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Crystalline Silicotitanate (CST) Ion Exchange Media Performance Evaluations in SRS Average Supernate Simulant and Tank 10H Waste Solution to Support TCCR

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June 2018

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EXECUTIVE SUMMARY

Savannah River Remediation (SRR) is deploying an “at-tank” ion exchange process to remove radioactive cesium from waste supernate which is referred to as the Tank Closure Cesium Removal (TCCR) system utilizing Crystalline Silicotitanate (CST) media. After being loaded with cesium, but before flushed and dried and sent to Interim Safe Storage (ISS), it is anticipated that the TCCR ion exchange columns will be taken off-line (stagnant) with the CST media still immersed in supernate. The currently designed columns include no active cooling system during processing (although normal process fluid flow through the column during operations provides significant cooling) or during off-line conditions and temperature increases are expected in the stagnant, loaded, and liquid-filled columns due to decay heat from the radionuclides absorbed to the CST. As a result, modification of the Tank 10H supernate composition has been considered through the addition of either NaOH or KOH reagents to decrease cesium loading.

To confirm that the performance of IONSIV R9120-B CST media is similar to previous batches of IONSIV IE-911 and validate current test methodologies and equipment, batch contact testing has been conducted in the Savannah River National Laboratory (SRNL) shielded cells facility using a Cs-137 spiked Savannah River Site (SRS) Average Waste Simulant composition utilized in previous studies. Kinetics testing was conducted to determine the timescale to achieve cesium loading equilibrium with R9120-B under the test conditions. The cesium equilibrium loading isotherm in SRS simulant at 23 °C was subsequently determined and compared to ZAM isotherm model predictions and previous test results with IE-911 media. The results indicate that R9120-B media performs similarly to IE-911.

SRNL also conducted CST batch contact equilibrium testing with as-received and chemically-modified Tank 10H waste supernate to evaluate various potential processing scenarios and initial results were reported in SRNL-L3100-2017-00149 [1]. Additional details regarding this testing and additional modeling analysis of the results are provided herein. The impacts of sodium and potassium additions on CST cesium removal performance from this waste were generally consistent with expectations and initial model predictions. Addition of either sodium or potassium hydroxide reagents resulted in decreased cesium loading on CST and lower Cs^+ distribution coefficients (K_d), with potassium addition having the greatest impact. Based on the results, increasing the potassium concentration to ≥ 0.2 M is expected to decrease cesium loading on the CST column at saturation by ~50%.

Desorption studies were also conducted with CST samples loaded to cesium saturation with chemically-modified Tank 10H Surface and Variable Depth samples. In this case, the chemical modifications involved the addition of 50 wt. % NaOH and a non-radioactive CsNO_3 solution to produce ~5 M Na^+ solutions with cesium levels elevated relative to the as-received Tank 10H supernate. The addition of non-radioactive cesium was necessary to produce CST samples loaded to cesium saturation levels expected with Tank 10H materials. This maximum cesium loading level should be achieved when the final solution cesium concentration after CST contact equals the original Tank 10H concentration. Insufficient Tank 10H supernate was available in the SRNL shielded cells to produce sufficient cesium saturated CST for analysis, therefore non-radioactive cesium was added based on preliminary modeling predictions. Equilibrium batch contact loading tests were then conducted at 30 °C with phase ratios near 61 (supernate volume: dry CST reference state mass). Small sub-samples of the liquid and solid phases were subsequently removed for analysis and the bulk of the solution was removed from the test samples, leaving cesium-saturated CST samples immersed in Tank 10H supernate at a phase ratio near 5 for desorption testing.

The remaining Tank 10H/CST slurries were then heated to 80 °C in sealed vessels with agitation to promote desorption of radionuclides. This condition is believed to represent the TCCR process condition when the stagnant, loaded, liquid-filled CST columns are allowed to self-heat due to radioactive decay. Sub-samples of the liquid and solid phases were subsequently collected at elevated temperature for analysis to determine

the amount of cesium desorbed from the CST at elevated temperature. Cesium concentrations in the liquid phase were observed to increase in Tank 10H supernate by a factor of 3-7 relative to the concentration of the original supernate. ZAM model predictions indicated that the liquid phase cesium concentration should increase by a factor of ~ 3 when the temperature is increased from 30 to 80 °C, although the ZAM model was developed based on batch contact data in the 25-44 °C range [2]. The concentrations of various other radionuclides in the liquid and solid phases were also analyzed to determine the amounts absorbed at 30 °C and desorbed at 80 °C, although it was unknown whether these species would load onto the CST at saturation levels under these conditions. A radionuclide of particular interest in this testing was plutonium, most of which (>94% based on liquid phase analysis) was observed to load onto the CST at 30 °C. In contrast to cesium, plutonium did not desorb from the CST at 80 °C, implying that the sorption and desorption of plutonium to/from CST involves a mechanism other than ion exchange.

All batch contact testing was successfully completed and the results were generally consistent with ZAM model predictions indicating that the current CST batch performs similarly to previously tested batches in various liquid phase compositions and at elevated temperatures.

TABLE OF CONTENTS

LIST OF TABLES	ix
LIST OF FIGURES	x
LIST OF ABBREVIATIONS.....	xi
1.0 Introduction.....	1
2.0 Experimental Methods and Modeling Approach	1
2.1 Equipment	1
2.2 CST Pretreatment	2
2.3 Simulant Preparation	4
2.4 CST Batch Contact Testing with SRS Average Simulant.....	4
2.5 Tank 10H Sample Chemical Modifications for CST Batch Contact Equilibrium Loading Testing. ..	5
2.6 CST Batch Contact Loading Testing with As-Received and Chemically Modified Tank 10H Samples	6
2.7 Tank 10H Sample Chemical Modifications for CST Batch Contact Equilibrium Desorption Testing	6
2.8 CST Batch Contact Desorption Testing with Chemically Modified Tank 10H Samples	6
2.9 ZAM Isotherm Model Calculations	8
3.0 Results and Discussion	8
3.1 CST Loading Batch Contact Tests with SRS Average Simulant	8
3.2 CST Batch Contact Loading Tests with As-Received and Chemically Modified Tank 10H Samples	11
3.3 CST Batch Contact Desorption Testing with Chemically Modified Tank 10H Samples	20
4.0 Conclusions.....	27
5.0 Recommendations, Path Forward or Future Work	27
6.0 References.....	29
7.0 Appendices.....	30
Appendix A (ZAM Analyses).....	30
7.1 Input: 30C – Surface Sample – As-Rec.....	30
7.2 Output: 30C – Surface Sample – As-Rec.....	30
7.3 Input: 30C – Surface Sample – MOD1	31
7.4 Output: 30C – Surface Sample – MOD1.....	31
7.5 Input: 30C – Surface Sample – MOD2	32
7.6 Output: 30C – Surface Sample – MOD2.....	32
7.7 Input: 30C – Surface Sample – MOD3	33

7.8 Output: 30C – Surface Sample – MOD3.....	33
7.9 Input: 30C – Surface Sample – MOD4	34
7.10 Output: 30C – Surface Sample – MOD4.....	34
7.11 Input: 30C – Surface Sample – MOD5	35
7.12 Output: 30C – Surface Sample – MOD5.....	35
7.13 Input: 30C – VD Sample – As-Rec	36
7.14 Output: 30C – VD Sample – As-Rec	36
7.15 Input: 30C – VD Sample – MOD1	37
7.16 Output: 30C – VD Sample – MOD1	37
7.17 Input: 30C – VD Sample – MOD2.....	38
7.18 Output: 30C – VD Sample – MOD2	38
7.19 Input: 30C – VD Sample – MOD3.....	39
7.20 Output: 30C – VD Sample – MOD3	39
7.21 Input: 30C – VD Sample – MOD4.....	40
7.22 Output: 30C – VD Sample – MOD4.....	40
7.23 Input: 30C – VD Sample – MOD5.....	41
7.24 Output: 30C – VD Sample – MOD5	41
Appendix B (ZAM Beta Values)	42

LIST OF TABLES

Table 2-1. Thermal Gravimetric Analysis Results for As-Received and Pretreated R9120-B CST Media.	3
Table 2-2. SRS Average Simulant Composition Developed by Walker [6] and Total Cesium Spike Levels Utilized for Testing.....	4
Table 2-3. Sample and Reagent Masses used for Tank 10H Surface and Variable Depth Sample Chemical Modifications Prior to Batch Contact Equilibrium Loading Testing.....	5
Table 2-4. Sample and Reagent Masses used for Tank 10H Surface and Variable Depth Sample Chemical Modifications Prior to CST Desorption Studies.	6
Table 2-5. Masses and Volumes used for Tank 10H Surface and Variable Depth Sample CST Batch Contact Loading/Desorption Studies.	7
Table 3-1. Analytical Results for Cesium Loading Batch Contact Testing with CST and SRS Average Simulant.....	9
Table 3-2. Analytical Results for the As-Received and Chemically Modified Tank 10H Samples	13
Table 3-3. Ion Balanced Tank 10H Sample Compositions used for ZAM Input.....	14
Table 3-4. Cesium Loading Batch Contact Results (Cs^+ removal) for Individual As-Received and Chemically Modified Tank 10H Surface Samples with CST.....	15
Table 3-5. Cesium Loading Batch Contact Results (Cs^+ removal) for Individual As-Received and Chemically Modified Tank 10H Variable Depth Samples with CST.....	16
Table 3-6. Liquid Phase Cesium Analysis Results from 30 °C Loading Batch Contact Before Desorption Testing.	21
Table 3-7. Solid Phase Cesium Analysis Results from 30 °C Loading Batch Contact Before Desorption Testing.	21
Table 3-8. Liquid Phase Cesium Analysis Results from 80 °C Batch Contact Desorption Testing.....	22
Table 3-9. Solid Phase Cesium Analysis Results from 80 °C Batch Contact Desorption Testing.	22
Table 3-10. CST Wash Sample Analysis Following Cesium Loading and Desorption.	22
Table 3-11. Liquid Phase Plutonium Analysis Results from 30 °C Loading Batch Contact Testing.....	25
Table 3-12. Liquid Phase Plutonium Analysis Results from 80 °C Desorption Testing.	25
Table 3-13. CST Solid Phase Plutonium Analysis Results from 30 °C Loading and 80 °C Desorption Testing.	25
Table 3-14. CST Additional Radionuclide Analysis Results from Desorption Studies.....	26
Table 3-15. CST Elemental Analysis Results from Desorption Studies.....	26

LIST OF FIGURES

Figure 2-1. Reciprocal Water Bath Shaker Unit Utilized for Most Batch Contact Testing.....	2
Figure 3-1. Cesium Loading Versus Time from SRS Average Simulant on CST at 23 °C Using Simulant Composition D.....	10
Figure 3-2. Cesium Equilibrium Loading Isotherm in SRS Average Simulant on CST at 23 °C (13-day contact).	10
Figure 3-3. Comparison of Observed and Predicted (ZAM Model) Cesium Equilibrium Loading Isotherm with SRS Average Simulant and CST at 23 °C.	11
Figure 3-4. Trends in Cs^+ K_d values versus the Sodium and Potassium Molarities for the As-received and Modified Tank 10H Surface Samples.....	17
Figure 3-5. Trends in Cs^+ K_d values versus the Sodium and Potassium Molarities for the As-received and Modified Tank 10H Variable Depth Samples.	17
Figure 3-6. Comparison of ZAM Cs^+ Loading Isotherms for CST at 30 °C Versus the Measured Cesium Loading Values for the Tank 10H Surface As-Received and Modification #1 and #2 Samples (Na^+ impacts).	18
Figure 3-7. Comparison of ZAM Cs^+ Loading Isotherms for CST at 30 °C Versus the Measured Cesium Loading Values for the Tank 10H Surface As-Received and Modification #3, #4, and #5 Samples (K^+ impacts).	18
Figure 3-8. Comparison of ZAM Cs^+ Loading Isotherms for CST at 30 °C Versus the Measured Cesium Loading Values for the Tank 10H Variable Depth As-Received and Modification #1 and #2 Samples (Na^+ impacts).	19
Figure 3-9. Comparison of ZAM Cs^+ Loading Isotherms for CST at 30 °C Versus the Measured Cesium Loading Values for the Tank 10H Variable Depth As-Received and Modification #3, #4, and #5 Samples (K^+ impacts).	19
Figure 3-10. Comparison of Cesium 30 °C Equilibrium Sorption and 80 °C Desorption Data to ZAM Model Predictions for Tank 10H Surface Sample and CST.	23
Figure 3-11. Comparison of Cesium 30 °C Equilibrium Sorption and 80 °C Desorption Data to ZAM Model Predictions for Tank 10H Variable Depth Sample and CST.	23

LIST OF ABBREVIATIONS

CST	Crystalline Silicotitanate
DOE	Department of Energy
ICP-ES	Inductively Coupled Plasma - Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma - Mass Spectroscopy
ISS	Interim Safe Storage
K _d	Distribution Coefficient
PVDF	Polyvinylidene fluoride
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TGA	Thermal Gravimetric Analysis
TIC	Total Inorganic Carbon
TCCR	Tank Closure Cesium Removal
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
MS	Mass Spectroscopy
VD	Variable Depth
ZAMM	ZAMM Isotherm Model

1.0 Introduction

Savannah River Remediation (SRR) is deploying an ion exchange process to remove radioactive cesium from waste supernate which is referred to as TCCR. The TCCR process focuses on the dissolution, removal, and decontamination of saltcake from High Level Waste (HLW) tanks prior to tank closure. During TCCR processing, filtered Tank 10H salt solution will be passed through ion exchange columns containing CST media commercially known as UOP IONSIV R9120-B (formerly called IE-911) to remove Cs-137. At the beginning of Calendar Year 2017, Tank 10H waste was considered to be “dry salt” with no significant liquid layer above the saltcake solids. In February of 2017, approximately 42,000 gallons of inhibited water and rain water from a sump were added without mixing to Tank 10H to create a free supernatant layer in the tank. Surface and Variable Depth (VD) samples were collected from the tank in March of 2017 and sent to SRNL for characterization. Sample analysis results for these Tank 10H samples were documented in SRNL-STI-2017-00392 [3].

Three types of batch contact testing (described below) were conducted to support TCCR design and implementation as specified in the associated Technical Task Request [4] and Technical Task and Quality Assurance Plan [5].

1. The ion exchange media, test method, and equipment were evaluated for comparison to previous studies and model predictions by conducting CST batch contact tests with SRS average simulant at 23 °C. Confirmation of equilibrium cesium loading (kinetics studies) was also conducted as part of this testing.
2. CST batch contact equilibrium loading studies were conducted at 30 °C with as-received and chemically modified Tank 10H supernate (aqueous dissolved saltcake) solutions to evaluate the impacts of NaOH and KOH reagent additions.
3. Desorption studies were conducted at 80 °C with CST media previously loaded to cesium saturation at 30 °C using chemically modified Tank 10H supernate. The Surface and Variable Depth samples were chemically adjusted prior to batch contact testing to ~5 M Na⁺ by the addition of NaOH reagent. In addition, prior to CST contact the total cesium concentrations of these samples were increased to calculated target values expected to promote cesium loadings on CST near the values expected with Tank 10H dissolved saltcake.

