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Characterization and CST Batch Contact Equilibrium Testing of Modified Tank 9H Process Supernate Samples in Support of TCCR

K. M. L. Taylor-Pashow, W. D. King, 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 ^{137}Cs. TCCR currently focuses on dissolving Savannah River Site (SRS) radioactive tank waste (primarily sodium saltcake solids) within Tank 10H followed by at-tank ion exchange column treatment. Two supernate batches from Tank 10H have been processed through the TCCR unit and processing of a third batch is expected soon. After processing of this supernate batch, plans are to replace the CST columns and process dissolved salt solution from Tank 9H through Tank 10H and then through the new CST columns installed in the TCCR unit. The new columns are expected to contain either a media similar to an archived CST batch (IE-911) or the R9120-B CST media used in the current TCCR columns (the two materials are fundamentally the same; just different specifications, product names, and preconditioning steps).

Samples of Tank 9H dissolved saltcake were received at the Savannah River National Laboratory (SRNL) and characterized. The Tank 9H supernate contained a high sodium concentration (~9.6 M Na^+) and will require dilution to near 6 M [Na^+] prior to processing through the TCCR unit. The cesium concentration in Tank 9H is currently significantly higher than was observed with Tank 10H. Three dilutions of the Tank 9H supernate were conducted to mimic possible dilutions that could be conducted in the tank farm prior to TCCR processing using inhibited water, sodium hydroxide, and sodium nitrate solutions. Dilution #1 was prepared by diluting the Tank 9H supernate by a factor of 1.6 with inhibited water, Dilution #2 was prepared by diluting the Tank 9H supernate by a factor of 3.7 with a mixed sodium hydroxide/sodium nitrate diluent, and Dilution #3 was prepared by also diluting by a factor of 3.7 but with sodium hydroxide only. All three dilutions have similar Na^+ concentrations (~6 M), but Dilutions #2 and #3 contain significantly less cesium. Major and key minor components of the diluted Tank 9H supernate samples are provided in Table ES-1.

Batch contact equilibrium tests were conducted with the Tank 9H dilutions and the two different CST media batches being considered for use in the new TCCR columns. Results are summarized in Table ES-2 and compared to ZAM model predictions. The highest cesium distribution coefficient and percent removal were observed with Dilution #3. IE-911 CST (an archived CST media batch) was more effective at removing cesium than the more recently prepared R9120-B CST media, though both media samples removed >88% of the cesium and the differences may not be statistically different considering the overall uncertainty. Based on the results, maximum cesium loadings were calculated for each CST media type and Tank 9H dilution. In general, maximum cesium loadings from dilutions of this supernate batch are quite high (approaching 0.1 mmol total Cs^+/g CST for Dilution #1). The highest calculated maximum ^{137}Cs loading for the Tank 9H dilutions using the ZAM model with input of the tank compositions and batch contact results was 207 Ci/kg CST (Dilution #1 with IE-911 CST). In all cases, higher maximum cesium loading values were predicted for IE-911 CST versus R9120-B, although the differences varied considerably between the dilutions. The maximum loading value for IE-911 CST with Tank 9H Dilution #1 was only 7% higher than the maximum loading for R9120-B. The maximum loading value for IE-911 CST with Dilution #3 was 24% higher than the maximum loading for R9120-B. Dilution #2 was intermediate between these values. Note that these maximum loading values are the theoretical calculated values, and actual operating conditions will cause differences. A CST binder dilution (correction) factor near 0.7 (relative to pure powder CST) was required for each batch contact test with IE-911 engineered CST using the three Tank 9H dilutions. Correction factors calculated for R9120-B CST ranged from 0.56 to 0.66 for the three dilutions.

Following the batch contact tests, the CST samples were isolated from the Tank 9H solution, washed, dried, and digested in acid following established procedures. The analysis results are provided in Table ES-3. Total cesium loading values determined by CST digestion were similar to the calculated loading values based on solution analysis (Table ES-2) for all samples. In addition, the CST was observed to load calcium (R9120-B sample only), iron, strontium, lead, uranium, and plutonium after contact with the waste supernate, as has been observed previously.

Table ES-1. Major and Key Minor Component Concentrations for the Modified Tank 9H Supernate Samples.

Component	Tank 9H Dilution #1 (M)	Tank 9H Dilution #2 (M)	Tank 9H Dilution #3 (M)
Na^+	6.2	6.3	6.3
K^+	0.022	0.010	0.010
Cs^+	$1.5x10^{-4}$	$6.5x10^{-5}$	$6.7x10^{-5}$
OH^-	0.45	1.9	3.6
NO_3^-	3.0	3.1	1.3
NO_2^-	1.1	0.48	0.48
$Al(OH)_4^-$	0.25	0.11	0.11
CO_3^{2-}	0.53	0.26	0.25
SO_4^{2-}	0.039	0.019	0.018
^{137}Cs (Ci/gal)	1.2	0.52	0.53

Table ES-2. Cesium % Removal, Distribution Coefficients (K_d), and Loading (based on liquid phase analysis) from CST Batch Contact Tests and ZAM Predictions for Tank 9H Supernate Dilutions at 35 °C.

CST Batch	Tank 9H Dilution #	Experimental Average			ZAM Model		
		Cs^+ % Removal	Cs^+ K_d (mL/g CST)[a]	Total Cs^+ Loading (mmol Cs^+/g CST)[a]	Cs^+ K_d (mL/g)	Correction Factor (CF)	Maximum Loading Ci ^{137}Cs/kg CST
IE-911	1	89.6	840	1.28E-02	839	0.711	207
	2	90.2	897	5.65E-03	896	0.698	109
	3	93.9	1489	6.04E-03	1488	0.697	171
R9120-B	1	88.7[b]	782[b]	1.30E-02[b]	782[b]	0.664[b]	193[b]
	2	88.3	754	5.70E-03	753	0.588	92
	3	92.3	1192	6.11E-03	1191	0.560	137

[a] dry CST mass basis
[b] based on individual sample result rather than average of duplicates

Table ES-3. Results of Analysis of Digested CST Samples after Contact with Modified Tank 9H Solutions.

Element	Dilution #1	Dilution #2	Dilution #3
	Net Loading (Average) mmol/g Dry CST[a]		
IE-911 CST			
Cs	1.2E-02[b]	5.4E-03[b]	5.8E-03[b]
Ca	-5.6E-04[c]	-6.5E-04[c]	-1.9E-03[c]
Fe	2.7E-03	1.5E-04	1.1E-05
Sr	1.0E-05	3.9E-05	4.4E-05
Pb	1.6E-03	5.3E-04	5.3E-04
U	7.0E-05	1.6E-05	1.1E-05
R9120-B CST			
Cs	1.2E-02[b]	5.4E-03[b]	5.7E-03[b]
Ca	9.8E-04	1.8E-03	3.5E-04
Fe	4.3E-04	1.4E-03	-7.6E-04[c]
Sr	-5.8E-06[c]	3.5E-05	3.5E-05
Pb	≥ 1.7E-03	≥ 3.1E-04	≥ 4.6E-04
U	≥ 8.6E-05	≥ 2.5E-05	≥ 1.8E-05
Radionuclide	**Loading[d] (Average) dpm/g Dry CST[a]**		
IE-911 CST			
^{137}Cs	4.9E+10	2.1E+10	2.3E+10
^{90}Sr	5.1E+06	2.4E+06	2.0E+06
^{238}Pu	7.8E+05	2.9E+05	2.9E+05
R9120-B CST			
^{137}Cs	4.7E+10	2.1E+10	2.2E+10
^{90}Sr	5.9E+06	2.8E+06	2.6E+06
^{238}Pu	6.8E+05	3.3E+05	3.1E+05

[a] dry CST mass basis
[b] Total Cs loadings calculated from ^{137}Cs gamma results and isotopic ratio determined from ICP-MS results. No blank subtraction.
[c] Negative values indicate the blank contained a higher concentration, i.e., this element leached from the CST during batch contact testing.
[d] no blank subtraction

