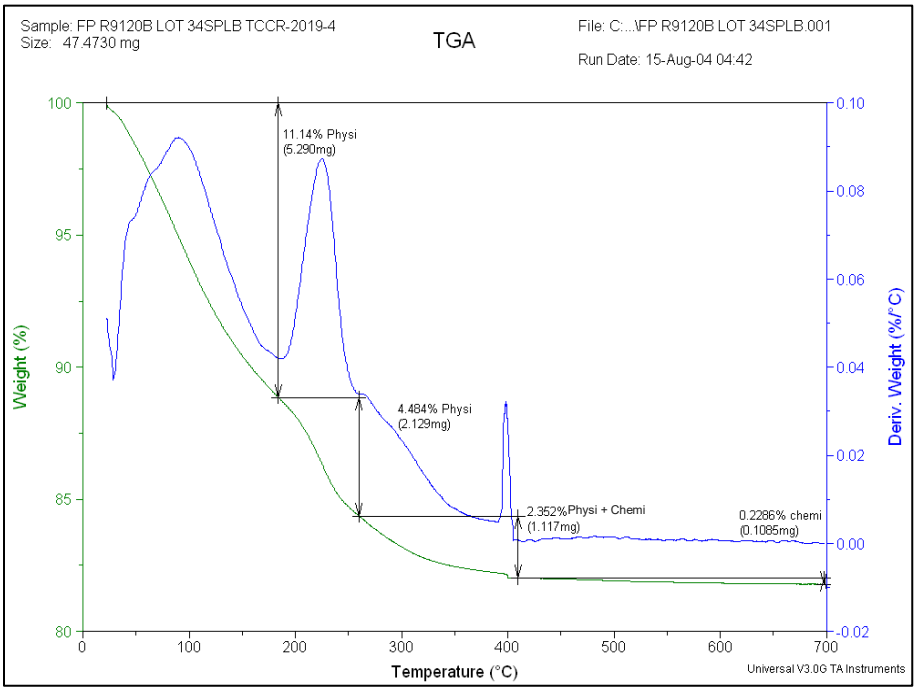

Figure A-2. TGA Mass Loss Profiles versus Time for Field-Pretreated CST Batch R9120-B Lot #2099000034 Sample B.

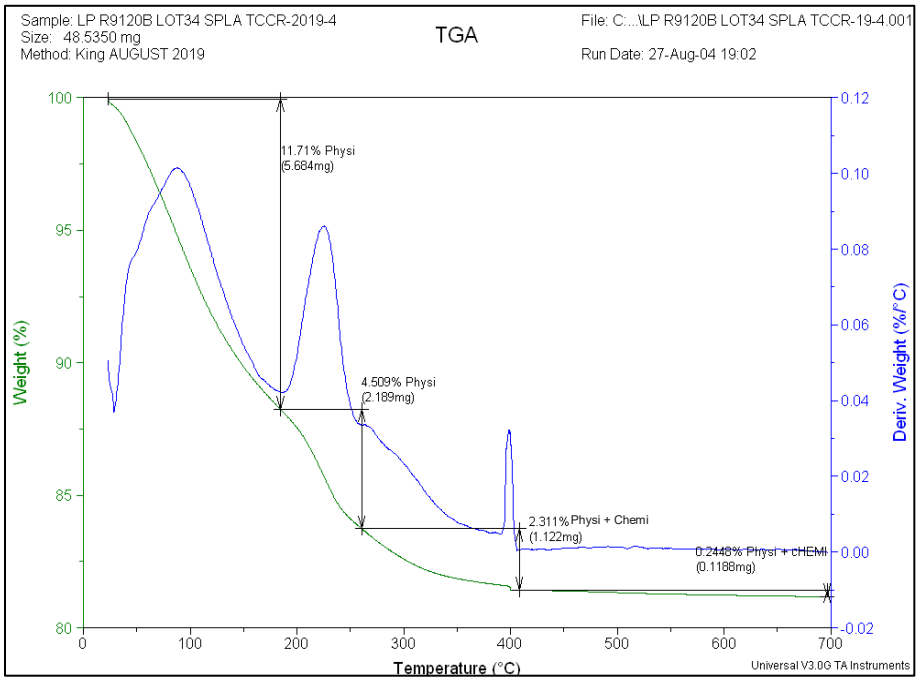

Figure A-3. TGA Mass Loss Profiles versus Time for Laboratory-Pretreated CST Batch R9120-B Lot #2099000034 Sample A.