2.0 Experimental Methods and Modeling Approach

2.1 Equipment

A New Brunswick Scientific Reciprocal Water Bath Shaker (Model R 76) was utilized for most of the batch contact testing (Figure 2-1). The test sample bottles were immersed (vertical orientation with caps above liquid level) in the water bath which was equipped with a heater and thermostat for temperature control. For simulant testing conducted at 23 °C and some testing at 30 °C, an external water recirculator unit (ThermoCube Solid State Cooling System) with a thermoelectric chiller was used to pump water through the water bath to maintain the target temperature. In this case, the heater unit on the water bath was turned off during testing. Test samples were continuously agitated in the water bath using a one-dimensional reciprocal (back-and-forth) motion, except during sampling events. A shaker setting of 5 was utilized for all testing which corresponded to an agitation rate near 130 cycles per minute (cycle defined as one complete back-and-forth motion). The bath temperature was monitored using a thermocouple.

During CST desorption testing, equipment issues were observed which changed test plans and delayed test completion. Equipment malfunctions such as these are not uncommon in the SRNL shielded cells due to



Figure 2-1. Reciprocal Water Bath Shaker Unit Utilized for Most Batch Contact Testing.

the high radiation field in this environment. During desorption testing at 90 °C, the water bath temperature control could not be maintained and the test was stopped. A new shaker unit (ThermoScientific Incubator Shaker) utilizing air rather than water for temperature control and an orbital rather than reciprocal agitation motion, was installed in the shielded cells and the test was completed using an agitation rate of 150 rpm. The maximum temperature for the backup shaker unit was only 80 °C, so the final desorption portion of the testing was conducted at this temperature.

2.2 CST Pretreatment

Details of the CST media pretreatment were reported previously [1] and are summarized again below.

A bottle of CST Media was received for testing at SRNL labeled as IONSIV R9120-B, Lot #2099000034, Mat. #8103701-556, Sub-sample from CUA #125953-A. A portion of the CST beads was isolated and wetted in deionized water and fines were removed by decantation prior to transfer of the bulk solids to a glass column for further fines removal and caustic pretreatment. 3M NaOH solution was subsequently pumped into the column in an upflow direction. Following caustic pretreatment, deionized water was transferred through the column in an upflow direction until the pH decreased to near 11. The CST slurry was removed from the column, filtered, and allowed to air dry as a filter cake before being dried in an oven and maintained at 35 °C until a constant mass was observed. This pretreatment method is believed to fully convert the CST to the Na⁺ ionic form. Pretreated CST media in this condition is defined as the reference state for ion exchange testing and this material was utilized for all subsequent testing. Thermal Gravimetric Analysis (Figure 2-2 and Table 2-1) of the as-received and pretreated CST media revealed that the percentages of physisorbed water in the samples were 20.75% and 18.14%, respectively. As discussed in detail in the earlier memorandum [1], the water mass loss data indicated that the as-received CST was primarily in the hydrogen ionic form. Conversion of the pretreated CST reference state mass to a dry mass basis can be accomplished by multiplying the reference mass by a factor 0.8186.

Based on the TGA analysis provided in Figure 2-2, water loss from standard state CST media at 100 °C should be at least 7.6% and could be as high as 11.2%, with additional drying time. This latter mass loss represents the total physisorbed water as the temperature was increased to 168 °C. Additional water loss is not expected at 100 °C and the water content of the CST media should be near 7.0% after being thoroughly dried at this temperature. It should be noted that these comments are based on the assumption that all mass

loss from the CST media was associated with water loss, although the identity of the off-gas components was not confirmed by mass spectroscopy analysis.

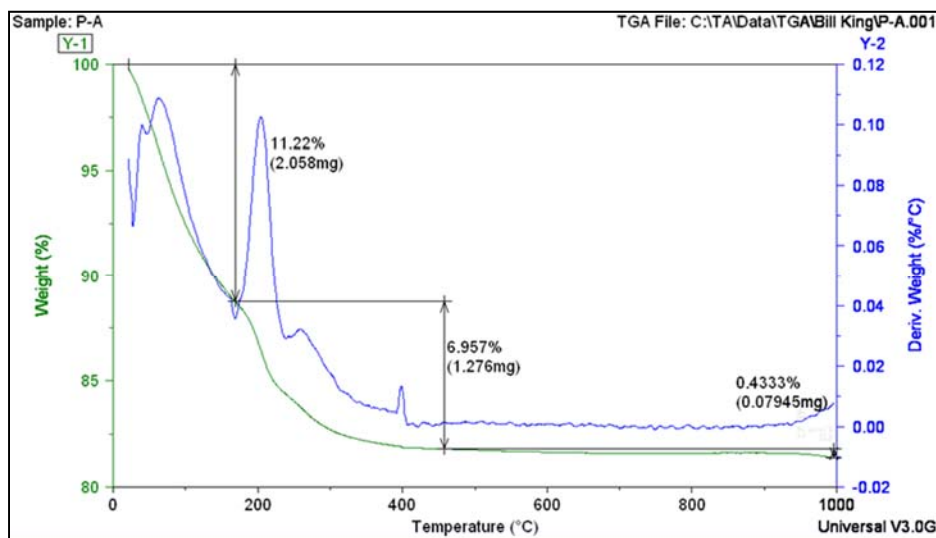


Figure 2-2. Thermal Gravimetric Analysis Results for Pretreated R9120-B CST Media (Pretreated Sample A).

Table 2-1. Thermal Gravimetric Analysis Results for As-Received and Pretreated R9120-B CST Media.

Sample	Cumulative % Mass Loss
As-Received B	20.76
As-Received C	20.74
Average	20.75
% RSD	0.1%
Mass Correction Factor	0.793
Pretreated A	18.18
Pretreated B	17.98
Pretreated C	18.27
Average	18.14
% RSD	0.8%
Mass Correction Factor	0.819

* pretreated CST in standard mass reference state

2.3 Simulant Preparation

A sample of waste simulant with the composition provided in Table 2-2 was prepared following the recipe reported by Walker [6]. This simulant was developed to represent an average SRS waste supernate liquid and this solution has been used in the past for CST performance evaluations. The simulant contains 5.6 M Na^+ and 1.9 M free OH^- , with nitrate and nitrite anions being the next most concentrated anions present. Cesium salts were excluded from the initial simulant preparation so that various cesium spike levels could be added for CST loading isotherm testing. The simulant was filtered through a 0.45 μm polymer filter unit. Radioactive and non-radioactive cesium sources were added to each of four separate portions of the simulant to give different total cesium concentrations within the compositional range of interest for cesium absorption onto CST media. A relatively constant Cs-137 spike concentration near 2 E6 dpm/mL was used for all samples while the total cesium concentration ranged from 3 E-6 M to 1 E-3 M. The measured simulant density was 1.2157 g/mL at ambient temperature (19 °C).

Table 2-2. SRS Average Simulant Composition Developed by Walker [6] and Total Cesium Spike Levels Utilized for Testing.

Component	Molarity
Na^+	5.60
K^+	0.015
OH^-	1.91
NO_3^-	2.14
NO_2^-	0.52
AlO_2^-	0.31
CO_3^{2-}	0.16
SO_4^{2-}	0.15
Cl^-	0.025
F^-	0.032
PO_4^{3-}	0.01
$\text{C}_2\text{O}_4^{2-}$	0.008
SiO_3^{2-}	0.004
MoO_4^{2-}	0.0002
Sub-Sample Spike Levels	
Simulant	Total Cs^+ (M)
A	3.1 E-6
B	1.4 E-4
C	9.9 E-4
D	5.1 E-6

2.4 CST Batch Contact Testing with SRS Average Simulant

10 mL samples of each of the simulant solution sub-samples (A-D in Table 2-2) were used for batch contact equilibrium testing with ~0.1 g samples (standard damp mass basis) of CST media. Additional 10 mL

samples were prepared for cesium loading kinetics evaluations using Spike Level D. The slurry test samples were placed in 60 mL polyethylene bottles, transferred to the water bath shaker, and exposed to continuous agitation. A water bath temperature of 23 °C was targeted and the temperature was recorded daily (excluding weekends). Batch contact testing was continued for a total of 16 days with sub-samples collected at various times (4, 5, 9, 13, and 16 days) to determine the cesium loading kinetics and loading isotherm. Duplicate test samples were prepared for 13 and 16-day samples while single samples were prepared for the other test durations. A, B, and C test solutions were sampled only after 13 days of agitation. During testing, the average temperature based on the recorded data was 23.06 °C and the temperature ranged from 22.80 to 23.58 °C. During each sampling event, individual samples were removed from the shaker, filtered through 0.45 µm syringe filters, and submitted for Cs-137 (gamma) analysis. Feed samples were diluted by a factor of ~2 in 3 M HNO₃ and submitted for gamma and ICP-MS analysis to determine both the Cs-137 and total cesium concentrations. The total cesium concentrations for the simulant samples were calculated as the sum of the Cs-137 and Cs-133 concentrations.

2.5 Tank 10H Sample Chemical Modifications for CST Batch Contact Equilibrium Loading Testing.

The Tank 10H Surface sample used for cesium batch contact equilibrium loading testing was a composite of tank farm samples HTF-10-17-30 and -31 prepared by Reboul [2]. The Tank 10H Variable Depth sample used for testing was a composite of tank farm samples HTF-10-17-32 and -33 prepared by Reboul [2]. The samples were chemically modified by the addition of NaOH and/or KOH reagents prior to being transferred through 5 µm polyvinylidene fluoride (PVDF) syringe filters. The Tank 10H supernate and reagent masses used for chemical modifications are provided in Table 2-3. As reported by Reboul [2], the densities of the Tank 10H Surface and Variable Depth samples were 1.16 g/mL and 1.17 g/mL, respectively. The densities of the NaOH and KOH reagents were 1.525 g/mL and 1.456 g/mL, respectively. The densities of 2 mL sub-samples of the chemically modified and filtered Tank 10H supernate samples were measured in duplicate. No precipitation was visually observed following the addition of the caustic reagents. The chemically-modified samples were mixed and allowed to stand for several days prior to filtration. The filtrates were used for CST batch contact testing described below. Subsamples of the chemically modified Tank 10 solutions were diluted in water by a factor of ~19 and analyzed by ICP-ES, Free OH⁻, IC anion, and Total Inorganic Carbon (TIC) methods. Separate sub-samples were diluted by a factor of ~16 in 3 M HNO₃ and analyzed by gamma scan to determine the Cs-137 concentrations.

Table 2-3. Sample and Reagent Masses used for Tank 10H Surface and Variable Depth Sample Chemical Modifications Prior to Batch Contact Equilibrium Loading Testing.

Tank 10H Sample	Sample ID	Tank 10H (g)	50 wt. % NaOH (g)	45 wt. % KOH (g)
Surface (HTF-10-17-30/-31)	Modification #1	34.898	1.256	---
	Modification #2	34.891	4.568	---
	Modification #3	34.820	---	0.167
	Modification #4	34.752	0.825	0.766
	Modification #5	34.839	---	2.758
Variable Depth (HTF-10-17-32/-33)	Modification #1	35.074	2.353	---
	Modification #2	35.130	5.776	---
	Modification #3	35.119	---	0.195
	Modification #4	35.091	1.933	0.783
	Modification #5	35.136	---	2.750

2.6 CST Batch Contact Loading Testing with As-Received and Chemically Modified Tank 10H Samples

Duplicate 10 mL samples of each as-received and modified Tank 10H supernate sample were used for batch contact testing with ~0.1 g samples (standard damp mass basis) of CST media. The slurry test samples were placed in 60 mL polyethylene bottles, transferred to the water bath shaker, and exposed to continuous agitation. A water bath temperature of 30 °C was targeted and the temperature was recorded daily (excluding weekends). Batch contact testing was continued for a total of 12 days. The bath and sample temperature averaged 30.0 °C and varied across a range of 29.8-30.1 °C during testing. At test completion, individual samples were removed from the shaker, immediately filtered through 0.45 µm syringe filters, and diluted by a factor of ~4 in 3 M HNO₃. The diluted samples were submitted for Cs-137 (gamma scan) analysis.

2.7 Tank 10H Sample Chemical Modifications for CST Batch Contact Equilibrium Desorption Testing

Additional portions of the Tank 10H Surface and Variable Depth samples were chemically modified by the addition of NaOH reagent and CsNO₃ spike solution. The Tank 10H supernate and reagent masses used for chemical modification are provided in Table 2-4. The density of the CsNO₃ spike solution was 0.998 g/mL and the cesium concentration was 2.13 g Cs⁺/L. No precipitation was observed following the addition of the caustic reagent. The chemically-modified samples were mixed and allowed to stand for several days and then transferred through 5 µm polyvinylidene difluoride (PVDF) syringe filters prior to use for CST batch contact desorption testing described below. Sub-samples of the chemically modified Tank 10H supernate solutions were diluted by a factor of 5-18 in 3 M HNO₃ and analyzed by gamma scan and ICP-MS to determine the Cs-137 and total Cs⁺ concentrations.

Table 2-4. Sample and Reagent Masses used for Tank 10H Surface and Variable Depth Sample Chemical Modifications Prior to CST Desorption Studies.

Tank 10H Sample	Tank 10H (g)	50 wt. % NaOH (g)	CsNO ₃ Solution (g)
Surface (HTF-10-17-30/-31)	73.934	11.296	2.599
Variable Depth (HTF-10-17-32/-33)	52.546	10.160	1.846

* calculated total [Na⁺]: Surface – 5.09 M; Variable Depth 5.16 M

** cesium nitrate spike solution concentration: 2.13 g Cs/L

2.8 CST Batch Contact Desorption Testing with Chemically Modified Tank 10H Samples

Individual 70 and 50 mL samples, respectively, of the chemically modified Tank 10H Surface and Variable Depth samples were used for batch contact testing with 1.4 and 1.0 g (standard damp mass basis) of CST media (respectively). Exact masses used are provided in Table 2-5. The slurry test samples were placed in ~150 mL Teflon digestion bottles and sealed prior to transfer to the water bath shaker. A water bath temperature of 30 °C was targeted for cesium loading and the temperature was recorded daily (excluding weekends). Batch contact loading testing was continued for a total of 13 days. The bath and sample temperature averaged 29.7 °C and varied across a range of 28.7-30.1 °C during testing, excluding one night when temperature control was lost and the temperature decreased to near ambient conditions. At test completion, individual samples were removed from the shaker, filtered through 0.45 µm syringe filters, and diluted by a factor of ~3 in 3 M HNO₃. The diluted samples were submitted for Cs-137 (gamma scan) analysis.

Immediately following completion of the cesium CST batch contact loading step, the bulk of the liquid phase and small portions of the CST were removed from the vessel. The CST sub-samples were briefly washed with 0.01 M NaOH to remove residual supernate. The sample liquid phase was removed down to the target volumes indicated in Table 2-5. Then the digestion vessels were sealed again and the samples were returned to the water bath shaker unit. The temperature of the unit was increased to the target value of 90 °C. The samples were maintained near a temperature of 88 °C with daily water bath refill events in which the temperature would decrease to near 70 °C for approximately an hour. After 10 days of contact and agitation, temperature control was lost overnight due to equipment malfunction and the sample cooled to ambient temperature (near 18 °C). The broken water bath shaker unit was removed from the cell and a new shaker oven was installed. The sample vessels remained closed during this 9-day period with no temperature control. The digestion bottles were then placed in the new shaker oven at a set temperature of 80 °C (maximum oven temperature) and continually agitated for 13 days. The digital readout on the oven read 80.0 °C throughout the testing. At test conclusion, the shaker temperature was checked using a thermocouple which indicated that the temperature was 79.3 °C. The slightly lower temperature observed with the thermocouple was not surprising given that the thermocouple cord had to be placed across the foam heat seal liner for the shaker bath top (or sash) to measure the temperature. The uncertainty for the thermocouple temperature readings was ± 0.25 °C at 30 °C and ± 0.60 °C at 80 °C. Sub-samples of the liquid and solid phases were collected for analysis immediately after the samples were removed from the oven. The liquid sub-samples were filtered through 0.45 μ m syringe filters and diluted by a factor of 2.5-6 in 3 M HNO₃. The CST sub-samples were briefly washed with 0.01 M NaOH to remove residual supernate.