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LIST OF ABBREVIATIONS

CF	correction factor (also sometimes called dilution factor)
CST	crystalline silicotitanate
DI	deionized
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
OLI	OLI Systems Thermodynamic Model
PVDF	Polyvinyl difluoride
rpm	revolutions per minute
RSD	relative standard deviation
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 cesium (primarily focused on removal of ^{137}Cs) from waste supernate solutions. In TCCR, radioactive salt solution is prepared by the dissolution of saltcake solids, filtered, and then passed through ion exchange columns containing crystalline silicotitanate (CST) media, commercially known as UOP IONSIV™ R9120-B[a], to remove cesium ions. Four TCCR columns were prepared, loaded with CST, installed at SRS, and used to process two waste supernate batches from SRS Tank 10H. A third Tank 10H waste batch is expected to be processed through the TCCR unit in calendar year 2020. The two batches processed to date were relatively dilute salt solutions with sodium concentrations less than 4 M. Following processing of the third supernate batch, current plans are to replace the CST columns within the TCCR unit with modified columns containing new CST media. The new media may be R9120-B CST or could be media with performance and bead size similar to a batch of caustic washed IE-911 CST (current vendor designation R9120-B 30x60), which was evaluated at SRS many years ago. A limited number of archived drums of this caustic-washed IE-911 are still available at SRS. Recent testing has indicated that in most circumstances, caustic washed IE-911 CST exhibits a higher cesium capacity and a smaller average particle diameter than R9120-B CST [1, 2]. Dissolved saltcake from SRS Tank 9H is scheduled to be transferred into Tank 10H and then processed in the TCCR unit through the new columns containing unused CST media. Water has already been added to Tank 9H to dissolve salt waste and samples have been analyzed at SRNL and shown to contain approximately 9.6 M Na^+ and 1.85 Ci ^{137}Cs/gallon [3]. Additional dilution of the Tank 9H material will be conducted prior to transfer to Tank 10H using either inhibited water, sodium hydroxide solution, or both sodium hydroxide and sodium nitrate solutions targeting a total sodium ion concentration near 6 M and ~0.5 Ci ^{137}Cs/gallon.

In order to evaluate the performance of the CST media following dilution of the Tank 9H waste, three different dilutions of the Tank 9H sample were prepared, aged, filtered, characterized, and used for CST batch contact equilibrium testing in the SRNL Shielded Cells. Both CST media types, IE-911 and R9120-B, were used for testing. Liquid phase analysis was used to determine the Cs^+ and plutonium distribution coefficients and calculate metal loadings on the CST. In addition, selected CST samples were digested in acid following the batch contact tests to directly measure the metal loading on the solid phase. OLI and ZAM modeling were subsequently utilized to evaluate the results and predict the maximum cesium loading that would be expected for each CST media type from the various Tank 9H waste supernate dilutions under TCCR waste processing conditions based on the batch contact results.

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. This work was performed following the applicable TTQAP, Technical Task and Quality Assurance Plan [4]. The Technical Task Request (TTR) associated with this work [5] requested a functional classification of Safety Class (see section 9.5 of the TTQAP entitled "Clarification of Safety Class Functional Classification"). 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 numbers A2341-00117-13 and E7518-00211-45, -46.

OLI modeling is controlled under Software Quality Assurance Plan X-SQP-A-00001, Rev. 0 [6]. ZAM is currently classified as Level D software [7] 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 [8].

[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

A sample of the major TCCR column CST media from production batch IONSIV™ R9120-B, Lot #2099000034 (Mat. #8103701-556, Sub-sample from CUA #125953-A) which had been exhaustively pretreated using a laboratory protocol described previously [9] was used for equilibrium testing. The IE-911 CST used for testing was pretreated (caustic-washed) by the vendor prior to shipment and was used as-received. This IE-911 CST sample had been stored at SRS for nearly two decades prior to testing. 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 [1].

2.2 CST Water Content Determination

Thermal Gravimetric Analysis (TGA) was conducted on sub-samples (collected at the same time as batch contact samples) of 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 Appendix A. The total mass loss was determined as the sum of several successive mass losses believed to be associated with both physisorbed and chemisorbed water. 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. Small mass losses (<0.55 wt %) were observed above 400 ºC for all samples.

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

CST Batch/Sample[a]	Sample	% Mass Loss at 410 °C
VP IE-911	A	15.854
	B	15.781
Average Mass Loss		15.818
Mass Loss %RSD		0.3%
F-factor		0.8418
LP R9120-B	A	18.166
	B	18.200
Average Mass Loss		18.183
Mass Loss %RSD		0.1%
F-factor		0.8182

[a] VP = vendor pretreated, LP = laboratory pretreated

2.3 Tank 9H Supernate Sample Dilution and Characterization

The two Tank 9H samples received and previously characterized [3] by SRNL (HTF-9-19-74 and HTF-9-19-75) were combined into a single sample. The composite sample included 258.3 g of sample HTF-9-19-74 and 246.7 g of HTF-9-19-75. After thoroughly mixing the combined sample, aliquots were used for preparing three different dilutions. Dilution #1 was prepared by combining 89.9 g of the Tank 9H sample with 37.1 g of inhibited water (0.01 M NaOH). Dilution #2 was prepared by combining 69.8 g of the Tank 9H sample with 156.5 g of a mixed diluent containing 2.46 M NaOH and 2.22 M $NaNO_3$. Dilution #3 was prepared by combining 38.8 g of Tank 9H solution with 84.8 g of 4.68 M NaOH. The target dilution factor for Dilution #1 was 1.6 to reach a Na^+ concentration of 6 ± 0.5 M. The dilution factor for Dilutions #2 and #3 was 3.7 to reach a ^{137}Cs activity of 0.5 Ci/gallon. The use of NaOH and $NaNO_3$ provided additional Na^+ to these dilutions to maintain the Na^+ concentration at 6 ± 0.5 M. After preparing and mixing the dilutions,

the solutions were left to age at ambient Shielded Cell temperature for approximately three weeks. After aging, each solution was filtered through a 0.45-µm Nylon filter to remove any solids that may have precipitated. Visual inspections of the filters did not indicate the presence of any solids. The density of each solution was measured in duplicate using 2-mL density tubes. The temperature during density measurements was 16 °C. Sub-samples of each solution were submitted for inductively coupled plasma – emission spectroscopy (ICP-ES), inductively coupled plasma – mass spectrometry (ICP-MS), ion chromatography (IC) for anions, total inorganic carbon/total organic carbon (TIC/TOC), titration for free hydroxide concentration, gamma spectroscopy, and plutonium analysis by extraction with thenoyltrifluoracetone (TTA) followed by alpha pulse height analysis to quantify ^{238}Pu and ^{239,240}Pu and liquid scintillation counting (LSC) to quantify ^{241}Pu.

2.4 CST Batch Contact Testing

Duplicate 10 mL sub-samples of the modified and filtered Tank 9H samples were used for equilibrium batch contact testing with 0.12 g samples (~0.1 g after water content correction) of CST media. A ThermoScientific MaxQ Incubated 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 4, 6, or 8 contact days at 35.3 (IE-911 test) and 34.8 °C (R9120-B test). The oven display temperature was manually monitored and recorded periodically throughout testing and was checked with two calibrated thermocouples before, during, and after testing. The reported temperatures for each test were the average values recorded using the calibrated thermocouples (% RSD's below 3% in each case). At test completion, individual test samples were removed from the shaker, filtered through 0.1-µm PVDF (polyvinylidene difluoride) syringe filters, diluted in 5 M HNO_3 (dilution factor = 2), and submitted for ^{137}Cs (gamma) analysis. Samples from tests with Dilution #2 were also submitted for plutonium analysis using the TTA analytical method described above. Separate filtered sub-samples of each Tank 9H 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, diluted in nitric acid (dilution factor = 2-7) and submitted for gamma analysis. The feed solution for Dilution #2 was also analyzed for plutonium. One sub-sample of each feed solution was analyzed with each set of tests (IE-911 and R9120-B). CST and Tank 9H supernate masses for individual samples during equilibrium batch contact testing are provided in Table 2-2.