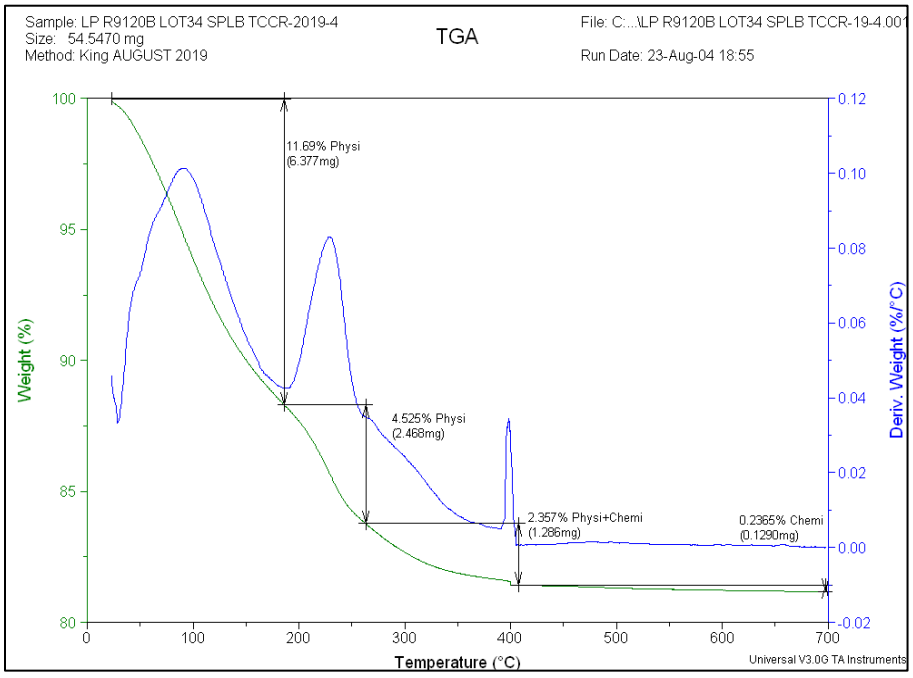

Figure A-4. TGA Mass Loss Profiles versus Time for Laboratory-Pretreated CST Batch R9120-B Lot #2099000034 Sample B.

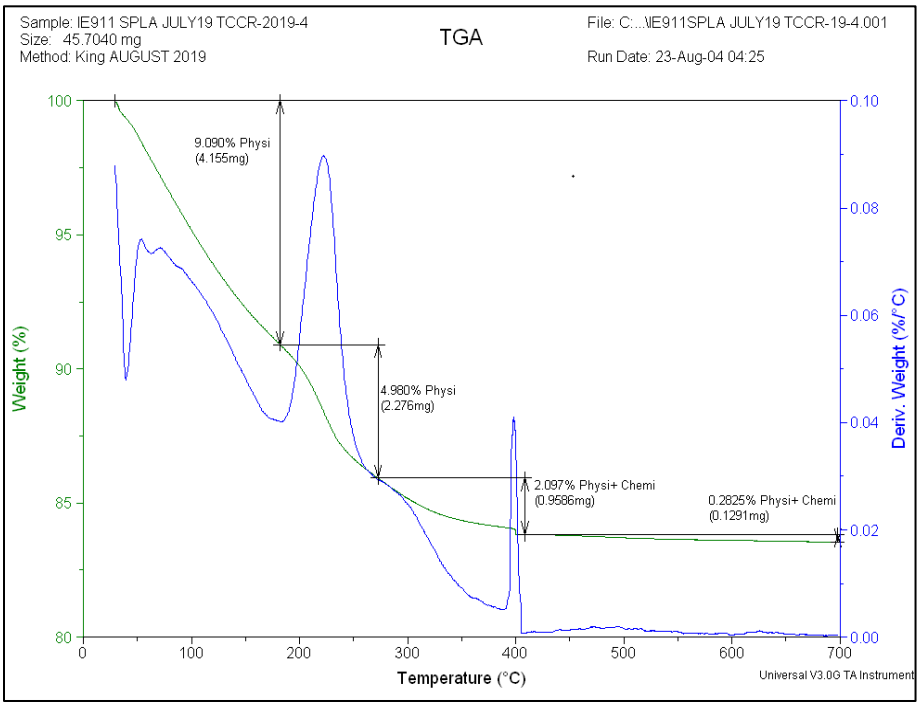

Figure A-5. TGA Mass Loss Profiles versus Time for Vendor-Pretreated CST Batch IE-911 Sample A.