The batch contact filtrate sub-samples were analyzed for Cs-137 by gamma counting and total Cs⁺ by ICP-MS. The washed CST sub-samples were dried to a constant mass at 35 °C (to determine the standard reference state mass), dissolved in acid (HF/concentrated HNO₃ mixture) at elevated temperature, and the digestion liquid was analyzed for Cs-137 (gamma), total Cs⁺ (ICP-MS), plutonium isotopes (Pu-TTA), uranium isotopes (ICP-MS and counting), various metals (ICP-ES), Np-237 (Cs-removed gamma), Am-241 (Cs-removed gamma), and Sr-90 (beta scintillation counting). The CST wash solutions were also analyzed for Cs-137 to ensure that minimal losses of absorbed cesium occurred during washing.

Table 2-5. Masses and Volumes used for Tank 10H Surface and Variable Depth Sample CST Batch Contact Loading/Desorption Studies.

Modified Tank 10H Sample	Cesium Loading		Cesium Desorption	
	Modified Tank 10H (g)*	CST (g)**	Modified Tank 10H (mL)*	CST (g)**
Surface (HTF-10-17-30/-31)	85.728	1.4010	5.6	1.366
Variable Depth (HTF-10-17-32/-33)	61.509	1.0032	4.0	0.942

* modified Tank 10H sample densities: Surface – 1.225 g/mL, Variable Depth – 1.230 g/mL; bulk of supernate removed following cesium loading targeting final solution volumes indicated

** standard state reference masses provided can be corrected to dry CST mass by multiplying by 0.8186; small portion of CST removed for analysis following cesium loading

2.9 ZAM Isotherm Model Calculations

The ZAM Isotherm Model code is purchased commercial software developed at Texas A&M University by Rayford G. Anthony and Zhixin Zheng 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 provided by Zheng et al. [7].

Two types of ZAM Isotherm Model analyses were employed during this effort:

- Specific numerical batch contact calculations were performed to make direct comparisons between measured loadings and ZAM predicted values; and
- Series of runs were conducted by varying the CsCl concentration (while maintaining charge balance) to map out a specific isotherm.

ZAM only views the CST resin in its powdered form; therefore, in order to make consistent ZAM runs a fixed amount of engineered-form resin must be converted into its powdered form (i.e., to maintain the actual amount of exchange sites present within a batch contact). Once the resin is put into its equivalent powdered-form dry mass basis, ZAM runs are made. Upon completion of the ZAM batch contact runs the resulting ZAM loadings and K_d values are then converted back to an engineered-form basis. These conversions required a “dilution factor” (DF) to convert from powdered-form to engineered-form. For all of the results presented in this report a DF = 0.68 was employed. Also, all ZAM runs were made using version-4 since SrOH was not being considered here and version-4 converges better than the later version-5. Strontium sorption on CST is not expected to impact cesium uptake significantly in this waste supernate, due to the strontium concentration in the waste and the selectivity of CST for strontium. The ZAM model was developed based on batch contact data in the 25-44 °C range [2], but was successfully utilized in this work to predict cesium loadings up to 80 °C and calculations were also conducted at 90 °C. The ZAM Model is classified as a Quality Assurance Level D software package.

Charge balanced solutions are required for ZAM analyses. Therefore, adjustments were made to selected species concentrations to create charge balanced solutions. Nitrite and chloride subtractions and additions were utilized for charge adjustment. Anion effects on cesium loading were evaluated previously [8], and these evaluations impacted the chemical adjustments utilized for charge balance. The total cesium concentrations used to calculate cesium loadings for the as-received and chemically modified Tank 10H samples in Section 3.2 were calculated values based on the initial measured cesium concentrations for the original Tank 10H samples and the dilution factors associated with chemical modifications.

ZAM input and output files for a subset of the batch contact cases considered are provided in Appendix A and Beta Values are provided in Appendix B.

3.0 Results and Discussion

3.1 CST Loading Batch Contact Tests with SRS Average Simulant

Cesium loading batch contact tests were conducted in the SRNL shielded cells facility using pretreated CST media and SRS Average Simulant spiked to various total cesium concentrations. Confirmation of cesium loading equilibrium was achieved by collecting sub-samples from individual batch contact samples at various times across a 16-day period. Evaluation of the cesium loading kinetics was necessary to confirm the timescale required to achieve equilibrium loading under the test conditions, especially considering that a different agitation method and CST media type were being utilized relative to past testing. Cesium loading

kinetics results are provided in Figure 3-1 and Table 3-1, where it is apparent that cesium sorption to CST media is essentially complete within 4 contact days with continuous agitation. Equilibrium cesium loading levels (mmol total Cs/g dry CST) and distribution coefficients ($K_d = [(C_i/C_f)-1][V/M \cdot F]$; where C_i and C_f correspond to initial and final cesium concentrations, V = liquid volume, M = CST reference state mass, and F is the F-factor mass correction for CST water content) were calculated based on analytical results and sample masses for simulant samples spiked to the four total cesium levels provided in Table 2-1. Cesium equilibrium loading levels are provided in Table 3-1 and Figure 3-2 after 13 days of contact for the four cesium spike levels evaluated. Cesium loading levels on CST exhibited a linear relationship ($R^2 = 99.9\%$) with respect to the final cesium concentration when plotted on a log-log scale.

Table 3-1. Analytical Results for Cesium Loading Batch Contact Testing with CST and SRS Average Simulant.

Simulant ID (Contact Days)	Initial Total Cs ⁺ (M)	Initial Cs-137 (dpm/mL)	Final Cs-137 (dpm/mL)	K_d^*	% Cs ⁺ Removal	Measured Cs ⁺ Loading (mmol/g)*
A (13)	3.09E-06	2.13E+06	1.42E+05	1609	93.3	3.31E-04
B (13)	1.35E-04	2.12E+06	1.38E+05	1701	93.5	1.49E-02
C (13)	9.91E-04	2.12E+06	1.28E+05	1812	94.0	1.08E-01
D (4)	5.13E-06	2.41E+06	1.85E+05	1391	92.3	5.47E-04
D (5)			1.65E+05	1609	93.2	5.65E-04
D (9)			1.79E+05	1432	92.6	5.45E-04
D (13)			1.72E+05	1545	92.9	5.61E-04
D (16)			2.08E+05	1273	91.4	5.50E-04

* dry CST mass basis

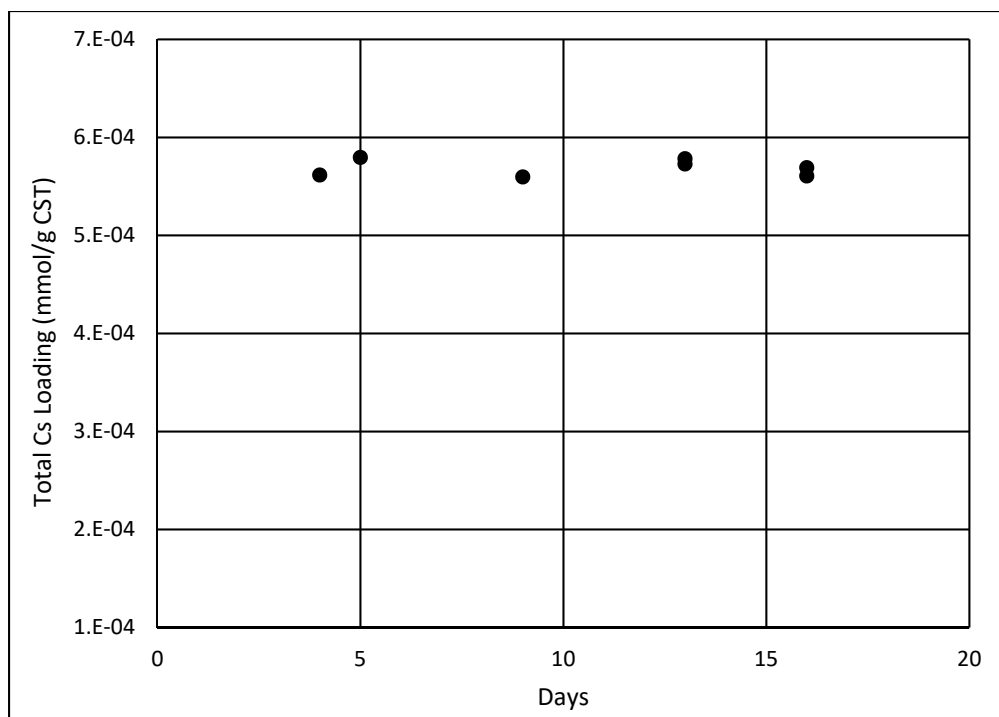


Figure 3-1. Cesium Loading Versus Time from SRS Average Simulant on CST at 23 °C Using Simulant Composition D.

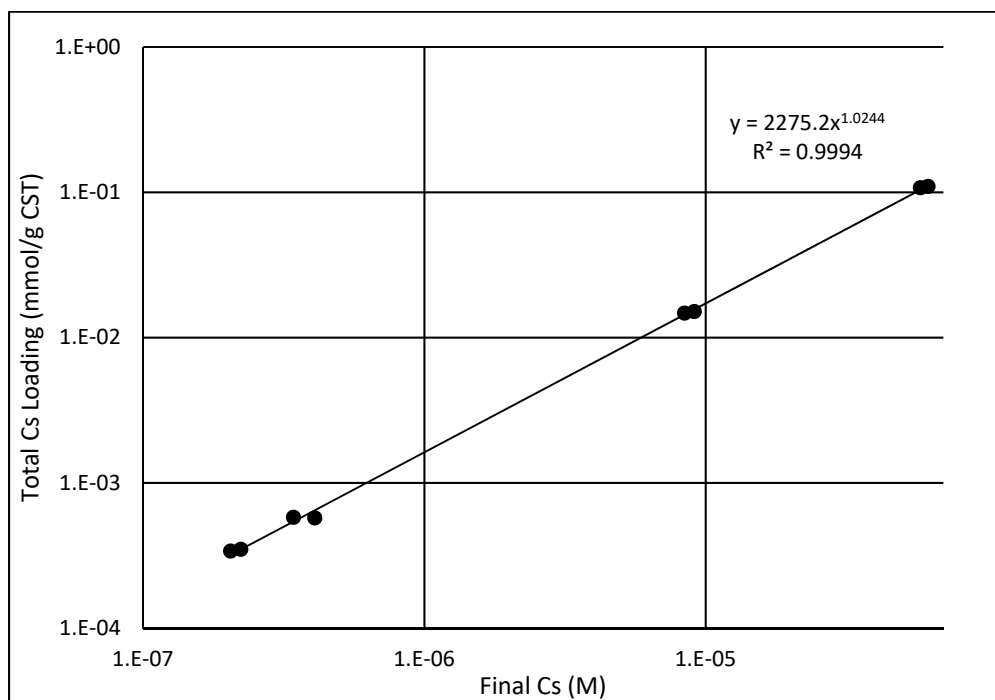


Figure 3-2. Cesium Equilibrium Loading Isotherm in SRS Average Simulant on CST at 23 °C (13-day contact).

CST loading results for the Average SRS simulant are compared to ZAM model predictions and previously reported results [9] in Figure 3-3. The current loading levels are lower than the earlier results and are consistent with a CST binder dilution factor of 0.68. Three of the four data replicate pairs are very near the predicted isotherm. At the highest cesium concentration tested for both the Beasley results and the current results, the experimental data is above the isotherm prediction. In the cesium concentration range of interest for most SRS applications this difference has little impact on performance. In previous CST performance modeling efforts [5], a dilution factor of 0.68 was selected as the best estimate value for the IE-911 engineered-form of CST when evaluating all available performance data. The previous results reported by Beasley, et. al. [9] were more consistent with the powdered form of CST, although IE-911 was utilized for testing. Regardless, based on the results it appears that pretreated R9120-B CST has remarkably similar performance to IE-911.

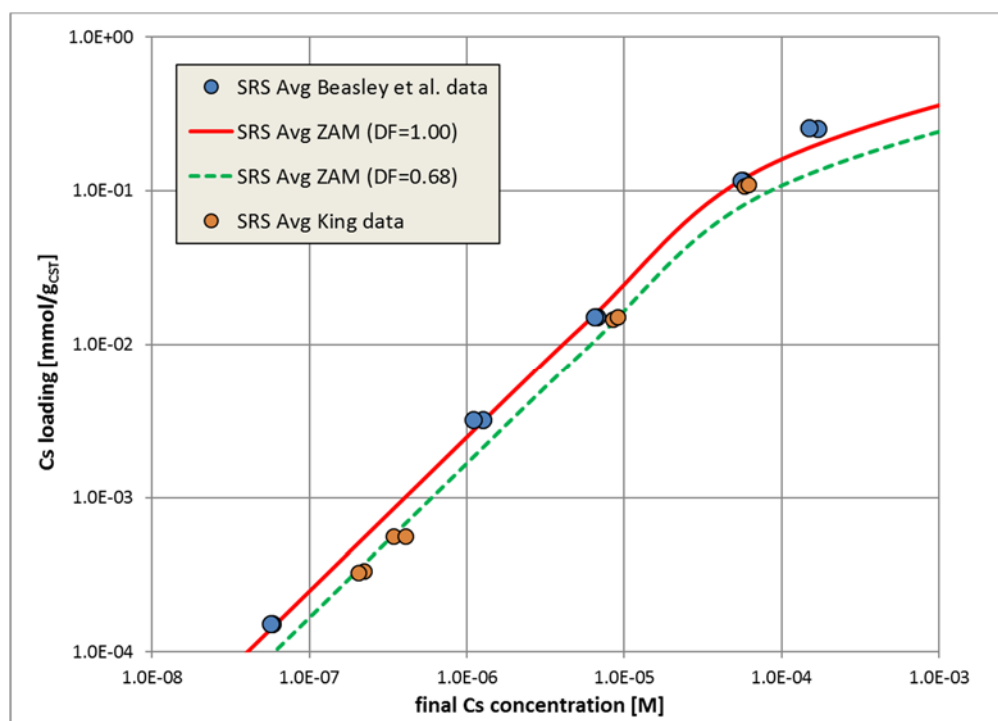


Figure 3-3. Comparison of Observed and Predicted (ZAM Model) Cesium Equilibrium Loading Isotherm with SRS Average Simulant and CST at 23 °C.