Table 2-2. CST and Tank 9H Diluted Supernate Masses Used for Cesium Equilibrium Batch Contact Testing.

CST Batch[a]	Tank 9H Supernate Dilution#	Contact Duration (Days)	CST (g)[b]	Tank 9H (g)	Tank 9H (mL)[c]	Average Temperature (ºC)
VP IE-911	1	4.1	0.1222	12.960	10.0	35.3
			0.1226	12.960		
	2	4.1	0.1226	12.935		
			0.1223	12.925		
	2	5.8	0.1223	12.934		
			0.1228	12.823		
	2	8.0	0.1223	12.932		
			0.1223	12.929		
	3	4.1	0.1228	12.806		
			0.1224	12.809		
LP R9120-B	1	4.2	0.1225	12.990	10.0	34.8
			0.1221	12.970		
	2	4.2	0.1222	12.930		
			0.1219	12.933		
	2	5.8	0.1223	12.930		
			0.1227	12.937		
	2	8.0	0.1228	12.929		
			0.1224	12.935		
	3	4.1	0.1225	12.814		
			0.1225	12.807		

[a] VP = vendor pretreated, LP = laboratory-pretreated
[b] hydrated CST reference state masses; multiply by appropriate F-factors (see Table 2-1) to correct to dry state mass basis
[c] supernate volumes calculated based on measured masses and average measured densities: 1.295 g/mL for Dilution #1, 1.293 g/mL for Dilution #2, and 1.281 g/mL for Dilution #3

2.5 Spent CST Digestion

After the completion of batch contact testing and the collection of liquid sub-samples for analysis, the remaining CST media and a portion of the residual modified Tank 9H solution were stored at test temperature (~35 ºC) without agitation. The solids were then washed and air dried following a similar protocol as described in SRNL Manual L29 Procedure ITS-0230. Briefly, any remaining Tank 9H solution in the batch contact bottles was removed to the extent possible without removing any of the CST. The CST was then washed by adding ~60 mL of 0.01 M NaOH and soaking for ~1 hour. The 0.01 M NaOH was then removed and the CST was briefly rinsed with deionized (DI) water by filling the bottles with ~60 mL of DI water. The water was removed after a two minute soak. The CST was then transferred to glass evaporating dishes and allowed to air dry to a constant weight. The ~0.1 g CST samples were then dissolved/digested in a hot HF-HNO_3 acid mixture in a sealed Teflon digestion vessel, diluted to 50 mL with water following established procedures, and the solution was analyzed by ICP-ES, ICP-MS, and gamma spectroscopy in addition to radiochemical analysis for $^{238\text{-}241}$Pu and ^{90}Sr. Blank samples of CST which were not exposed to Tank 9H supernate were also digested in the Shielded Cells and resulting solutions were analyzed alongside the batch contact samples. The ICP-MS determined concentrations of

Ti, Zr, and Nb in the blank samples were used to confirm the digestions were complete by comparing to the control limits previously established for this standard [10].

2.6 ZAM Isotherm Model Calculations

The ZAM (Zheng, Anthony, and Miller) Isotherm Model code is purchased commercial software and is 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 and IE-911 are engineered forms of crystalline silicotitanate ion exchange media that are composed of submicron-sized CST "powder" formed into 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 correction factor (CF), sometimes called a "dilution factor", as a way to adjust the isotherm to account both for binder and for any competing ions. Different CST batches may have different binder content and CF values. 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 9H Supernate Chemical Modification and Dilution Characterization

Preparation of the three different modified Tank 9H supernate samples was performed as planned. Analysis confirmed the target of 6 ± 0.5 M Na was achieved for all three dilutions, and in addition the target of 0.5 Ci ^{137}Cs/gallon was met for Dilutions #2 and #3. A summary of the characterization results is provided in Table 3-1. Interestingly, Dilutions #2 and #3 were found to have higher strontium concentrations than Dilution #1, likely due to the introduction of Sr as an impurity in the sodium hydroxide used for dilution. Additionally, as in some previous tank samples a small amount of rubidium was measured. Rubidium is a monovalent alkali metal like cesium, and is a known competitor for sorption sites on CST. Density measurements were performed in duplicate at 16 °C, and the results are provided in Table 3-2. In addition to the measured density, the density at 35 °C (batch contact test temperature) was calculated using the OLI modeling software, and the results are provided in Table 3-2. OLI modeling performed at 35 °C also predicted the precipitation of gibbsite ($Al(OH)_3$) in Dilution #1. While no precipitates were observed to have formed in the aged samples at SRNL, these modeling results indicate this composition is unstable due to the low hydroxide to aluminum ratio; and therefore, would not be recommended in the tank.

Table 3-1. Characterization Data for Modified Tank 9H Supernate Samples.

Component	Tank 9H Dilution #1		Tank 9H Dilution #2		Tank 9H Dilution #3	
	Concentration (M)	%RSD	Concentration (M)	%RSD	Concentration (M)	%RSD
Na^+	6.20	2.63	6.28	0.69	6.30	3.99
K^+	0.0218	0.51	0.0102	3.86	0.0101	0.33
Total Cs^+	1.48E-04	2.94	6.50E-05	1.47	6.69E-05	0.40
Rb^+	6.46E-05	1.59	2.79E-05	0.56	2.76E-05	1.70
Total Sr	1.78E-07	n/a[a]	6.05E-07	2.14	6.76E-07	0.19
OH^-	0.454	2.86	1.930	0.40	3.564	0.08
NO_3^-	3.02	1.09	3.08	0.57	1.29	1.23
NO_2^-	1.10	0.68	0.478	0.93	0.478	0.90
$Al(OH)_4^-$	0.247	0.72	0.105	0.53	0.106	0.02
CO_3^{2-}	0.530	1.78	0.258	2.46	0.247	0.66
SO_4^{2-}	3.96E-02	1.42	1.85E-02	4.19	1.84E-02	3.48
PO_4^{3-}	6.92E-03	0.02	3.05E-03	1.87	3.06E-03	0.83
CrO_4^{2-}	1.30E-03	0.19	< 6.34E-04	n/a	< 6.01E-04	n/a
^{137}Cs (Ci/gal)	1.2	2.94	0.52	1.47	0.53	0.40
^{238}Pu (dpm/mL)	1.05E+04	1.38	4.70E+03	17.6	4.50E+03	9.11
$^{239/240}Pu$ (dpm/mL)	<53.2	n/a	<59.5	n/a	<111	n/a
^{241}Pu (dpm/mL)	4.83E+02	5.00	<3.65E+02	n/a	<3.83E+02	n/a

[a] Single sample above detection limit.

Table 3-2. Densities of Modified Tank 9H Supernate Samples

	Dilution #1		Dilution #2		Dilution #3	
	Avg.	%RSD	Avg.	%RSD	Avg.	%RSD
Measured Density[a] (g/mL)	1.295	1.06	1.293	1.28	1.281	0.41
OLI Calculated Density[b] (g/mL)	1.276	n/a	1.274	n/a	1.248	n/a

[a] Measured at 16 °C. [b] Calculated at 35.3 °C.

3.2 CST Batch Contact Test Results

Based on the gamma scan results and the original total Cs^+ analysis results (Table 3-1), cesium distribution coefficients (K_d; Equation 1), % removal (Equation 2), and loading (mmol Cs^+/g CST; Equation 3) values were calculated for each batch contact test sample. Results are provided in Table 3-3. Cesium loading results were generally consistent between replicate samples for both CST batches (<10% RSD for the K_d values) except for the Dilution #1 samples with R9120-B CST where ~13% RSD was observed for the duplicate samples. Comparison of the cesium removal results for the 4-, 6-, and 8-day contact durations with the Dilution #2 samples indicates that cesium loading was complete for both IE-911 and R9120-B CST within 4 days.

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

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

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

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 ^{137}Cs activity data only or total cesium concentrations. In contrast, total cesium loading calculations require the determination of the sum of all cesium isotopes.