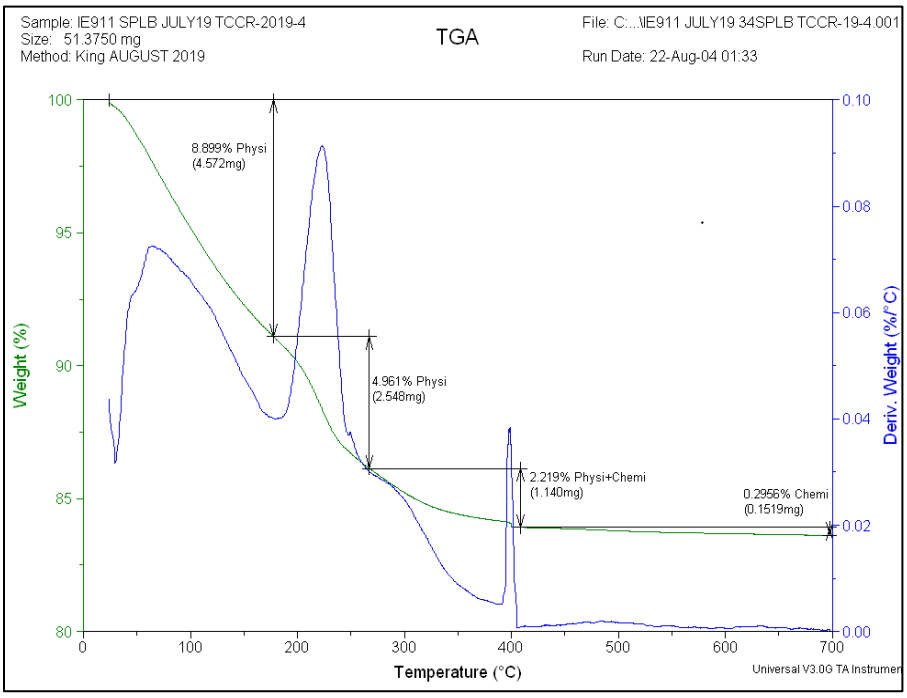

Figure A-6. TGA Mass Loss Profiles versus Time for Vendor-Pretreated CST Batch IE-911 Sample B.

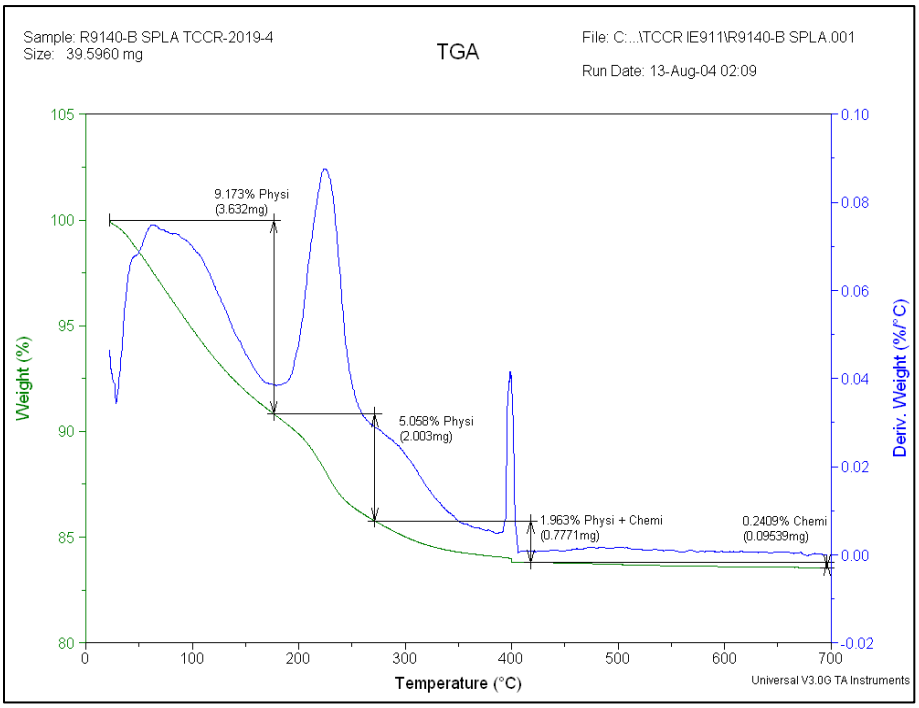

Figure A-7. TGA Mass Loss Profiles versus Time for Vendor-Pretreated CST Batch R9140-B Sample A.