3.2 CST Batch Contact Loading Tests with As-Received and Chemically Modified Tank 10H Samples

Analytical results for the as-received and chemically-modified Tank 10H samples are provided in Table 3-2. Results are generally similar to the expected concentrations. The target sodium concentrations for modified solutions 1, 2, and 4 were 4, 5, and 3.8 M Na^+ , respectively. The target potassium concentrations for modified solutions 3, 4, and 5 were 0.05, 0.2, and 0.7 M K^+ , respectively. Both sodium and potassium hydroxide addition were utilized to prepare Modification #3 targeting a total cation ($\text{Na}^+ + \text{K}^+$) concentration of 4.0 M. Based on free hydroxide analysis results, it appears that the Tank 10H Surface sample used for testing contained a significantly lower hydroxide concentration than was reported by Reboul [2] for the initial sample. Reboul reported 0.93 M OH^- for the Surface sample. However, analysis of the chemically modified samples (#1-5) indicate that the hydroxide concentration in the “as-received” Surface sample used for this testing is ~ 0.2 M (similar to the reported hydroxide for the Variable Depth sample). It is possible that the hydroxide concentration of the sample decreased during storage in the shielded cells relative to the initial concentration due to sorption of carbon dioxide from the atmosphere.

The free hydroxide concentrations for the as-received and chemically modified Tank 10H samples ranged from ~0.2-2.3 M, depending primarily upon the amount of NaOH or KOH reagent added. Compositional input values utilized for ZAM modeling (discussed below) based on the chemical analysis, reagent additions, and dilution effects are provided in Table 3-3.

Based on the gamma scan analysis results, the total Cs^+ analysis reported by Reboul [2], and the dilution factors associated with sample modifications, the cesium distribution coefficients, % removal, and loading values were calculated for each test sample. Results are provided in Tables 3-4 to 3-5 and Figures 3-4 to 3-5 for the Surface and Variable Depth samples. Trends in the data are generally as expected. The highest distribution coefficients and cesium loading values were observed for the as-received Tank 10H samples. Addition of either sodium or potassium hydroxide reagents resulted in decreased cesium loading on CST and lower Cs^+ distribution coefficients (K_d). As expected based on the relative selectivity of CST for Group 1 cations, the impact of K^+ on cesium removal is greater on a molar basis than the impact of Na^+ . However, increasing the potassium concentration from 0.2 to 0.7 M does not lead to further decreases in cesium loading or K_d .

As shown in Tables 3-4 and 3-5, the cesium loading values for the as-received and modified samples were similar (range: $1.6 \text{ E-}3$ to $1.8 \text{ E-}3$ mmol Cs/g CST) under the test conditions where cesium loading values are well below saturation, while the K_d values were quite different (range: 1450 to 3300 mL/g). The lowest K_d values were observed for the high potassium additions (Modification #5). Under cesium saturation conditions such as would be experienced during column operations, a decrease in cesium loading on the column of approximately 50% would be expected with high potassium feed based on these results, with a corresponding decrease in the column heat loading. (Note: It was not possible to measure the total cesium loading under saturation conditions experimentally, given the limited volume of Tank 10H supernate available.)

Cesium loading isotherms and individual batch contact results were calculated using the ZAM isotherm model for each as-received and chemically modified Tank 10H sample using the input concentrations provided in Table 3-3. The initial input concentrations used for ZAM isotherm modeling were based on a combination of analytical results and calculated values, as indicated in the table. In general, the concentrations of most species including Na^+ and K^+ ions were calculated values based on the analysis reported by Reboul for the as-received samples [3] with adjustment based on reagents and volumes added. Calculated hydroxide values utilized for the Surface samples were based on the current analysis of the modified samples, taking reagent and volume additions into account. Calculated hydroxide values utilized for the VD samples were based on the previous analysis of the as-received sample, taking reagent and volume additions into account. To produce charge-balanced compositions for the Surface samples, it was necessary to reduce the nitrite ion concentrations by ~0.15 M relative to the analytical results. To produce charge-balanced compositions for the VD samples, it was necessary to add chloride ion at low levels (~0.03 M) to the composition. Based on previous analyses, these modifications are expected to have minor impacts on cesium loading on CST. Such compositional adjustments to the liquid phase have been routinely applied during previous modeling efforts with the ZAM model. Reduction of the nitrite ion concentrations for the Surface test samples was the most significant compositional adjustment. Nitrite ion has been shown in previous analyses to have minimal impacts on cesium loadings on CST [8].

The model predictions are provided in Tables 3-4 and 3-5 and the isotherm results are plotted along with the experimental data in Figures 3-6 through 3-9. Model predictions were generally consistent with experimental results as shown in the tables and figures. Low percent differences (calculated minus measured) were observed for total CST cesium loading (-0.1 to 0.8%), K_d (-2 to 21%), and final liquid Cs^+ concentration (-17 to 2%). As was observed for the SRS average simulant results, the ZAM isotherm model is a good predictive tool for cesium sorption on this CST media if a binder dilution factor of 0.68 is utilized.

Table 3-2. Analytical Results for the As-Received and Chemically Modified Tank 10H Samples

<u>Surface</u>	<u>Molarity</u>					
Modification	As-Received*	#1	#2	#3	#4	#5
Na ⁺	3.59	3.84	4.97	3.44**	3.61	3.25
K ⁺	<0.011	<0.011	<0.011	0.048	0.17	0.61
AlO ₂ ⁻	0.061	0.064	0.058	0.063**	0.060	0.059
Free OH ⁻	0.93***	0.66	1.87	0.22	0.60	0.74
NO ₃ ⁻	1.21	1.13	1.09	1.24	1.28	1.19
NO ₂ ⁻	0.15	0.14	0.14	0.15	0.14	0.14
SO ₄ ²⁻	0.48	0.46	0.44	0.48	0.46	0.45
CO ₃ ²⁻	0.58****	0.56	0.54	0.59	0.57	0.55
Total Cs ⁺	1.53E-05	---	---	---	---	---
Density (g/mL)	1.16	1.191	1.225	1.181	1.196	1.202
<u>Variable Depth</u>	<u>Molarity</u>					
Modification	As-Received*	#1	#2	#3	#4	#5
Na ⁺	3.22	3.69	4.60	2.98	3.69	2.81
K ⁺	0.0033	<0.011	<0.011	0.047	0.18	0.59
AlO ₂ ⁻	0.063	0.058	0.054	0.061	0.061	0.058
Free OH ⁻	0.18	1.01	2.20	0.20	1.01	0.71
NO ₃ ⁻	1.04	1.11	1.09	1.13	1.14	1.09
NO ₂ ⁻	0.13	0.12	0.11	0.13	0.12	0.12
SO ₄ ²⁻	0.36	0.36	0.33	0.38	0.37	0.35
CO ₃ ²⁻	0.51	0.49	0.47	0.51	0.49	0.48
Total Cs ⁺	1.56E-05	---	---	---	---	---
Density (g/mL)	1.17	1.193	1.230	1.170	1.197	1.177

* as reported by Reboul [3] unless otherwise indicated

** not based on replicate analysis due to individual outlier

*** based on current analysis, previous hydroxide result by Reboul [3] not believed to be representative of current unmodified sample

**** data not previously reported

Table 3-3. Ion Balanced Tank 10H Sample Compositions used for ZAM Input.

Surface	Molarity					
Modification	As-Received*	#1	#2	#3	#4	#5
Na ⁺	3.59	4.00	5.00	3.58	3.80	3.38
K ⁺	3.3E-03**	3.2E-03**	3.0E-03**	0.048	0.201	0.696
Al(OH) ₄ ⁻	0.061	0.059	0.055	0.061	0.059	0.057
Free OH ⁻ ***	0.202	0.705	1.921	0.246	0.725	0.883
NO ₃ ⁻	1.210	1.178	1.100	1.205	1.168	1.138
NO ₂ ⁻	5.4E-04	5.2E-04	4.9E-04	5.3E-04	5.2E-04	5.0E-04
SO ₄ ²⁻	0.480	0.467	0.436	0.478	0.463	0.452
CO ₃ ²⁻ ****	0.580	0.565	0.527	0.578	0.560	0.546
Total Cs ⁺	1.53E-05	1.49E-05	1.39E-05	1.53E-05	1.48E-05	1.44E-05
Variable Depth	Molarity					
Modification	As-Received	#1	#2	#3	#4	#5
Na ⁺	3.22	4.00	5.00	3.21	3.80	3.03
K ⁺	3.32E-03	3.16E-03	2.95E-03	0.055	0.201	0.694
Al(OH) ₄ ⁻	0.063	0.060	0.056	0.063	0.060	0.059
Free OH ⁻	0.18	1.11	2.31	0.24	1.13	0.86
NO ₃ ⁻	1.040	0.989	0.923	1.035	0.981	0.978
NO ₂ ⁻	0.128	0.122	0.114	0.127	0.121	0.120
SO ₄ ²⁻	0.38	0.36	0.34	0.38	0.36	0.36
CO ₃ ²⁻	0.506	0.481	0.449	0.504	0.477	0.476
Cl ⁻	3.42E-02	3.26E-02	3.04E-02	3.41E-02	3.23E-02	3.22E-02
Total Cs ⁺	1.56E-05	1.48E-05	1.39E-05	1.55E-05	1.47E-05	1.47E-05

* based on Reboul results [2] unless otherwise indicated

** based on potassium concentration measured for VD sample reported by Reboul [2]; analytical result for Surface sample was below detection

*** based on hydroxide and carbonate concentrations measured for VD sample reported by Reboul [2] and analytical results for modified Surface samples

**** other species concentrations calculated based on reagents added and Reboul results [2] accounting for dilution with minor adjustments for ion charge balance; Cl⁻ added for ion balance with VD sample

Table 3-4. Cesium Loading Batch Contact Results (Cs⁺ removal) for Individual As-Received and Chemically Modified Tank 10H Surface Samples with CST.

Tank 10H Surface Sample	Measured			ZAM*			% Difference (Calculated - Measured)		
	Cs ⁺ K _d **	Cs ⁺ mmol/g CST**	Final Cs ⁺ (M)	Cs ⁺ K _d **	Cs ⁺ mmol/g CST*	Final Cs ⁺ (M)	Cs ⁺ K _d *	Cs ⁺ mmol/ g CST*	Final Cs ⁺ (M)
As-received	3263	1.80E-03	5.53E-07	3389	1.81E-03	5.33E-07	4	0.1	-4
Replicate As-received	3186	1.80E-03	5.66E-07	3389	1.81E-03	5.33E-07	6	0.2	-6
Modification #1	2627	1.74E-03	6.62E-07	3115	1.75E-03	5.62E-07	19	0.7	-15
Replicate Modification #1	2567	1.74E-03	6.77E-07	3115	1.75E-03	5.62E-07	21	0.8	-17
Modification #2	2254	1.60E-03	7.12E-07	2621	1.62E-03	6.16E-07	16	0.7	-13
Replicate Modification #2	2265	1.58E-03	6.97E-07	2621	1.59E-03	6.06E-07	16	0.7	-13
Modification #3	2310	1.77E-03	7.67E-07	2445	1.78E-03	7.26E-07	6	0.3	-5
Replicate Modification #3	2160	1.77E-03	8.19E-07	2445	1.78E-03	7.29E-07	13	0.6	-11
Modification #4	1453	1.66E-03	1.14E-06	1592	1.67E-03	1.05E-06	10	0.7	-8
Replicate Modification #4	1535	1.68E-03	1.09E-06	1592	1.68E-03	1.06E-06	4	0.3	-3
Modification #5	1490	1.62E-03	1.09E-06	1453	1.62E-03	1.12E-06	-2	-0.1	2
Replicate Modification #5	1447	1.62E-03	1.12E-06	1453	1.62E-03	1.12E-06	0	0.0	0

* ZAM model predictions assuming a CST binder dilution factor of 0.68

** dry CST mass basis; mmol/g based on total Cs⁺ measured by Reboul [2] corrected for minor dilutions from reagent additions

Table 3-5. Cesium Loading Batch Contact Results (Cs⁺ removal) for Individual As-Received and Chemically Modified Tank 10H Variable Depth Samples with CST.

Tank 10H Variable Depth Sample	Measured			ZAM*			% Difference (Calculated - Measured)		
	Cs ⁺ K _d **	Cs ⁺ mmol/g CST**	Final Cs ⁺ (M)	Cs ⁺ K _d **	Cs ⁺ mmol/g CST*	Final Cs ⁺ (M)	Cs ⁺ K _d *	Cs ⁺ mmol/ g CST*	Final Cs ⁺ (M)
As-received	3677	1.84E-03	5.00E-07	3843	1.84E-03	4.79E-07	5	0	-4
Replicate As-received	3863	1.85E-03	4.79E-07	3843	1.85E-03	4.81E-07	-1	0	0
Modification #1	2952	1.75E-03	5.92E-07	3216	1.76E-03	5.46E-07	9	0	-8
Replicate Modification #1	2894	1.74E-03	6.02E-07	3217	1.75E-03	5.44E-07	11	0	-10
Modification #2	2411	1.62E-03	6.72E-07	2698	1.63E-03	6.03E-07	12	1	-10
Replicate Modification #2	2509	1.61E-03	6.41E-07	2698	1.62E-03	5.99E-07	8	0	-7
Modification #3	2549	1.80E-03	7.07E-07	2603	1.80E-03	6.93E-07	2	0	-2
Replicate Modification #3	2662	1.83E-03	6.87E-07	2602	1.83E-03	7.03E-07	-2	0	2
Modification #4	1601	1.66E-03	1.04E-06	1631	1.66E-03	1.02E-06	2	0	-2
Replicate Modification #4	1581	1.66E-03	1.05E-06	1631	1.66E-03	1.02E-06	3	0	-3
Modification #5	1822	1.65E-03	9.07E-07	1629	1.64E-03	1.01E-06	-11	-1	12
Replicate Modification #5	1775	1.68E-03	9.45E-07	1629	1.67E-03	1.02E-06	-9	-1	9

* ZAM model predictions assuming a CST binder dilution factor of 0.68

** dry CST mass basis; mmol/g based on total Cs⁺ measured by Reboul [2] corrected for minor dilutions from reagent additions

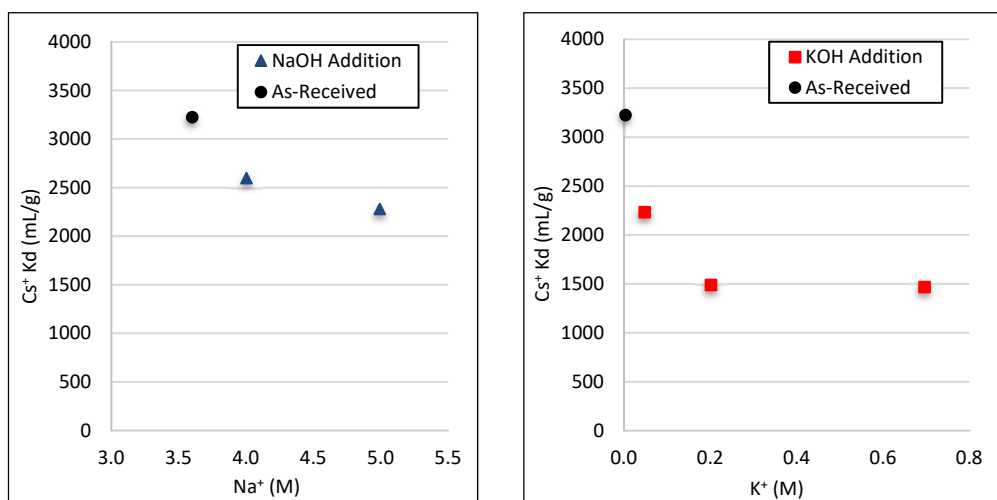


Figure 3-4. Trends in $Cs^+ K_d$ values versus the Sodium and Potassium Molarities for the As-received and Modified Tank 10H Surface Samples.