The highest cesium loading results were observed for Dilution #1 with both CST samples since this supernate sample contained more than twice as much total cesium as the other dilutions (Table 3-1). Similar cesium distribution coefficients and % removal were observed for Dilutions #1 and #2, while higher cesium removal was observed for Dilution #3 for each CST sample. Generally lower cesium removal was observed for R9120-B versus IE-911 CST with the exception being Dilution #1, although these values may not be statistically different considering overall uncertainty. The Tank 9H Dilution #1 samples with R9120-B also exhibited the highest variability of any test, as indicated by the % RSD value. If the highest result observed for this sample (K_d = 937 mL/g) is ignored as an outlier, the data trends are more consistent and indicate lower loading with R9120-B relative to IE-911 CST.

Table 3-3. Cesium Equilibrium Distribution Coefficients, % Removal, and Loading for CST Batches and Tank 9H Supernate Dilutions at ~35 °C.

CST Batch[a]	Tank 9H Dilution #	Contact Duration (Days)	Final Cs-137 (dpm/mL)	Initial Cs-137 (dpm/mL)	Cs^+ K_d (mL/g)[b]	Average			ZAM Predicted Loading[d] (mmol Cs/g CST)
						Cs^+ K_d (% RSD)[b]	Cs^+ % Removal	mmol Cs^+/g CST[b,c]	
VP IE-911	1	4.2	7.03E+07	6.89E+08	856	840 (2.7%)	89.6	1.28E-02	1.80E-02
			7.26E+07		823				
	2	4.2	2.91E+07	3.00E+08	900	897 (0.5%)	90.2	5.65E-03	8.09E-03
			2.94E+07		894				
	2	5.8	3.00E+07		873	894 (3.3%)	90.2	5.65E-03	8.12E-03
			2.87E+07		915				
	2	8.0	2.91E+07		899	903 (0.6%)	90.3	5.65E-03	8.04E-03
			2.90E+07		907				
	3	4.1	1.81E+07	2.95E+08	1485	1489 (0.4%)	93.9	6.04E-03	8.66E-03
			1.80E+07		1494				
LP R9120-B	1	3.9	7.81E+07	6.89E+08	782	859 (12.7%)	89.5	1.32E-02	1.96E-02
			6.66E+07		937				
	2	3.9	3.67E+07	3.00E+08	717	754 (7.0%)	88.3	5.70E-03	9.71E-03
			3.37E+07		792				
	2	5.8	3.65E+07		721	774 (9.5%)	88.5	5.70E-03	9.49E-03
			3.23E+07		826				
	2	8.0	3.72E+07		703	735 (6.2%)	88.0	5.66E-03	9.88E-03
			3.45E+07		767				
	3	3.8	2.33E+07	2.95E+08	1164	1192 (3.3%)	92.3	6.11E-03	1.09E-02
			2.23E+07		1220				

[a] VP = vendor pretreated, LP = laboratory-pretreated
[b] dry CST mass basis
[c] cesium loading corresponds to total of all isotopes based on Cs^+ concentrations provided in Table 3-1
[d] ZAM predicted loading for the powdered form of CST (i.e., with a correction factor of 1).

Plutonium distribution coefficients, % removal, and loading values were also calculated for the Dilution #2 samples with each CST media type based on liquid phase analysis data and results are provided in Table 3-4. Greater than 96% plutonium removal was observed for all samples. Trends in the data indicate that plutonium loading may not have been complete after 4 days, although additional plutonium loading was small during the remaining time period and variability between replicates was high for some of the 6- and 8-day data. As is the case for the cesium loading values provided in Table 3-3, these values represent plutonium loadings in equilibrium with the final measured plutonium concentrations and do not represent maximum loading values.

Table 3-4. ^{238}Pu Equilibrium Distribution Coefficients, % Removal, and Loading for CST Batches and Tank 9H Supernate Dilutions at ~35 °C.

CST Batch[a]	Tank 9H Dilution #	Batch Contact Duration (Days)	Final ^{238}Pu (dpm/mL)	Initial ^{238}Pu (dpm/mL)	Pu K_d (mL/g)[b]	Average		
						Pu K_d (% RSD)[b]	Pu % Removal	^{238}Pu mmol/ g CST[b]
VP IE-911	2	4.2	1.36+E02	4.66E+03	3227	3078 (6.8%)	96.9	4.99E-08
			1.50E+02		2929			
		5.8	1.46E+02		2995	3388 (16.4%)	97.2	5.01E-08
			1.17E+02		3781			
		8.0	1.32E+02		3320	4751 (42.6%)	97.8	5.04E-08
			7.21E+01		6182			
LP R9120-B	2	3.9	1.54E+02	3.94E+03	2464	2777 (15.9)	96.2	4.19E-08
			1.46E+02		3090			
		5.8	---		---	6057[c] (n/a)	99.0[c]	4.27E-08[c]
			7.54E+01		6057			
		8.0	1.06E+02		4287	4538 (7.8)	97.5	4.25E-08
			9.52E+01		4789			

[a] VP = vendor pretreated, LP = laboratory-pretreated
[b] dry CST mass basis
[c] based on individual sample result rather than average of duplicates

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 3-5 for the IE-911 samples and in Table 3-6 for the R9120-B samples. Elemental 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), with the exception of cesium. The radionuclide loading data does not include a blank subtraction as no radionuclides would be expected in the as-received CST material. Data for the standards (blanks) is provided in Appendix B. During the IE-911 batch contact experiments approximately half of the liquid was removed at the time of sampling (i.e., at 4, 6, or 8 days of contact) and the bottles containing the remaining liquid and CST were returned to the shaker oven. Therefore, for the digestions only the "4-day" samples were digested as there was not expected to be any difference between the "4-day" and "8-day" samples. For the R9120-B samples a similar approach was initially taken; however, at the time of the 6-day sampling event all of the remaining liquid was removed from the "4-day" test bottles. Therefore, for the R9120-B series, both the "4-day" and "8-day" samples were digested to look for differences in loading with extended contact.

The cesium loading results determined by CST digestion agree within 10% to the loading results based on the liquid phase analysis for both the IE-911 and R9120-B data sets. The plutonium loading results determined by CST digestion were 35% and 15% lower than loading results calculated based on the liquid phase analysis for IE-911 (2.9E+05 dpm ^{238}Pu/g CST) and R9120-B CST (3.3E+05 dpm ^{238}Pu/g CST), respectively. For the IE-911 samples the only elements present in concentrations higher than Cs were sodium and aluminum. R9120-B results were similar in that only Na was present in higher concentrations than Cs, and Al was also higher than Cs in the Dilution #1 samples. The R9120-B appeared to leach Al in Dilutions #2 and #3, as indicated by the negative loading values after subtracting the amount measured in the blank. The R9120-B CST contains approximately 1.5 times the amount of Al than IE-911 in the as received (and pretreated) materials. For IE-911, Dilution #1 the list of elements found in decreasing order

of concentration on the CST is as follows: Na, Al, Cs, Fe, Pb, Rb, U, Sr, although there was a large discrepancy between the Fe loadings on the replicate samples. For IE-911, Dilution #2 the order is slightly different as follows: Na, Al, Cs, Rb, Pb, Fe, Sr, U. The order for IE-911, Dilution #3 is similar to that of Dilution #2 except that the Fe loading drops to the lowest (Na, Al, Cs, Rb, Pb, Sr, U, Fe). Notably, there was no measurable Ca present (above what is measured in the standard) for the IE-911 samples, whereas Ca loading was observed in the R9120-B samples. Similar to Al, the R9120-B as received (and pretreated) material contains more Ca (~1.3x) than the IE-911 material, and it was observed to pick up additional Ca during the batch contact testing, whereas IE-911 lost a small amount.

Table 3-5. Results of Analysis of Digested IE-911 Samples after Contact with Modified Tank 9H Solutions (Corrected for the F-Factor).