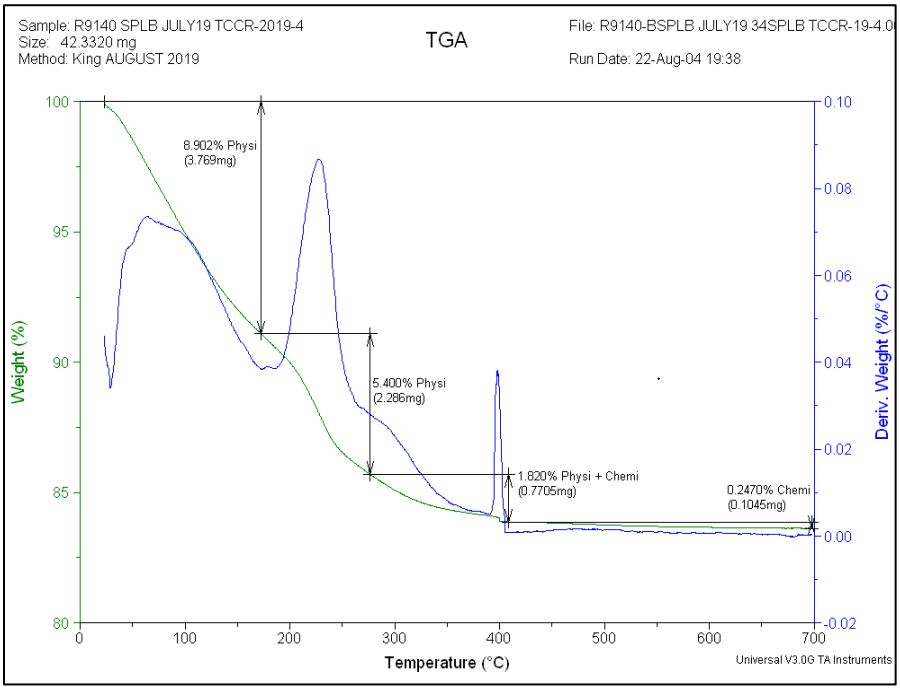

Figure A-8. TGA Mass Loss Profiles versus Time for Vendor-Pretreated CST Batch R9140-B Sample B.

Appendix B. CST Digestion Data

Table B-1. CST Standards Digestion Data

CST[a]	FP R9120-B	VP IE-911	VP R9140-B
Element	Average Content mmol/g (%RSD[b])		
Al	1.6E-01 (1.2%)	8.1E-02 (1.9%)	6.9E-02 (0.5%)
Ca	3.1E-02 (9.4%)	2.3E-02 (1.1%)	6.6E-02 (1.6%)
Fe	7.0E-03 (11%)	3.3E-03 (13%)	1.9E-03 (19%)
Mg	1.6E-02 (3.1%)	7.7E-03 (2.7%)	1.5E-02 (3.8%)
Na	4.4E+00 (1.8%)	4.7E+00 (1.9%)	5.0E+00 (1.8%)

[a] FP = field-pretreated Lot 209900034, VP = vendor pretreated
[b] %RSD values from analysis of duplicate samples

Table B-2. Ti and Zr Content from Digestion Data

CST[a]	Avg. Ti wt%[b]	%RSD	Avg. Zr wt%[b]	%RSD	Ti/Zr Molar Ratio
Batch Contact Samples					
FP R9120-B	18.1 wt%	5.82%	11.8 wt%	5.65%	2.92
LP R9120-B	20.4 wt%	4.23%	13.3 wt%	3.57%	2.92
VP IE-911	17.7 wt%	1.15%	12.5 wt%	0.48%	2.70
VP R9140-B	17.3 wt%	1.82%	10.9 wt%	1.81%	3.02
Standard (Blank) Samples					
FP R9120-B	18.8 wt%	0.46%	12.3 wt%	1.68%	2.92
VP IE-911	19.1 wt%	0.00%	12.9 wt%	1.96%	2.81
VP R9140-B	19.7 wt%	1.71%	12.5 wt%	3.38%	3.01

[a] FP = field-pretreated Lot 209900034, LP = laboratory-pretreated, VP = vendor pretreated
[b]Based on dry CST mass (i.e., corrected for F-factor)

Distribution:
alex.cozzi@srnl.doe.gov
david.crowley@srnl.doe.gov
c.diprete@srnl.doe.gov
a.fellinger@srnl.doe.gov
samuel.fink@srnl.doe.gov
joseph.manna@srnl.doe.gov
gregg.morgan@srnl.doe.gov
nancy.halverson@srnl.doe.gov
john.mayer@srnl.doe.gov
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Boyd.Wiedenman@srnl.doe.gov
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michael.stone@srnl.doe.gov
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