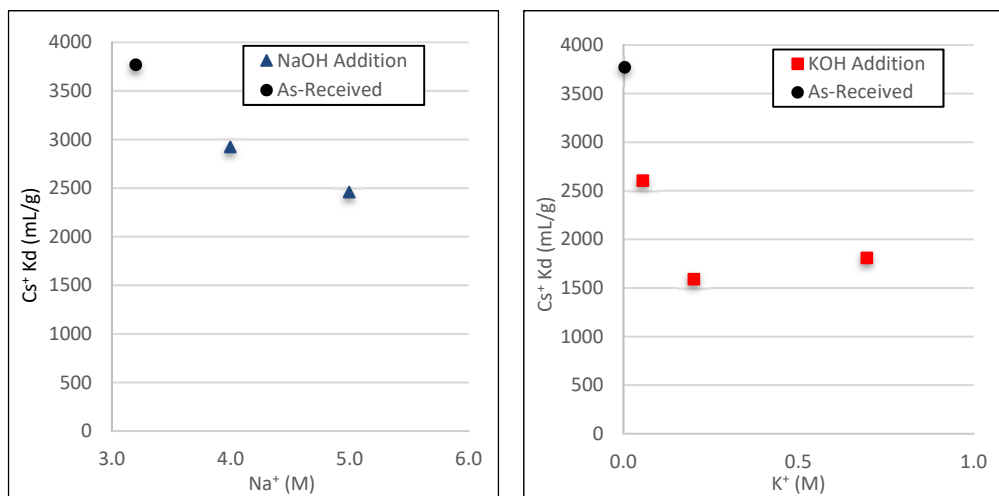


Figure 3-5. Trends in $Cs^+ K_d$ values versus the Sodium and Potassium Molarities for the As-received and Modified Tank 10H Variable Depth Samples.

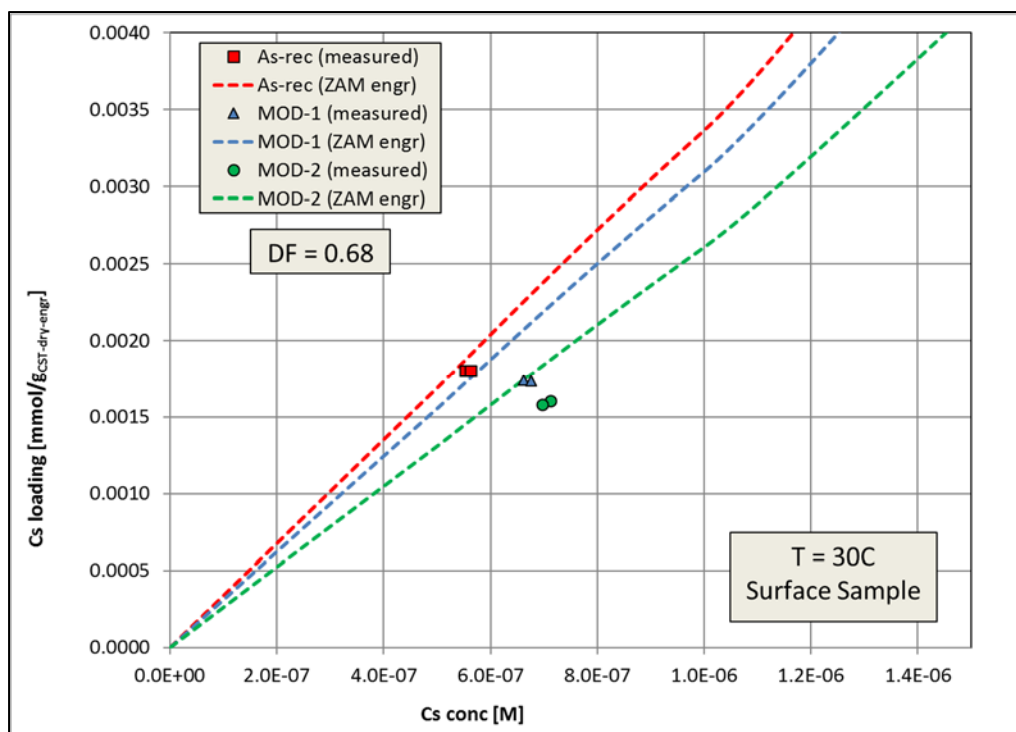


Figure 3-6. Comparison of ZAM Cs⁺ Loading Isotherms for CST at 30 °C Versus the Measured Cesium Loading Values for the Tank 10H Surface As-Received and Modification #1 and #2 Samples (Na⁺ impacts).

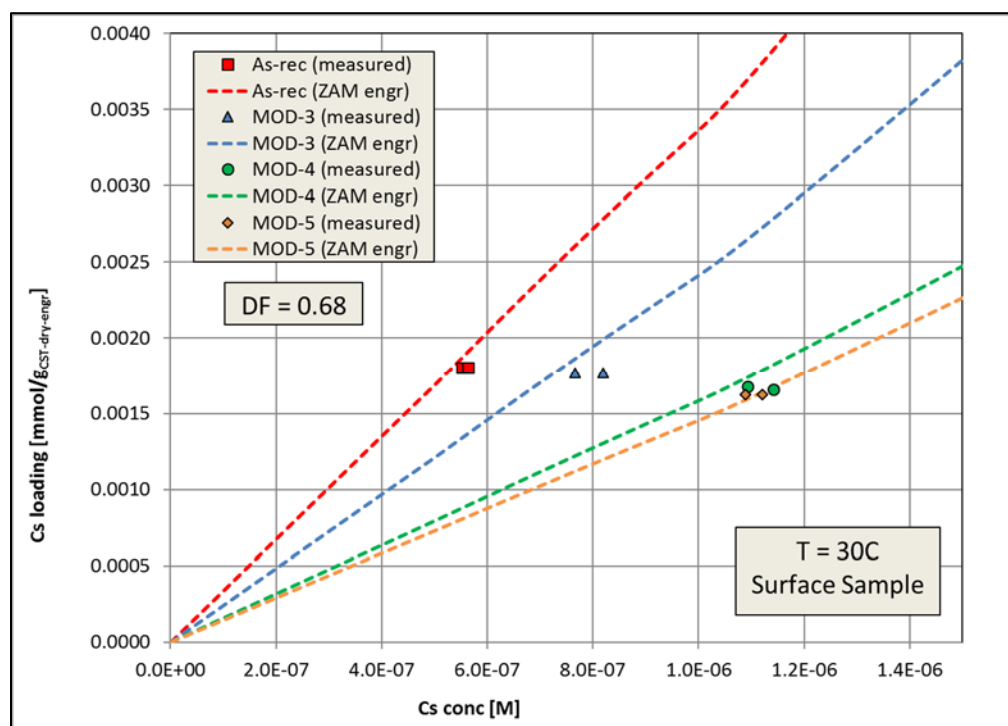


Figure 3-7. Comparison of ZAM Cs⁺ Loading Isotherms for CST at 30 °C Versus the Measured Cesium Loading Values for the Tank 10H Surface As-Received and Modification #3, #4, and #5 Samples (K⁺ impacts).

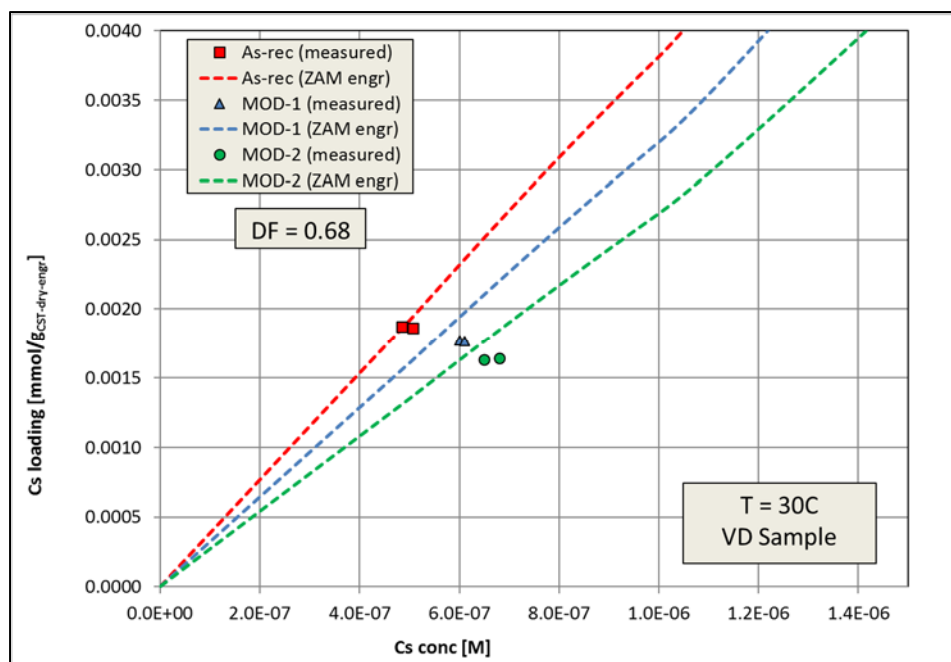


Figure 3-8. Comparison of ZAM Cs⁺ Loading Isotherms for CST at 30 °C Versus the Measured Cesium Loading Values for the Tank 10H Variable Depth As-Received and Modification #1 and #2 Samples (Na⁺ impacts).

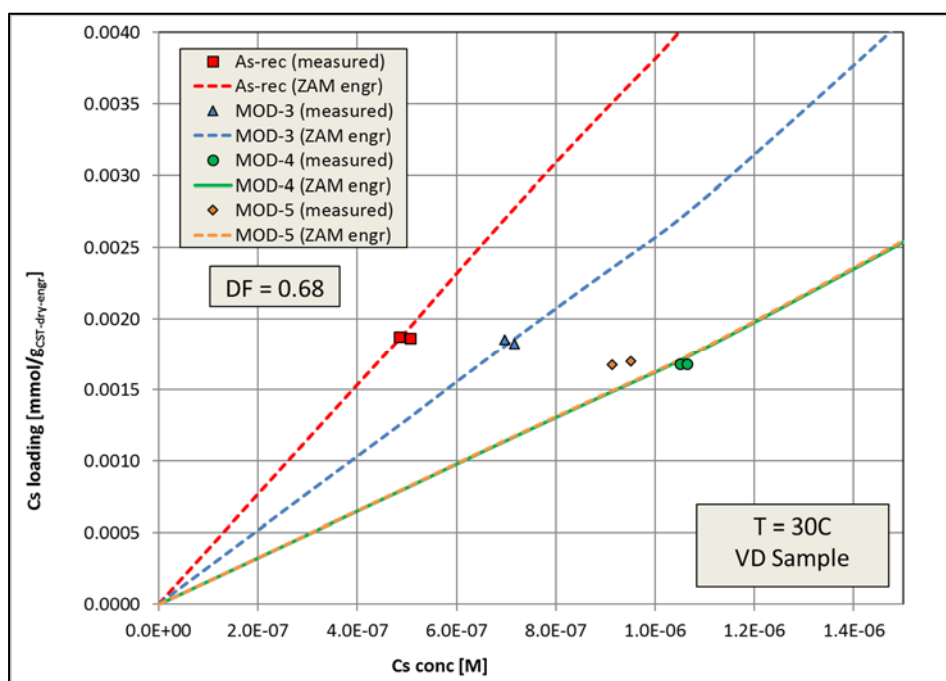


Figure 3-9. Comparison of ZAM Cs⁺ Loading Isotherms for CST at 30 °C Versus the Measured Cesium Loading Values for the Tank 10H Variable Depth As-Received and Modification #3, #4, and #5 Samples (K⁺ impacts).

3.3 CST Batch Contact Desorption Testing with Chemically Modified Tank 10H Samples

The remaining volumes of the Tank 10H Surface and Variable Depth samples were chemically modified and used for loading/desorption batch contact studies with CST. Chemical modification in this case included addition of a non-radioactive CsNO_3 spike solution to increase the total cesium concentrations for the samples to near 6 E-4 M (see Table 3-6). Cesium loading on CST to near saturation in Tank 10H supernate was accomplished at 30°C using a phase ratio (liquid mL:dry CST mass) near 61 (see Table 2-5). After sub-sampling both the liquid and solid phases, the bulk of the liquid phase was removed from each sample to reduce the phase ratio to near 5. The samples were placed back in the shaker bath and heated to near 90°C for 10 days until the water shaker bath malfunctioned and temperature control was lost. The sealed samples were stored under ambient conditions for several days prior to being placed in a second shaker oven and maintained at 80°C for 13 days with agitation. The CST solids and Tank 10H supernate were then sub-sampled for analysis. As a result, the desorption test CST samples which were previously loaded to cesium saturation at 30°C in Tank 10H supernate were subsequently (and inadvertently) exposed to two thermal cycles in which the samples were heated from 30°C to near 90°C , then allowed to cool to ambient temperature before being reheated to 80°C . The data from this unplanned temperature cycling event could potentially be used (to some degree) to evaluate the reversibility of cesium loading on CST.

Liquid phase cesium analysis data for the loading phase of this testing is provided in Table 3-6. Results indicate that the final total cesium loading values for the modified Tank 10H Surface and Variable Depth samples ranged from 1.3 E-5 to 1.5 E-5 M . The targeted final cesium concentrations for these samples after CST contact were near 1.4 E-5 M (equal to the initial Tank 10H total cesium concentration). Based on these results, it is believed that the cesium loading levels achieved for the CST solids contacted with the Tank 10H solutions are generally representative of the maximum cesium loading achievable with CST and Tank 10H waste supernate at 30°C . Total cesium levels on the solids were calculated from the liquid phase data (Table 3-6) and from digested solids analysis results (Table 3-7). Results indicate that the total cesium loading levels ranged from 3.2 E-2 to $3.7 \text{ E-2 mmol Cs}^+/\text{g CST}$ at 30°C .

Desorption sample cesium analysis results for the liquid and solid phases are provided in Tables 3-8 and 3-9, respectively. For the Surface sample, a liquid sub-sample was collected after 14 days of contact at 80°C to evaluate achievement of cesium desorption equilibrium. Two days later, at 16 contact days, the experiment was stopped and liquid and solid sub-samples were collected from each test sample (Surface and VD) while the samples were still at elevated temperature. The final total cesium concentrations in the liquid phase at the conclusion of 80°C desorption (16-day contacts) ranged from 4.2 E-5 to 4.9 E-5 M and the ratios of the final: initial total cesium concentrations ranged from 3.1 to 3.3. Surprisingly, the 14-day contact Surface sub-sample contained a significantly higher cesium concentration based on Cs-137 analysis than was observed for the 16-day sample. This result is inconsistent with plutonium analysis results on the Surface sub-samples and is believed to be the result of cesium contamination of the 14-day sample. Otherwise, these results would indicate additional sorption of cesium occurred between 14 and 16 days at 80°C . The 16-day data indicates that a 3-fold increase in the liquid phase cesium concentration can be expected when a CST column loaded to cesium saturation in Tank 10H supernate at 30°C is heated to 80°C . Because the phase ratio during desorption is low, these increases in the liquid phase cesium concentrations correspond to small decreases ($<1\%$) in the total cesium loading on the solid phase. Results indicate that the total cesium loading levels ranged from 3.3 E-2 to $3.7 \text{ E-2 mmol Cs}^+/\text{g CST}$ at 80°C , which is similar to the range observed following 30°C loading. Analysis results for the CST wash solutions used to remove residual supernate liquid from the solids prior to analysis (Table 3-10) indicate that the wash solutions contained 2 E5 to 6 E5 dpm of Cs-137 per sample, which is 5 orders of magnitude lower than the Cs-137 loading levels on the CST solids. This data confirms that washing the samples prior to analysis did not compromise the desorption test results.