Element	Dilution #1	Dilution #2	Dilution #3
	Net Loading (Average) mmol/g (%RSD[a])		
Cs	1.24E-02[b] (1.59%)	5.35E-03[b] (3.34%)	5.79E-03[b] (4.64%)
Al	7.64E-02 (9.17%)	2.64E-02 (0.00%[c])	1.63E-02 (2.18%)
Ca	-5.64E-04 (2.67%)	-6.52E-04 (9.55%)	-1.85E-03 (0.49%)
Fe	2.73E-03 (47.8%)	1.49E-04 (2.50%)	1.06E-05 (4.56%)
Na	2.21E-01 (0.39%)	3.31E-01 (14.7%)	1.81E-02 (4.80%)
Rb	≥ 1.36E-03 (1.47%)	≥ 6.55E-04 (1.69%)	≥ 8.94E-04 (1.46%)
Sr	1.01E-05 (4.58%)	3.87E-05 (1.15%)	4.38E-05 (1.04%)
Pb	1.57E-03 (4.64%)	5.31E-04 (22.0%)	5.25E-04 (0.89%)
U	7.04E-05 (4.83%)	1.57E-05 (5.20%)	1.10E-05 (4.86%)
Radionuclide	**Loading[d] (Average) dpm/g (%RSD)**		
^{137}Cs	4.91E+10 (1.59%)	2.12E+10 (3.34%)	2.29E+10 (4.64%)
^{90}Sr	5.13E+06 (12.6%)	2.35E+06 (3.61%)	1.99E+06 (2.13%)
^{238}Pu	7.78E+05 (12.5%)	2.94E+05 (2.17%)	2.88E+05 (6.87%)

[a] %RSD values based on original measured values before blank subtraction.
[b] Total Cs loadings calculated from ^{137}Cs gamma results and isotopic ratio determined from ICP-MS results. No blank subtraction.
[c] Replicate samples had identical results.
[d] No blank subtraction.

Table 3-6. Results of Analysis of Digested R9120-B Samples after Contact with Modified Tank 9H Solutions (Corrected for the F-Factor).

Element	Dilution #1	Dilution #2		Dilution #3
	4 Day	4 Day	8 Day	4 Day
	Net Loading (Average) mmol/g (%RSD[a])			
Cs	1.23E-02[b] (1.65%)	5.44E-03[b] (3.71%)	5.29E-03[b] (2.77%)	5.71E-03[b] (1.94%)
Al	9.69E-02 (1.16%)	-2.74E-02 (10.3%)	-2.74E-02 (4.95%)	-4.71E-02 (3.35%)
Ca	9.76E-04 (1.87%)	1.81E-03 (6.20%)	1.01E-03 (3.84%)	3.51E-04 (7.57%)
Fe	4.27E-04 (18.3%)	1.37E-03 (39.1%)	-9.85E-05 (2.38%)	-7.55E-04 (15.0%)
Na	5.16E-01 (0.57%)	5.74E-01 (3.77%)	3.46E-01 (3.10%)	4.92E-01 (4.64%)
Rb	≥ 1.23E-03 (2.08%)	≥ 5.74E-04 (5.90%)	≥ 5.86E-04 (5.19%)	≥ 7.98E-04 (1.73%)
Sr	-5.76E-06 (6.45%)	3.48E-05 (4.45%)	2.29E-05 (0.40%)	3.46E-05 (5.22%)
Pb	≥ 1.67E-03 (1.22%)	≥ 3.11E-04 (3.85%)	≥ 4.04E-04 (8.62%)	≥ 4.63E-04 (1.45%)
U	≥ 8.61E-05 (5.50%)	≥ 2.47E-05 (3.96%)	≥ 3.39E-05 (9.50%)	≥ 1.76E-05 (2.63%)
Radionuclide		**Loading[c] (Average) dpm/g (%RSD)**		
^{137}Cs	4.71E+10 (1.65%)	2.10E+10 (3.71%)	2.04E+10 (2.77%)	2.19E+10 (1.94%)
^{90}Sr	5.85E+06 (17.9%)	2.84E+06 (1.99%)	2.36E+06 (17.1%)	2.59E+06 (39.7%)
^{238}Pu	6.78E+05 (6.16%)	3.26E+05 (6.30%)	3.26E+05 (6.30%)	3.11E+05 (4.09%)

[a] %RSD values based on original measured values before blank subtraction.
[b] Total Cs loadings calculated from ^{137}Cs gamma results and isotopic ratio determined from ICP-MS results. No blank subtraction.
[c] No blank subtraction.

3.4 ZAM Isotherm Modeling of the Batch Contact Data

The ZAM predicted isotherm can be expressed by a Langmuir isotherm defined by equation 4:

$$Q_{Cs} = \frac{\eta C_T C_{Cs}}{C_{Cs}+\beta} \qquad \text{(Equation 4)}$$

where, Q_{Cs} - total Cs loading (mmol/g) on a dry CST mass basis

C_{Cs} - liquid-phase Cs concentration, [M]

C_T - total Cs ionic exchange capacity, (0.58 mmol/g) on a dry CST mass basis

β - temperature dependent beta-factor, [M]

η - correction factor

Isotherms calculated for each modified Tank 9H supernate are provided in Figure 3-1 for the powder form of CST (i.e., CF (η) set to a value of 1) where it is apparent that Dilution #3 is expected to exhibit the highest cesium loading (at a given equilibrium cesium concentration) and Dilutions #1 and #2 are expected to load cesium at similar levels. The isotherm parameters are provided in Table 3-7. Comparisons of the isotherms to the average equilibrium batch contact data observed with IE-911 and R9120-B CST are provided in Figures 3-2 through 3-4 for Tank 9H supernate Dilution #1 through Dilution #3, respectively; where correction factors (η) were applied to the isotherms to match the experimental data. Applying a correction factor of ~0.7 to the isotherm results in good agreement with the experimental data observed for the IE-911 CST and all three modified Tank 9H samples. A correction factor of 0.68 is the standard used for the engineered CST material [8]. In contrast, the correction factor necessary to match the experimental data for R9120-B varied from 0.66 for Dilution #1 down to 0.56 for Dilution #3 (average CF (η) = 0.60). Note that the ZAM modeling comparisons were made to the lower result observed for Dilution #1 with R9120-B CST (higher outlier result disregarded). Calculated cesium distribution coefficients (K_d) are provided in Table 3-8 and compared to the experimental data. The calculated correction factors (η) for both CST batches are generally consistent with recent column testing where CF factors of 0.76 and 0.62 were observed for IE-911 and R9120-B CST, respectively [2].

Based on the Tank 9H batch contact results and the CF values calculated by ZAM provided in Table 3-8, the ZAM isotherm model was also used to predict the maximum (saturated) cesium loading on the CST samples in each Tank 9H supernate dilution. The results are provided in Table 3-8. Maximum ^{137}Cs loadings ranged from 92 to 207 Ci/kg CST. The highest cesium loading is predicted for Dilution #1 using IE-911 CST. The lowest cesium loading is predicted for Dilution #2 and R9120-B CST. In general, these loading levels are quite high (total cesium loading approaching 0.1 mmol/g for Dilution #1), as expected based on the low sodium to cesium ratios.

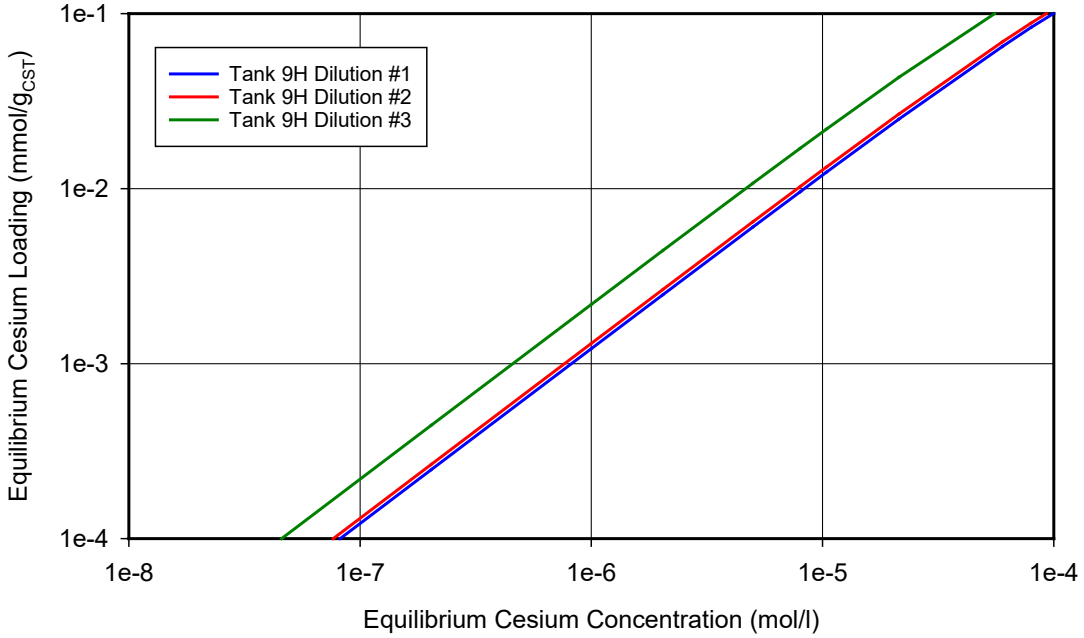

Figure 3-1. Tank 9H Supernate Dilution Isotherms at 35.3 ºC.

Table 3-7. Isotherm Parameters

Feed	T (°C)	η*	C_T	β
Dilution #1	35.3	1	0.58	4.7594E-4
Dilution #2	35.3	1	0.58	4.4515E-4
Dilution #3	35.3	1	0.58	2.6752E-4

* Correction factor

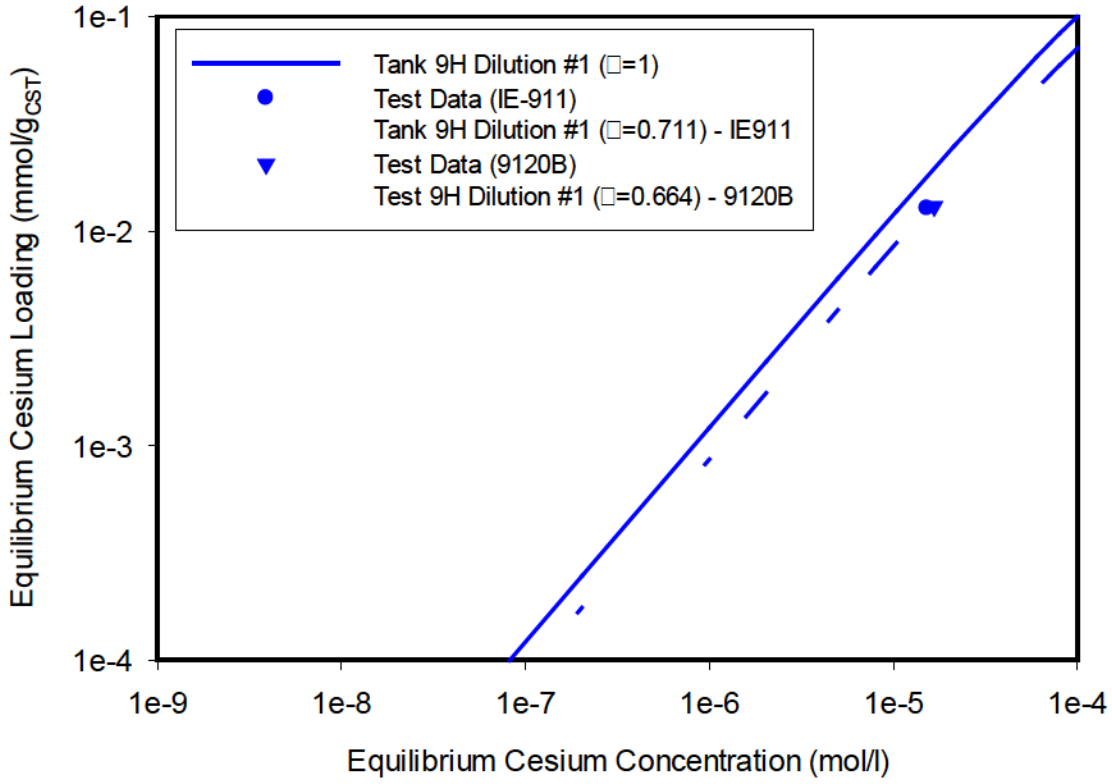

Figure 3-2. Tank 9H Dilution #1 Loading Cesium Isotherm Versus Experimental Data at 35.3 ºC.

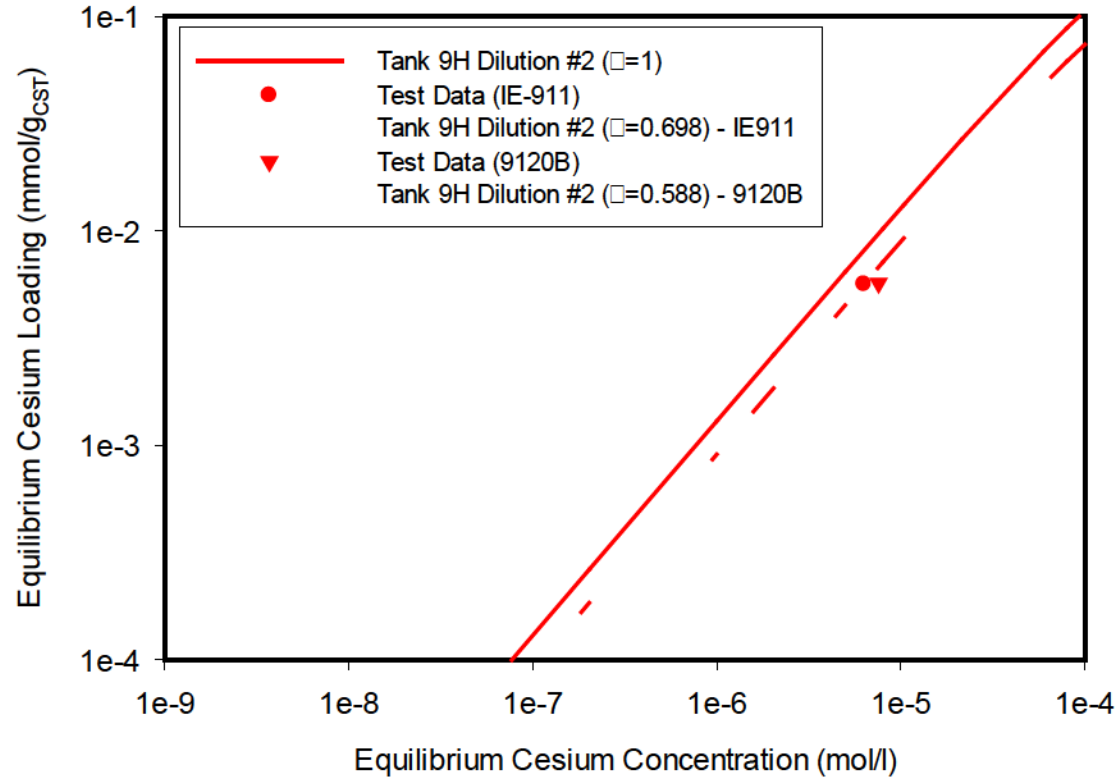

Figure 3-3. Tank 9H Dilution #2 Cesium Loading Isotherm Versus Experimental Data at 35.3 ºC.