ZAM modeling results for the desorption tests with the Tank 10H Surface and Variable Depth samples are provided in Figures 3-7 and 3-8, respectively. Measured cesium loading data for each CST sample are included in the figures as well for comparison. The absorption operating line (purple) in each figure is representative of the cesium loading kinetics versus time. Increasing cesium loading is observed going from right to left following the operating line up to the 30 °C loading isotherm. The green desorption operating line is representative of cesium desorption kinetics from the cesium-saturated CST solids when the temperature is increased to 80 °C. Small changes are observed in cesium loading going from left to right following the operating line until the 80 °C isotherm is reached. The small negative slope observed for the desorption operating line is indicative of low levels of cesium desorption under these conditions. The desorption operating line was also calculated for 90 °C desorption where it is apparent that little additional cesium desorbs from the CST under these conditions. It should be noted that utilization of ZAM at 90 °C is an extrapolation beyond current experimental datasets that was conducted because of the good agreement between experimental results and model calculations at 80 °C. The experimental data is consistent with model predictions for cesium sorption and desorption with both the Surface and Variable Depth samples. These results indicate that the ZAM isotherm model can be utilized to predict cesium sorption and desorption behavior on CST in Tank 10H solutions under various feasible waste process scenarios. In addition, the results indicate that cesium loading and temperature-induced desorption is a reversible process. The thermal stability of CST has been previously evaluated [11].

Table 3-6. Liquid Phase Cesium Analysis Results from 30 °C Loading Batch Contact Before Desorption Testing.

Sample	Initial Total Cs ⁺ (M)	Final Total Cs ⁺ (M)	% Cs ⁺ Removal	Initial Cs-137 (dpm/mL)	Final Cs-137 (dpm/mL)	% Cs ⁺ Removal	mmol Cs ⁺ /g* CST
Tank 10H Surface	6.23E-04	1.46E-05	97.7%	8.58E+07	2.07E+06	97.6%	3.71E-02
Tank 10H Variable Depth	5.60E-04	1.30E-05	97.7%	7.02E+07	1.67E+06	97.6%	3.33E-02

* dry CST mass basis

Table 3-7. Solid Phase Cesium Analysis Results from 30 °C Loading Batch Contact Before Desorption Testing.

Sample	Cs-137 (dpm/g)*	mmol Cs ⁺ /g* CST
Tank 10H Surface	4.45E+09	3.23E-02
Tank 10H Variable Depth	4.57E+09	3.65E-02

* dry CST mass basis

Table 3-8. Liquid Phase Cesium Analysis Results from 80 °C Batch Contact Desorption Testing.

Sample	Contact Days	Initial Total Cs ⁺ (M)	Final Total Cs ⁺ (M)	Ratio Final:Initial	Initial Cs-137 (dpm/mL)	Final Cs-137 (dpm/mL)	Ratio Final:Initial	mmol Cs ⁺ /g* CST
Tank 10H Surface	14	1.46E-05	1.03E-04*	7.1	2.07E+06	1.42E+07	6.9	3.67E-02
	16		4.83E-05**	3.3**		6.86E+06	3.3	3.69E-02
Tank 10H Variable Depth	16	1.30E-05	4.20E-05	3.2	1.67E+06	5.24E+06	3.1	3.32E-02

* dry CST mass basis

** calculated value based on Cs-137 data

Table 3-9. Solid Phase Cesium Analysis Results from 80 °C Batch Contact Desorption Testing.

Sample	Cs-137 (dpm/g)*	mmol Cs ⁺ /g* CST
Tank 10H Surface	3.27E+09	3.33E-02
Tank 10H Variable Depth	3.71E+09	3.31E-02

* dry CST mass basis

Table 3-10. CST Wash Sample Analysis Following Cesium Loading and Desorption.

Sample	Condition	Cs-137 (dpm/mL)	Sample (mL)	Total Cs-137 (dpm)
Tank 10H Surface	30 °C Loading	3.7E+04	7.9	2.9E+05
	80 °C Desorption	4.5E+04	11.3	5.2E+05
Tank 10H Variable Depth	30 °C Loading	4.1E+04	5.5	2.3E+05
	80 °C Desorption	1.9E+04	18.6	3.5E+05

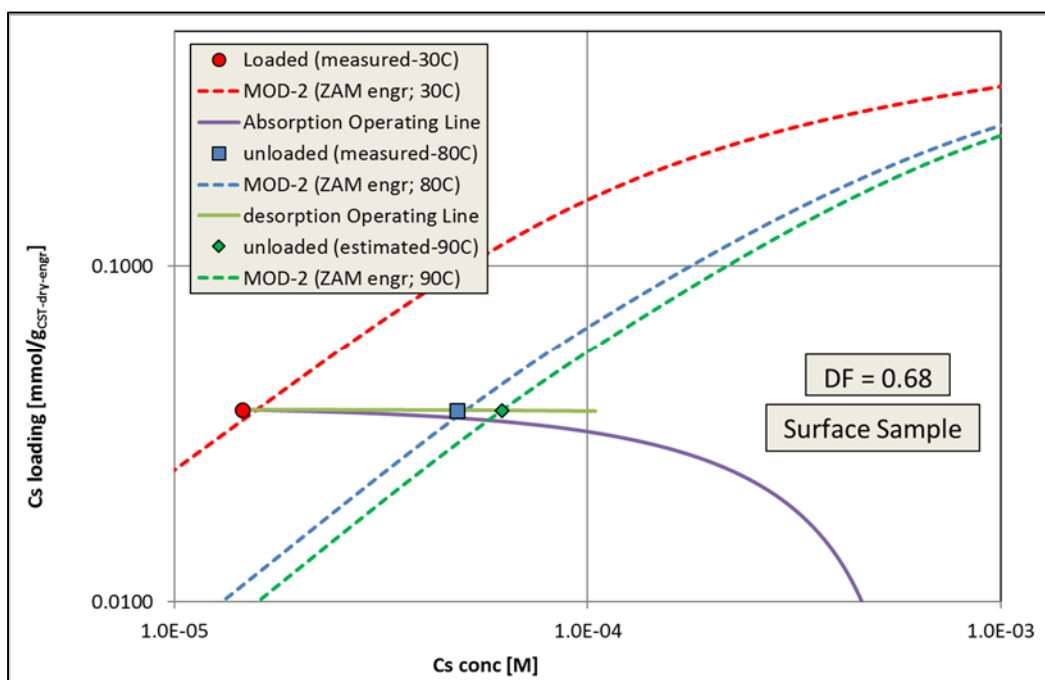


Figure 3-10. Comparison of Cesium 30 °C Equilibrium Sorption and 80 °C Desorption Data to ZAM Model Predictions for Tank 10H Surface Sample and CST.

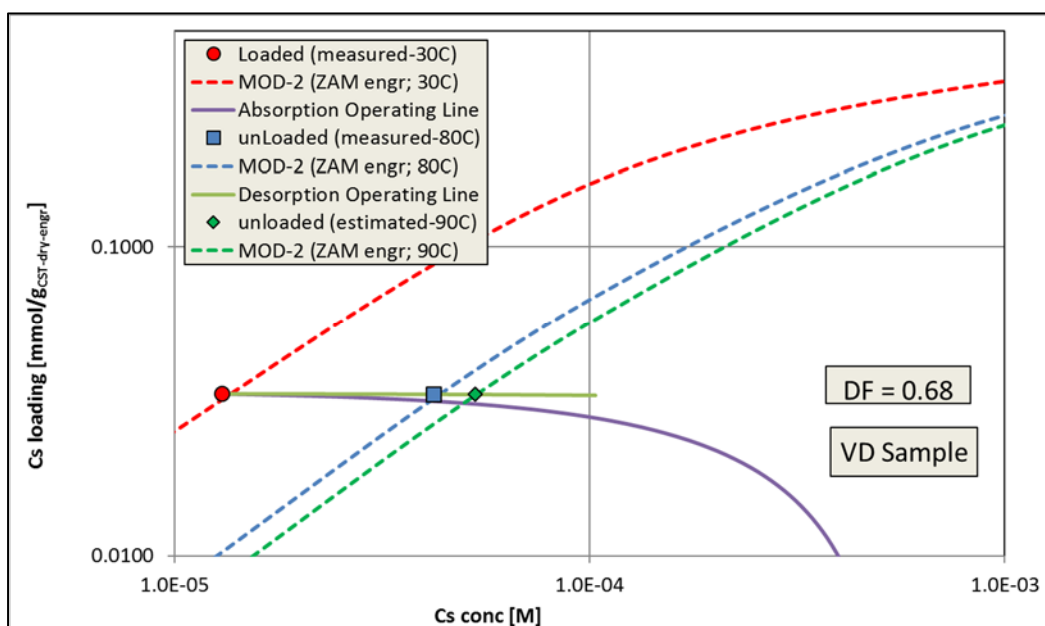


Figure 3-11. Comparison of Cesium 30 °C Equilibrium Sorption and 80 °C Desorption Data to ZAM Model Predictions for Tank 10H Variable Depth Sample and CST.

The CST sub-samples collected following 30 °C loading and 80 °C desorption tests were also analyzed for other non-radioactive elements and radionuclides. Currently available data is provided below and additional radionuclide analysis results for the digested CST samples will be reported separately.

Liquid phase plutonium analysis results are provided in Table 3-11 for the 30 °C loading tests where it is apparent that >94% of the soluble plutonium was absorbed to the CST. It should be emphasized that, in contrast to cesium, plutonium loading is not expected to represent the maximum value achievable with the Tank 10H supernate. Analysis of the liquid phase following 80 °C desorption studies (Table 3-12) indicated that plutonium did not desorb from the CST at elevated temperature. Rather, additional plutonium sorption may have occurred, as indicated by small decreases in the aqueous plutonium concentrations for the samples. Based on Pu-238 liquid phase analysis, the plutonium concentration decreased by about 50% at 80 °C relative to the concentration at 30 °C. As shown in Table 3-13, plutonium analysis of the dissolved CST media also indicated that additional plutonium sorption occurred at elevated temperature. Plutonium loading values for the Surface and Variable Depth samples following 80 °C contact increased by 11 and 15%, respectively, relative to the values observed following 30 °C contact. Collectively, these results indicate that plutonium does not desorb from the CST at elevated temperature, which may be indicative of a sorption mechanism other than ion exchange. The SRS simulant sample did not contain added plutonium and therefore served as a blank to evaluate plutonium contamination. Plutonium contamination was observed, but not at levels believed to impact the results (2-3 orders of magnitude below the Pu-238 levels observed for the Tank 10H samples). The observed plutonium loading values are quite high and indicate that the CST media in the TCCR columns will require treatment as TRU waste. It should be noted that Pu-238 levels on the solid phase for the Surface sample (69% of total) are lower than were calculated based on the liquid phase analysis (98% of total). For comparison, 86% Pu-238 removal was calculated based on the solid phase analysis for the VD sample versus 96% removal calculated from the liquid phase analysis. Pu concentrations exceeding 1000 nCi/g CST were observed, which is well in excess of the TRU waste classification limit of 100 nCi/g. Previous studies have shown plutonium sorption to CST [12].

Other radionuclides measured on the dissolved CST samples are provided in Table 3-14. In contrast to cesium, loading of these radionuclides on CST is not expected to represent saturated or maximum values. Neptunium and americium were not observed at levels above instrument detection for any samples. Uranium was observed, but as was the case for plutonium, there was no indication of desorption at elevated temperature.

Elemental analysis results for the CST samples following media digestion in acid are also provided in Table 3-15. Elements reported are those known to be constituents of the CST media. These constituents are known to leach from CST media in alkaline solutions [1] and are believed under certain circumstances to lead to clumping and bridging of the CST beads in a column configuration [11].

Table 3-11. Liquid Phase Plutonium Analysis Results from 30 °C Loading Batch Contact Testing.

Sample	Initial Pu-238 (dpm/mL)	Final Pu-238 (dpm/mL)	% Pu-238 Removal	Initial Pu-239/-240 (dpm/mL)	Final Pu-239/-240 (dpm/mL)	% Pu-239/-240 Removal
Tank 10H Surface	9.77E+04	1.93E+03	98.0%	1.24E+03	3.64E+01	97.0%
Tank 10H Variable Depth	5.22E+04	1.71E+03	96.1%	6.29E+02	3.11E+01	93.9%

Table 3-12. Liquid Phase Plutonium Analysis Results from 80 °C Desorption Testing.

Sample	Contact Days	Initial Pu-238 (dpm/mL)	Final Pu-238 (dpm/mL)	Pu-238 ratio final:initial	Initial Pu-239/-240 (dpm/mL)	Final Pu-239/-240 (dpm/mL)	Pu-239/-240 ratio final:initial
Tank 10H Surface	14	1.93E+03	9.79E+02	0.51	3.64E+01	1.25E+01	0.34
	16		9.93E+02	0.51		≤1.02E+01	≤0.28
Tank 10H Variable Depth	16	1.71E+03	6.94E+02	0.41	3.11E+01	9.00E+00	0.29

Table 3-13. CST Solid Phase Plutonium Analysis Results from 30 °C Loading and 80 °C Desorption Testing.

Sample	Test	Pu-238 (dpm/g)*	Pu-239/240 (dpm/g)*
Tank 10H Surface	30 °C Loading	3.35E+06	5.43E+04
	80 °C Desorption	3.71E+06	4.71E+04
Tank 10H Variable Depth	30 °C Loading	3.12E+06	4.24E+04
	80 °C Desorption	3.59E+06	5.04E+04
SRS Average Simulant Blank	30 °C Loading	4.80E+03	<4.78E02
	80 °C Desorption	3.63E+04	3.98E+03

* dry CST mass basis

Table 3-14. CST Additional Radionuclide Analysis Results from Desorption Studies.

Sample	Condition	dpm/g CST*		mg/g CST*			
		Np-237	Am-241	U-235	U-236	U-238	Sum U-235/238
Tank 10 Surface	Loading	<2.1E+05	<2.3E+05	3.1E-03	<2.9E-03	2.0E-02	0.023
	Desorption	<9.0E+04	<9.4E+04	3.2E-03	9.2E-04	2.0E-02	0.023
Tank 10 Variable Depth	Loading	<1.3E+05	<1.4E+05	2.61E-03	<1.7E-03	1.55E-02	0.018
	Desorption	<7.7E+04	<8.0E+04	2.87E-03	<9.2E-04	1.76E-02	0.020
Simulant Blank	Loading	<1.3E+05	<1.5E+05	<2.3E-03	<2.3E-03	<2.3E-03	---
	Desorption	<5.9E+04	<6.7E+04	<9.7E-04	<9.7E-04	5.0E-03	---

* standard state (hydrated) CST mass basis

Table 3-15. CST Elemental Analysis Results from Desorption Studies.