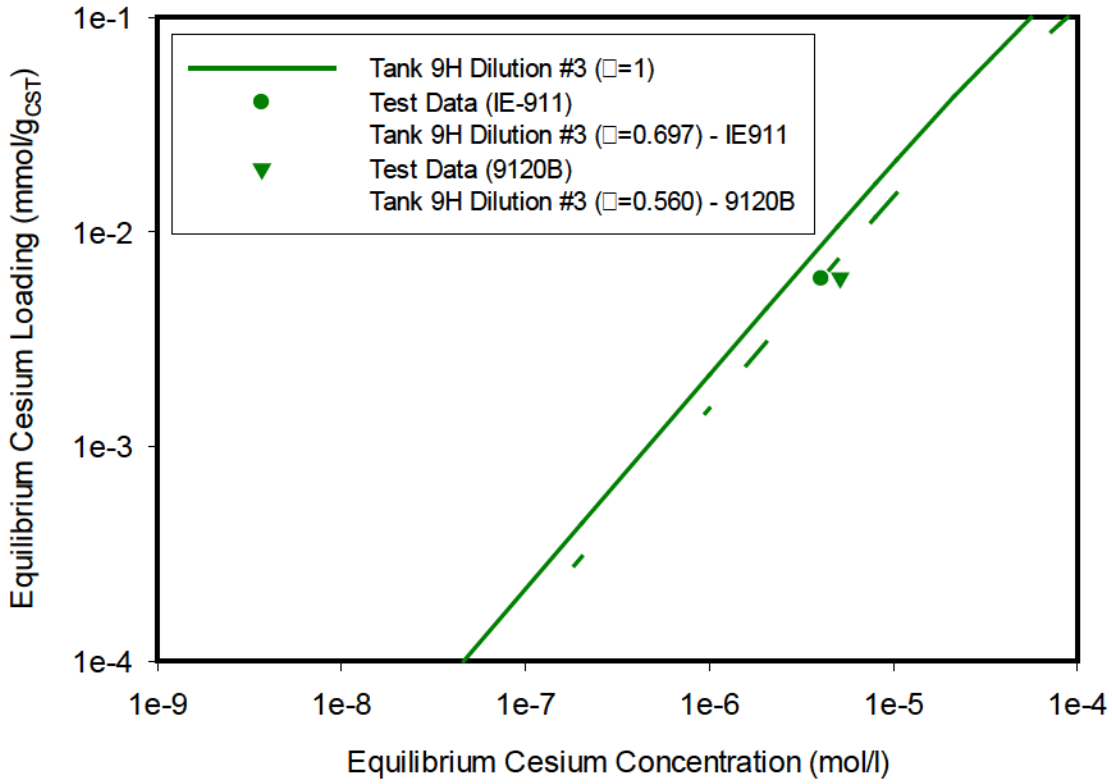

Figure 3-4. Tank 9H Dilution #3 Cesium Loading Isotherm Versus Experimental Data at 35.3 ºC.

Table 3-8. Calculated Cesium Distribution Coefficients and Maximum Cesium Loading for Tank 9H Supernate Dilutions.

Tank 9H Dilution #	CST	ZAM CF	Cs^+ Distribution Coefficient, K_d		Maximum ZAM-Calculated Loading, Q	
			Predicted (mL/g_{CST})	Average Observed (mL/g_{CST})[a]	Total Cs^+ (mmol/g CST)	^{137}Cs (Ci/kg_{CST})
1	IE-911	0.711	839	829	9.78E-02	207
2		0.698	896	898	5.16E-02	109
3		0.697	1488	1517	8.09E-02	171
1	R9120-B	0.664	782[b]	782[b]	9.13E-02	193
2		0.588	753	754	4.35E-02	92
3		0.560	1191	1192	6.50E-02	137

[a] dry CST mass basis
[b] based on inidvidual sample result rather than average of duplicates

4.0 Conclusions

Three dilutions of the Tank 9H sample composite were prepared and characterized. The results indicated that the dilutions achieved the desired compositional goals (all three samples near 6 M Na^+; Dilution #2 and Dilution #3 near 0.5 Ci ^{137}Cs/gallon). Batch contact equilibrium tests were conducted on all three Tank 9H dilutions with the two different CST media types being considered for use in the second TCCR unit. Comparison of loading results to ZAM model predictions indicated that the CST media performance was

as expected based on previous testing with similar correction factors to earlier results. Higher cesium loadings were observed for IE-911 CST relative to R9120-B CST, as expected. Cesium loading results observed for the digested CST samples from selected tests were consistent with loading results calculated based on liquid phase analysis. ZAM model predictions of maximum (saturation) cesium loading levels for the Tank 9H dilutions indicate very high ^{137}Cs loading ranging from 92 to 207 Ci ^{137}Cs/kg CST. In general, the theoretical total cesium loading levels are quite high (approaching 0.1 mmol/g for Dilution #1), as expected based on the high cesium concentrations in these solutions.

5.0 Recommendations

In order to predict performance of Tank 9H materials in the TCCR unit, batch contact equilibrium tests should also be conducted for the actual Tank 9H field-diluted material after transport and mixing with the Tank 10H heel using sub-samples of the same batch of CST media loaded into the columns. Alternatively, this could be accomplished by diluting a sample of the Tank 9H material already at SRNL and mixing it with a portion of the Tank 10H Batch 3 qualification sample at a ratio to simulate mixing with the Tank 10H heel. If additional Tank 9H dilutions are prepared they should be aged at the tank temperature rather than ambient temperature to better simulate what will occur in the tank.

Once the new batch of CST material that is to be used in the TCCR columns for treating Tank 9H is available, additional testing should be performed to compare performance of the new lot of material to previous batches tested here. Batch contact testing should be performed with both SRS average simulant as well as one or more of the Tank 9H dilutions described in this report. In addition to the standard batch contact tests to compare performance with previous batches, a batch contact should be performed with the new batch of CST and a representative Tank 9H dilution at a higher phase ratio to determine the impacts of competitors.

6.0 References

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Appendix A. TGA Results

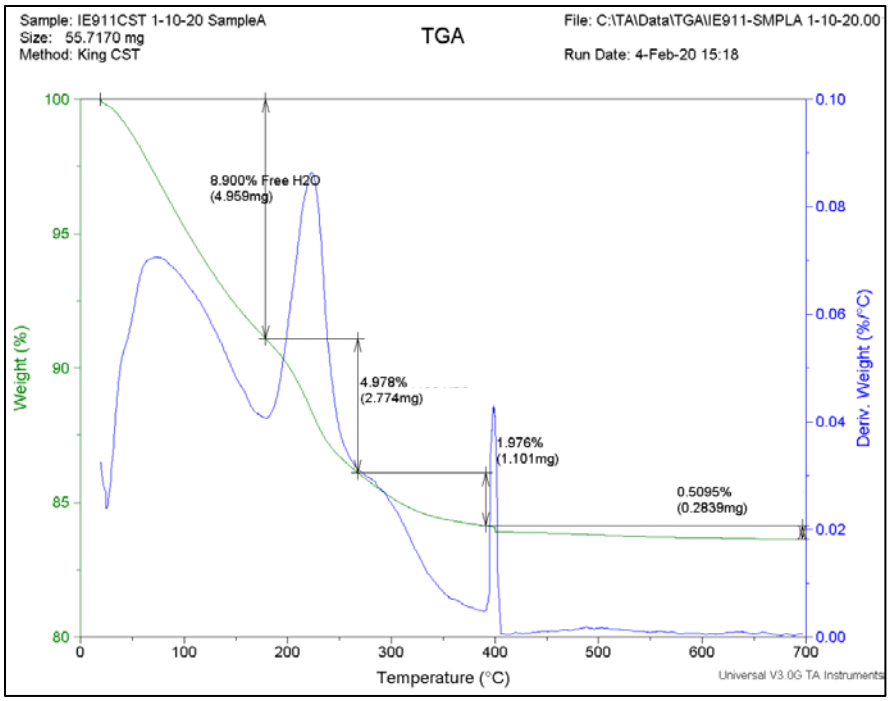

Figure A-1. TGA Mass Loss Profiles Versus Time for Vendor-Pretreated CST Batch IE-911 Sample A.

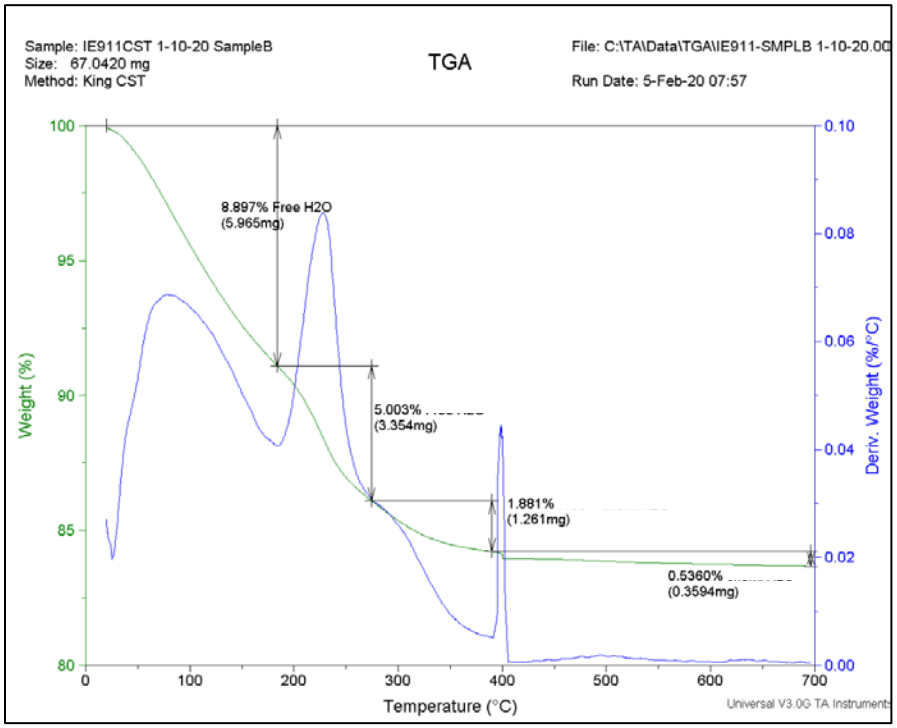

Figure A-2. TGA Mass Loss Profiles Versus Time for Vendor-Pretreated CST Batch IE-911 Sample B.

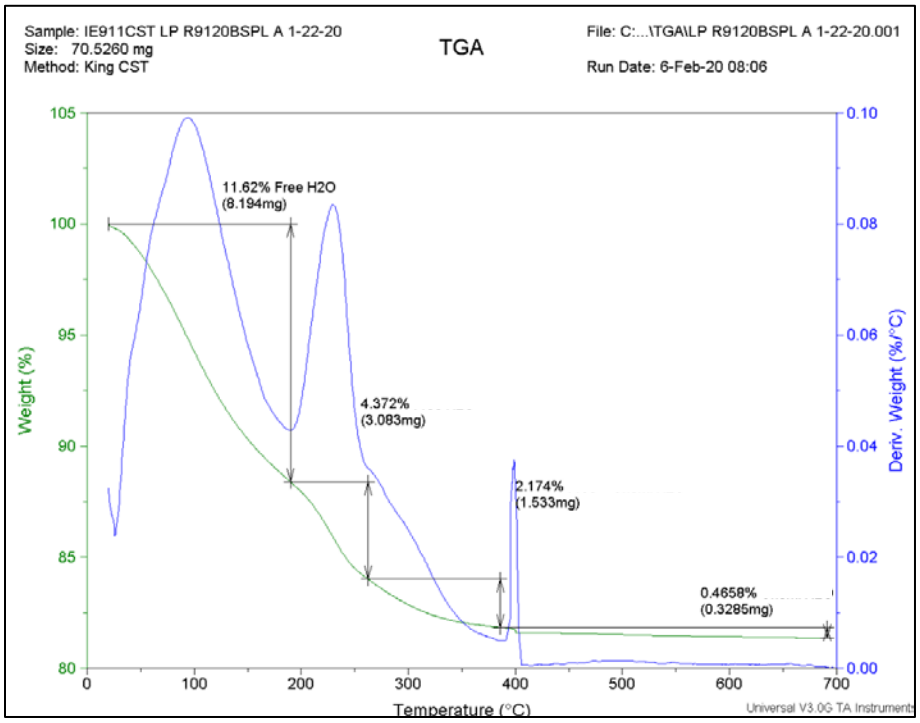

Figure A-3. TGA Mass Loss Profiles Versus Time for Laboratory-Pretreated CST Batch R9120-B Sample A.

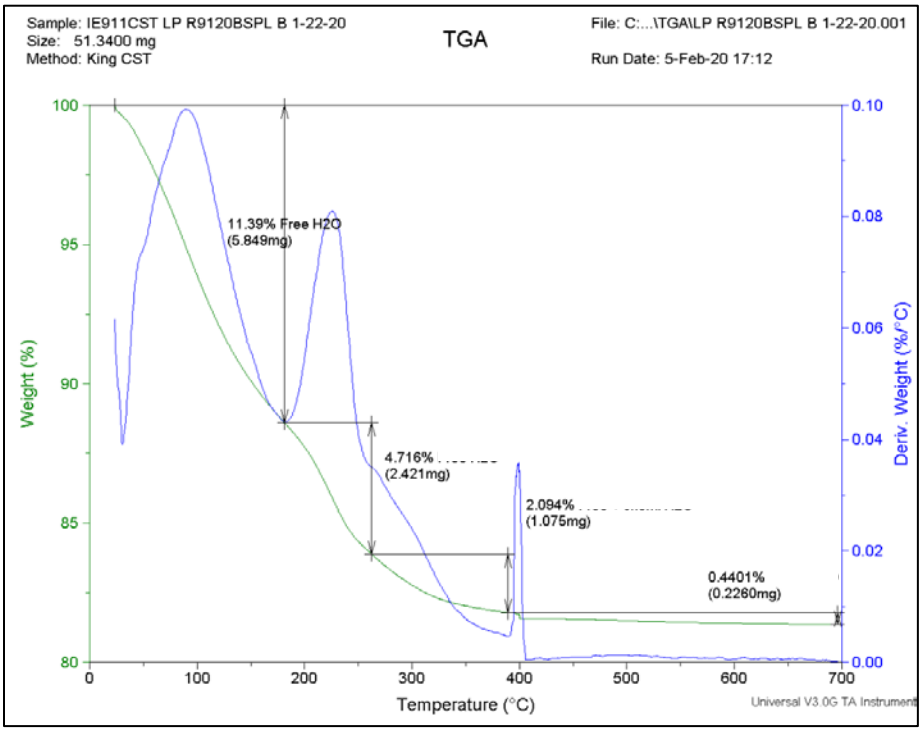

Figure A-4. TGA Mass Loss Profiles Versus Time for Laboratory-Pretreated CST Batch R9120-B Sample B.

Appendix B. CST Digestion Data

Table B-1. CST Standards Digestion Data (Corrected for the F-factor)[a]

Element	IE-911	R9120-B
	Average Content mmol/g (%RSD[b])	
Cs	1.82E-05 (5.41%)	< 4.58E-06 (n/a[c])
Al	6.96E-02 (5.37%)	1.01E-01 (1.55%)
Ca	1.47E-02 (21.1%)	1.90E-02 (3.81%)
Fe	5.26E-03 (20.3%)	3.81E-03 (0.33%)
Na	2.57E+00 (4.69%)	3.36E+00 (0.82%)
Rb	< 1.71E-05 (n/a[c])	1.23E-05 (8.88%)
Sr	3.97E-05 (0.67%)	1.38E-04 (2.31%)
Pb	2.59E-05 (2.87%)	< 1.04E-05 (n/a[c])
U	1.45E-05 (72.4%)	< 2.56E-06 (n/a[c])
Radionuclide	Average Content dpm/g (%RSD)	
^{137}Cs	< 9.43E+07 (n/a[c])	< 2.85E+06 (n/a[c])
^{90}Sr	< 2.08E+05 (n/a[c])	3.54E+05 (86.7%)
^{238}Pu	1.04E+04 (n/a[d])	2.06E+03 (n/a[d])

[a] Digestion standards were processed in the Shielded Cells along side the experimental samples. Presence of radionuclides represents contamination from the Shielded Cell environment.
[b] %RSD values from analysis of duplicate samples
[c] Not applicable as replicate samples were both below detection.
[d] Not applicable as reported value is from a single replicate above detection, duplicate sample was below the detection limit.