Sample	Condition	mg/g			
		Na	Si	Ti	Zr
Tank 10H Surface	30 °C Loading	115.0	240.0	141.0	93.0
	80 °C Desorption*	98.8	138.0	146.0	97.0
		69.5	120.0	152.0	100.0
Tank 10H Variable Depth	30 °C Loading	59.7	188.0	146.0	96.6
	80 °C Desorption*	58.4	133.0	215.0	141.0
		56.9	135.0	109.0	74.2
Simulant Blank	30 °C Loading	79.8	308.0	145.0	96.3
	80 °C Desorption	84.3	177.0	192.0	130.0
Average	All	77.8	179.9	155.8	103.5
%RSD		27.0%	36.2%	21.1%	20.8%

* replicate data

** standard state (hydrated) CST mass basis

4.0 Conclusions

Based on the test results and associated ZAM modeling the following conclusions can be made.

- SRS Average Simulant batch contact testing at 23 °C confirmed comparable performance for pretreated R9120-B CST relative to engineered IE-911 CST which was tested previously.
- Cesium removal performance at 30 °C with R9120-B CST and SRS Tank 10H as-received and chemically modified supernate was as expected with regard to Na⁺ and K⁺ competitor effects. Either NaOH or KOH reagent additions could be utilized to reduce cesium loading on CST. Potassium addition would likely significantly impact other cesium removal processes and could have other downstream impacts. If KOH additions are required, the impacts of that addition to the tank of interest as well as downstream impacts need to be evaluated by SRR.
- Loaded CST media was produced at 30 °C from Tank 10H supernates at total cesium loading levels near saturation and desorption studies were subsequently performed at 80 °C with a low liquid to solid phase ratio to mimic anticipated TCCR processing conditions during no-flow conditions. Conclusions from this study included:
 - A 3- to 7-fold increase in the liquid phase cesium concentration is observed under these conditions, but this corresponds to <1% desorption of the cesium from the media.
 - Sorption of plutonium and uranium to CST were also observed at 30 °C, but no desorption of these radionuclides was observed at elevated temperature.
 - Plutonium loading levels on the spent CST exceed TRU waste loading limits. It is recommended that SRR take this into consideration when selecting final disposal paths for the TCCR columns following removal from ISS.
- ZAM isotherm predictions were consistent with experimental data and lead to the following conclusions:
 - A dilution factor of 0.68 was needed for all data comparisons in this report with R9120-B CST. A variance about the mean in the dilution factor on the order of 3% was observed. Utilization of this dilution factor yields performance predictions in good agreement with all current experimental results.
 - Some historical and current tests at high cesium concentrations above levels relevant to TCCR indicate that the ZAM model may underpredict cesium loading.
 - In general, the ZAM model accurately predicts Na⁺/K⁺ competitor effects on cesium removal performance with CST.
 - Sorption/desorption evaluations across a broad temperature range (30-90 °C) provided an additional database to confirm that the cesium isotherm is reversible. Modeling predictions up to 90 °C indicate that <1% of the total cesium desorbs from the CST under low phase ratio conditions.
 - The ZAM isotherm model continues to be a useful tool to evaluate various ion exchange processing scenarios for engineered CST media.

5.0 Recommendations, Path Forward or Future Work

- Collection of higher temperature cesium loading data to confirm ZAM model predictions at temperatures exceeding 80 °C is recommended.
- Column or kinetics testing should also be considered to evaluate particle size effects on performance.
- VERSE operational modeling evaluating column performance under various processing scenarios and considering the impacts of particle size on loading kinetics is highly recommended. Although batch contact tests have confirmed that cesium equilibrium loading on current CST batches is similar to previous batches, additional evaluations (particle size analysis, column testing, and

VERSE modeling) are needed to understand the performance of current CST batches in a column configuration.

6.0 References

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3. S. H. Reboul, "Characterization of the March 2017 Tank 10 Surface Sample (Combination of HTF-10-17-30 and HTF-10-17-31) and Variable Depth Sample (Combination of HTF-10-17-32 and HTF-10-17-33)", SRNL-STI-2017-00392, Revision 0, July 2017.
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7.0 Appendices

Appendix A (ZAM Analyses)

The following are the ZAM input and output files for a subset of the batch contact cases considered. The replicate test cases are not being shown here. All ZAM runs made in the course of this effort have been saved and archived onto SRNL servers that can be retrieved at a later date, if requested.

7.1 Input: 30C – Surface Sample – As-Rec

```

1, 303.15
TCCR project: Temperature Effect @ 30C
7, 10
1160
  3, 6, 1, 5, 4, 40, 13
13, 9, 27, 15, 19, 2, 20, 28, 25 1
96.0107
3.590000      1.53104E-05      1.0E-14 0.0      0.003320      0.0      0.0
0.201900  1.210000  0.00053531  0.480000      0.580000      0      0.0 0.060900      0.0      0.0
0.01026, 0.05706
0
.9

```

7.2 Output: 30C – Surface Sample – As-Rec

```

Solution: TCCR project: Temperature Effect
*****INPUT*****

Density= .1160E+04 kg/m3

      Molecular Wt.      Valance      Molarity(mol/L)
Na+.....      22.9898      1.      .3590E+01
Cs+.....      132.9054      1.      .1531E-04
H+.....      1.0079      1.      .1000E-13
Rb+.....      85.4678      1.      .0000E+00
K+.....      39.0983      1.      .3320E-02
SrOH+...      105.0000      1.      .0000E+00
Sr++.....      87.6200      2.      .0000E+00
OH-.....      17.0073      -1.      .2019E+00
NO3-....      62.0049      -1.      .1210E+01
NO2-....      46.0000      -1.      .5353E-03
SO4--...      96.0636      -2.      .4800E+00
CO3--...      60.0092      -2.      .5800E+00
Cl-.....      35.4527      -1.      .0000E+00
PO4---...      94.9712      -3.      .0000E+00
Al(OH)4-      95.0000      -1.      .6090E-01
Other--...      96.0107      -2.      .0000E+00
F-.....      18.9984      -1.      .0000E+00

```

Liquid(L)= .1026E-01 Solid(g)= .5706E-01

Material: Na Form

*****OUTPUT*****

Ionic Strength= 5.795768290032583 mol/kg

	Q (mmol/gCST)	C (mmol/L)	Kd (ml/gCST)
Cs	.2657E-02	.5331E-03	.4984E+04
Rb	.0000E+00	.0000E+00	.0000E+00
Sr	.0000E+00	.0000E+00	.0000E+00
K	.3734E-01	.3112E+01	.1200E+02

7.3 Input: 30C – Surface Sample – MOD1

```

1, 303.15
TCCR project: Temperature Effect @ 30C
7, 10
1190
  3, 6, 1, 5, 4, 40, 13
13, 9, 27, 15, 19, 2, 20, 28, 25 1
96.0107
4.002352      1.49025E-05      1E-14      0      0.003232      0      0
0.704518 1.177763 0.00052105 0.467212 0.564548 0      0      0.059278      0      0
0.01014, 0.05650
0
.9

```

7.4 Output: 30C – Surface Sample – MOD1

```

Solution: TCCR project: Temperature Effect
*****INPUT*****

Density= .1190E+04 kg/m3

      Molecular Wt.   Valance   Molarity(mol/L)
Na+.....      22.9898      1.      .4002E+01
Cs+.....     132.9054      1.      .1490E-04
H+.....       1.0079      1.      .1000E-13
Rb+.....      85.4678      1.      .0000E+00
K+.....       39.0983      1.      .3232E-02
SrOH+...     105.0000      1.      .0000E+00
Sr++.....      87.6200      2.      .0000E+00
OH-.....      17.0073     -1.      .7045E+00
NO3-....      62.0049     -1.      .1178E+01
NO2-....      46.0000     -1.      .5211E-03
SO4--...      96.0636     -2.      .4672E+00
CO3--...      60.0092     -2.      .5645E+00
Cl-.....      35.4527     -1.      .0000E+00
PO4---...      94.9712     -3.      .0000E+00
Al(OH)4-      95.0000     -1.      .5928E-01
Other--...      96.0107     -2.      .0000E+00
F-.....      18.9984     -1.      .0000E+00

Liquid(L)= .1014E-01   Solid(g)= .5650E-01
Material: Na Form

*****OUTPUT*****

Ionic Strength=          6.095173696615734 mol/kg

      Q (mmol/gCST)   C (mmol/L)   Kd (ml/gCST)
Cs      .2574E-02     .5618E-03     .4581E+04
Rb      .0000E+00     .0000E+00     .0000E+00
Sr      .0000E+00     .0000E+00     .0000E+00
K       .3441E-01     .3040E+01     .1132E+02

```

7.5 Input: 30C – Surface Sample – MOD2

```

1, 303.15
TCCR project: Temperature Effect @ 30C
7, 10
1220
  3, 6, 1, 5, 4, 40, 13
13, 9, 27, 15, 19, 2, 20, 28, 25 1
96.0107
5.000109      1.39155E-05      1E-14  0      0.003018      0      0
1.920687  1.099761  0.00048654  0.436269  0.527158  0      0      0.055352      0      0
0.01005, 0.05628
0
.9

```

7.6 Output: 30C – Surface Sample – MOD2

```

Solution: TCCR project: Temperature Effect
*****INPUT*****

Density= .1220E+04 kg/m3

      Molecular Wt.      Valance      Molarity(mol/L)
Na+.....      22.9898      1.      .5000E+01
Cs+.....      132.9054      1.      .1392E-04
H+.....      1.0079      1.      .1000E-13
Rb+.....      85.4678      1.      .0000E+00
K+.....      39.0983      1.      .3018E-02
SrOH+...      105.0000      1.      .0000E+00
Sr++.....      87.6200      2.      .0000E+00
OH-.....      17.0073      -1.      .1921E+01
NO3-.....      62.0049      -1.      .1100E+01
NO2-.....      46.0000      -1.      .4865E-03
SO4--...      96.0636      -2.      .4363E+00
CO3--...      60.0092      -2.      .5272E+00
Cl-.....      35.4527      -1.      .0000E+00
PO4---..      94.9712      -3.      .0000E+00
Al(OH)4-      95.0000      -1.      .5535E-01
Other--..      96.0107      -2.      .0000E+00
F-.....      18.9984      -1.      .0000E+00

Liquid(L)= .1005E-01      Solid(g)= .5628E-01

Material: Na Form

*****OUTPUT*****

Ionic Strength=      7.093494834379384 mol/kg

      Q (mmol/gCST)      C (mmol/L)      Kd (ml/gCST)
Cs      .2375E-02      .6161E-03      .3855E+04
Rb      .0000E+00      .0000E+00      .0000E+00
Sr      .0000E+00      .0000E+00      .0000E+00
K      .2910E-01      .2855E+01      .1019E+02

```

7.7 Input: 30C – Surface Sample – MOD3

```

1, 303.15
TCCR project: Temperature Effect @ 30C
7, 10
1180
  3, 6, 1, 5, 4, 40, 13
13, 9, 27, 15, 19, 2, 20, 28, 25 1
96.0107
3.576333      1.52521E-05      1E-14      0      0.047760      0      0
0.245584  1.205393  0.00053327  0.478173  0.577792  0      0      0.060668      0      0
0.01007, 0.05600
0
.9

```

7.8 Output: 30C – Surface Sample – MOD3

```

Solution: TCCR project: Temperature Effect
*****INPUT*****

Density= .1180E+04 kg/m3

      Molecular Wt.   Valance   Molarity(mol/L)
Na+.....      22.9898      1.      .3576E+01
Cs+.....     132.9054      1.      .1525E-04
H+.....       1.0079      1.      .1000E-13
Rb+.....      85.4678      1.      .0000E+00
K+.....       39.0983      1.      .4776E-01
SrOH+...     105.0000      1.      .0000E+00
Sr++.....      87.6200      2.      .0000E+00
OH-.....      17.0073     -1.      .2456E+00
NO3-....      62.0049     -1.      .1205E+01
NO2-....      46.0000     -1.      .5333E-03
SO4--...      96.0636     -2.      .4782E+00
CO3--...      60.0092     -2.      .5778E+00
Cl-.....      35.4527     -1.      .0000E+00
PO4---...      94.9712     -3.      .0000E+00
Al(OH)4-      95.0000     -1.      .6067E-01
Other--...      96.0107     -2.      .0000E+00
F-.....      18.9984     -1.      .0000E+00

Liquid(L)= .1007E-01   Solid(g)= .5600E-01

Material: Na Form

*****OUTPUT*****

Ionic Strength=          5.705072638629713 mol/kg

      Q (mmol/gCST)   C (mmol/L)   Kd (ml/gCST)
Cs      .2612E-02     .7264E-03     .3596E+04
Rb      .0000E+00     .0000E+00     .0000E+00
Sr      .0000E+00     .0000E+00     .0000E+00
K       .3704E+00     .4570E+02     .8106E+01

```

7.9 Input: 30C – Surface Sample – MOD4

```

1, 303.15
TCCR project: Temperature Effect @ 30C
7, 10
1200
  3, 6, 1, 5, 4, 40, 13
13, 9, 27, 15, 19, 2, 20, 28, 25 1
96.0107
3.798941      1.47838E-05      1E-14      0      0.201228      0      0
0.725388  1.168385  0.00051690  0.463492  0.560052  0      0      0.058806      0      0
0.01014, 0.05667
0
.9

```

7.10 Output: 30C – Surface Sample – MOD4

```

Solution: TCCR project: Temperature Effect
*****INPUT*****

Density= .1200E+04 kg/m3

      Molecular Wt.   Valance   Molarity(mol/L)
Na+.....      22.9898      1.      .3799E+01
Cs+.....     132.9054      1.      .1478E-04
H+.....       1.0079      1.      .1000E-13
Rb+.....      85.4678      1.      .0000E+00
K+.....       39.0983      1.      .2012E+00
SrOH+...     105.0000      1.      .0000E+00
Sr++.....      87.6200      2.      .0000E+00
OH-.....      17.0073     -1.      .7254E+00
NO3-....      62.0049     -1.      .1168E+01
NO2-....      46.0000     -1.      .5169E-03
SO4--...      96.0636     -2.      .4635E+00
CO3--...      60.0092     -2.      .5601E+00
Cl-.....      35.4527     -1.      .0000E+00
PO4---...      94.9712     -3.      .0000E+00
Al(OH)4-      95.0000     -1.      .5881E-01
Other--...      96.0107     -2.      .0000E+00
F-.....      18.9984     -1.      .0000E+00

Liquid(L)= .1014E-01   Solid(g)= .5667E-01

Material: Na Form

*****OUTPUT*****

Ionic Strength=          6.022550332311608 mol/kg

      Q (mmol/gCST)   C (mmol/L)   Kd (ml/gCST)
Cs      .2457E-02     .1050E-02     .2341E+04
Rb      .0000E+00     .0000E+00     .0000E+00
Sr      .0000E+00     .0000E+00     .0000E+00
K       .7566E+00     .1970E+03     .3841E+01

```

7.11 Input: 30C – Surface Sample – MOD5

```

1, 303.15
TCCR project: Temperature Effect @ 30C
7, 10
1200
  3, 6, 1, 5, 4, 40, 13
13, 9, 27, 15, 19, 2, 20, 28, 25 1
96.0107
3.376983      1.44019E-05      1E-14  0      0.695954      0      0
0.882751  1.138203  0.00050355  0.451519  0.545585  0      0      0.057286      0      0
0.01021, 0.05694
0
.9

```

7.12 Output: 30C – Surface Sample – MOD5

```

Solution: TCCR project: Temperature Effect
*****INPUT*****

Density= .1200E+04 kg/m3

      Molecular Wt.   Valance   Molarity(mol/L)
Na+.....      22.9898      1.      .3377E+01
Cs+.....     132.9054      1.      .1440E-04
H+.....       1.0079      1.      .1000E-13
Rb+.....      85.4678      1.      .0000E+00
K+.....       39.0983      1.      .6960E+00
SrOH+...     105.0000      1.      .0000E+00
Sr++.....      87.6200      2.      .0000E+00
OH-.....      17.0073     -1.      .8828E+00
NO3-....      62.0049     -1.      .1138E+01
NO2-....      46.0000     -1.      .5036E-03
SO4--...      96.0636     -2.      .4515E+00
CO3--...      60.0092     -2.      .5456E+00
Cl-.....      35.4527     -1.      .0000E+00
PO4---...      94.9712     -3.      .0000E+00
Al(OH)4-      95.0000     -1.      .5729E-01
Other--...      96.0107     -2.      .0000E+00
F-.....      18.9984     -1.      .0000E+00

Liquid(L)= .1021E-01   Solid(g)= .5694E-01

Material: Na Form

*****OUTPUT*****

Ionic Strength=      6.110516372614335 mol/kg

      Q (mmol/gCST)   C (mmol/L)   Kd (ml/gCST)
Cs      .2383E-02     .1115E-02     .2137E+04
Rb      .0000E+00     .0000E+00     .0000E+00
Sr      .0000E+00     .0000E+00     .0000E+00
K       .1019E+01     .6903E+03     .1476E+01

```

7.13 Input: 30C – VD Sample – As-Rec

```

1, 303.15
TCCR project: Temperature Effect @ 30C
7, 10
1170
  3, 6, 1, 5, 4, 40, 13
13, 9, 27, 15, 19, 2, 20, 28, 25 1
96.0107
3.220000      1.56076E-05      1.0E-14 0.0      0.0033200      0.0      0.0
0.184000  1.040000  0.128000  0.381000  0.506000  0.034236  0.0      0.063100      0.0      0.0
0.01071, 0.05984
0
.9

```

7.14 Output: 30C – VD Sample – As-Rec

```

Solution: TCCR project: Temperature Effect
*****INPUT*****

Density= .1170E+04 kg/m3

      Molecular Wt.      Valance      Molarity(mol/L)
Na+.....      22.9898      1.      .3220E+01
Cs+.....      132.9054      1.      .1561E-04
H+.....      1.0079      1.      .1000E-13
Rb+.....      85.4678      1.      .0000E+00
K+.....      39.0983      1.      .3320E-02
SrOH+...      105.0000      1.      .0000E+00
Sr++.....      87.6200      2.      .0000E+00
OH-.....      17.0073      -1.      .1840E+00
NO3-....      62.0049      -1.      .1040E+01
NO2-....      46.0000      -1.      .1280E+00
SO4--...      96.0636      -2.      .3810E+00
CO3--...      60.0092      -2.      .5060E+00
Cl-.....      35.4527      -1.      .3424E-01
PO4---...      94.9712      -3.      .0000E+00
Al(OH)4-      95.0000      -1.      .6310E-01
Other--...      96.0107      -2.      .0000E+00
F-.....      18.9984      -1.      .0000E+00

Liquid(L)= .1071E-01      Solid(g)= .5984E-01

Material: Na Form

*****OUTPUT*****

Ionic Strength=      4.879166585320211 mol/kg

      Q (mmol/gCST)      C (mmol/L)      Kd (ml/gCST)
Cs      .2708E-02      .4790E-03      .5652E+04
Rb      .0000E+00      .0000E+00      .0000E+00
Sr      .0000E+00      .0000E+00      .0000E+00

```

7.15 Input: 30C – VD Sample – MOD1

```

1, 303.15
TCCR project: Temperature Effect @ 30C
7, 10
1190
  3, 6, 1, 5, 4, 40, 13
13, 9, 27, 15, 19, 2, 20, 28, 25 1
96.0107
3.995601172 1.48438E-05 1.0E-14 0.0 0.0031575 0.0 0.0
1.108187 0.989101 0.121736 0.362353 0.481236 0.032560 0.0 0.060012 0.0 0.0
0.01038, 0.05750
0
.9

```

7.16 Output: 30C – VD Sample – MOD1

```

Solution: TCCR project: Temperature Effect
*****INPUT*****

Density= .1190E+04 kg/m3

      Molecular Wt.  Valance  Molarity(mol/L)
Na+.....      22.9898      1.      .3996E+01
Cs+.....     132.9054      1.      .1484E-04
H+.....       1.0079      1.      .1000E-13
Rb+.....      85.4678      1.      .0000E+00
K+.....       39.0983      1.      .3158E-02
SrOH+...     105.0000      1.      .0000E+00
Sr++.....      87.6200      2.      .0000E+00
OH-.....      17.0073     -1.      .1108E+01
NO3-.....      62.0049     -1.      .9891E+00
NO2-.....      46.0000     -1.      .1217E+00
SO4--...      96.0636     -2.      .3624E+00
CO3--...      60.0092     -2.      .4812E+00
Cl-.....      35.4527     -1.      .3256E-01
PO4---...      94.9712     -3.      .0000E+00
Al(OH)4-      95.0000     -1.      .6001E-01
Other--...      96.0107     -2.      .0000E+00
F-.....      18.9984     -1.      .0000E+00

Liquid(L)= .1038E-01  Solid(g)= .5750E-01

Material: Na Form

*****OUTPUT*****

Ionic Strength=          5.675261039329186 mol/kg

      Q (mmol/gCST)  C (mmol/L)  Kd (ml/gCST)
Cs      .2581E-02    .5456E-03    .4730E+04
Rb      .0000E+00    .0000E+00    .0000E+00
Sr      .0000E+00    .0000E+00    .0000E+00
K       .3458E-01    .2966E+01    .1166E+02

```

7.17 Input: 30C – VD Sample – MOD2

```

1, 303.15
TCCR project: Temperature Effect @ 30C
7, 10
1230
  3, 6, 1, 5, 4, 40, 13
13, 9, 27, 15, 19, 2, 20, 28, 25 1
96.0107
5.000486405 1.38541E-05 1.0E-14 0.0 0.0029470 0.0 0.0
2.305582 0.923156 0.113619 0.338194 0.449151 0.030389 0.0 0.056011 0.0 0.0
0.01054, 0.05834
0
.9

```

7.18 Output: 30C – VD Sample – MOD2

```

Solution: TCCR project: Temperature Effect
*****INPUT*****

Density= .1230E+04 kg/m3

      Molecular Wt.   Valance   Molarity(mol/L)
Na+.....      22.9898      1.      .5000E+01
Cs+.....     132.9054      1.      .1385E-04
H+.....       1.0079      1.      .1000E-13
Rb+.....      85.4678      1.      .0000E+00
K+.....       39.0983      1.      .2947E-02
SrOH+...     105.0000      1.      .0000E+00
Sr++.....      87.6200      2.      .0000E+00
OH-.....      17.0073     -1.      .2306E+01
NO3-....      62.0049     -1.      .9232E+00
NO2-....      46.0000     -1.      .1136E+00
SO4--...      96.0636     -2.      .3382E+00
CO3--...      60.0092     -2.      .4492E+00
Cl-.....      35.4527     -1.      .3039E-01
PO4---...      94.9712     -3.      .0000E+00
Al(OH)4-      95.0000     -1.      .5601E-01
Other--...     96.0107     -2.      .0000E+00
F-.....      18.9984     -1.      .0000E+00

Liquid(L)= .1054E-01   Solid(g)= .5834E-01

Material: Na Form

*****OUTPUT*****

Ionic Strength=          6.620059211348782 mol/kg

      Q (mmol/gCST)   C (mmol/L)   Kd (ml/gCST)
Cs      .2394E-02     .6034E-03     .3967E+04
Rb      .0000E+00     .0000E+00     .0000E+00
Sr      .0000E+00     .0000E+00     .0000E+00
K       .2909E-01     .2786E+01     .1044E+02

```

7.19 Input: 30C – VD Sample – MOD3

```

1, 303.15
TCCR project: Temperature Effect @ 30C
7, 10
1170
  3, 6, 1, 5, 4, 40, 13
13, 9, 27, 15, 19, 2, 20, 28, 25 1
96.0107
3.205694641 1.55383E-05 1.0E-14 0.0 0.0551794 0.0 0.0
0.235057 1.035380 0.127431 0.379307 0.503752 0.034084 0.0 0.062820 0.0 0.0
0.01044, 0.05845
0
.9

```

7.20 Output: 30C – VD Sample – MOD3

```

Solution: TCCR project: Temperature Effect
*****INPUT*****

Density= .1170E+04 kg/m3

      Molecular Wt.   Valance   Molarity(mol/L)
Na+.....      22.9898      1.      .3206E+01
Cs+.....     132.9054      1.      .1554E-04
H+.....       1.0079      1.      .1000E-13
Rb+.....      85.4678      1.      .0000E+00
K+.....       39.0983      1.      .5518E-01
SrOH+...     105.0000      1.      .0000E+00
Sr++.....      87.6200      2.      .0000E+00
OH-.....      17.0073     -1.      .2351E+00
NO3-....      62.0049     -1.      .1035E+01
NO2-....      46.0000     -1.      .1274E+00
SO4--...      96.0636     -2.      .3793E+00
CO3--...      60.0092     -2.      .5038E+00
Cl-.....      35.4527     -1.      .3408E-01
PO4---...      94.9712     -3.      .0000E+00
Al(OH)4-      95.0000     -1.      .6282E-01
Other--...      96.0107     -2.      .0000E+00
F-.....      18.9984     -1.      .0000E+00

Liquid(L)= .1044E-01   Solid(g)= .5845E-01

Material: Na Form

*****OUTPUT*****

Ionic Strength=      4.922689858334877 mol/kg

      Q (mmol/gCST)   C (mmol/L)   Kd (ml/gCST)
Cs      .2652E-02     .6928E-03     .3828E+04
Rb      .0000E+00     .0000E+00     .0000E+00
Sr      .0000E+00     .0000E+00     .0000E+00
K       .4319E+00     .5276E+02     .8187E+01

```

7.21 Input: 30C – VD Sample – MOD4

```

1, 303.15
TCCR project: Temperature Effect @ 30C
7, 10
1200
  3, 6, 1, 5, 4, 40, 13
13, 9, 27, 15, 19, 2, 20, 28, 25 1
96.0107
3.797143047 1.47216E-05 1.0E-14 0.0 0.2006353 0.0 0.0
1.131001 0.980959 0.120733 0.359371 0.477274 0.032292 0.0 0.059518 0.0 0.0
0.01026, 0.05756
0
.9

```

7.22 Output: 30C – VD Sample – MOD4

```

Solution: TCCR project: Temperature Effect
*****INPUT*****

Density= .1200E+04 kg/m3

      Molecular Wt.  Valance  Molarity(mol/L)
Na+.....      22.9898      1.      .3797E+01
Cs+.....     132.9054      1.      .1472E-04
H+.....       1.0079      1.      .1000E-13
Rb+.....      85.4678      1.      .0000E+00
K+.....       39.0983      1.      .2006E+00
SrOH+...     105.0000      1.      .0000E+00
Sr++.....      87.6200      2.      .0000E+00
OH-.....      17.0073     -1.      .1131E+01
NO3-.....      62.0049     -1.      .9810E+00
NO2-.....      46.0000     -1.      .1207E+00
SO4--...      96.0636     -2.      .3594E+00
CO3--...      60.0092     -2.      .4773E+00
Cl-.....      35.4527     -1.      .3229E-01
PO4---...      94.9712     -3.      .0000E+00
Al(OH)4-      95.0000     -1.      .5952E-01
Other--...      96.0107     -2.      .0000E+00
F-.....      18.9984     -1.      .0000E+00

Liquid(L)= .1026E-01  Solid(g)= .5756E-01

Material: Na Form

*****OUTPUT*****

Ionic Strength=          5.615910435036820 mol/kg

      Q (mmol/gCST)  C (mmol/L)  Kd (ml/gCST)
Cs      .2443E-02    .1018E-02    .2399E+04
Rb      .0000E+00    .0000E+00    .0000E+00
Sr      .0000E+00    .0000E+00    .0000E+00
K       .7630E+00    .1964E+03    .3886E+01

```

7.23 Input: 30C – VD Sample – MOD5

```

1, 303.15
TCCR project: Temperature Effect @ 30C
7, 10
1180
  3, 6, 1, 5, 4, 40, 13
13, 9, 27, 15, 19, 2, 20, 28, 25 1
96.0107
3.029442009 1.4684E-05 1.0E-14 0.0 0.6941250 0.0 0.0
0.864112 0.978453 0.120425 0.358453 0.476055 0.032210 0.0 0.059366 0.0 0.0
0.01000, 0.05672
0
.9

```

7.24 Output: 30C – VD Sample – MOD5

```

Solution: TCCR project: Temperature Effect
*****INPUT*****

Density= .1180E+04 kg/m3

      Molecular Wt.  Valance  Molarity(mol/L)
Na+.....      22.9898      1.      .3029E+01
Cs+.....     132.9054      1.      .1468E-04
H+.....       1.0079      1.      .1000E-13
Rb+.....      85.4678      1.      .0000E+00
K+.....       39.0983      1.      .6941E+00
SrOH+...     105.0000      1.      .0000E+00
Sr++.....      87.6200      2.      .0000E+00
OH-.....      17.0073     -1.      .8641E+00
NO3-.....      62.0049     -1.      .9785E+00
NO2-.....      46.0000     -1.      .1204E+00
SO4--...      96.0636     -2.      .3585E+00
CO3--...      60.0092     -2.      .4761E+00
Cl-.....      35.4527     -1.      .3221E-01
PO4---...      94.9712     -3.      .0000E+00
Al(OH)4-      95.0000     -1.      .5937E-01
Other--...      96.0107     -2.      .0000E+00
F-.....      18.9984     -1.      .0000E+00

Liquid(L)= .1000E-01  Solid(g)= .5672E-01

Material: Na Form

*****OUTPUT*****

Ionic Strength=          5.415941795649370 mol/kg

      Q (mmol/gCST)  C (mmol/L)  Kd (ml/gCST)
Cs      .2411E-02    .1006E-02    .2396E+04
Rb      .0000E+00    .0000E+00    .0000E+00
Sr      .0000E+00    .0000E+00    .0000E+00
K       .1030E+01    .6883E+03    .1497E+01

```

Appendix B (ZAM Beta Values)

As described by Hamm et al. [2], the cations cesium, potassium, sodium, and strontium hydroxide form a 4-component homovalent system where the surface loading for cesium on the CST material can be expressed as:

$$Q_{Cs} = \frac{\eta_{df} \bar{C}_T c_{Cs}}{c_{Cs} + [\tilde{K}_{21} c_K + \tilde{K}_{31} c_{Na} + \tilde{K}_{41} c_{SrOH} + \dots]} \Rightarrow \frac{\eta_{df} \bar{C}_T c_{Cs}}{c_{Cs} + \beta},$$

where the beta parameter for cesium becomes dependent upon the other ionic competitors for CST adsorption (i.e., K^+ , Na^+ , $SrOH^+$, and Rb^+). The beta parameter contains the selectivity coefficients making it dependent upon temperature and liquid composition of all of the ionic species in solution. The larger the beta parameter the less favorable (and lower loadings) an isotherm will be (have). The dilution factor (η_{df}) is unity when considering a specific powder-form and is less than one upon addition of an inert binder. Based on analyses discussed in prior CST studies, the best estimate dilution factor for the engineered-form of this CST batch is set to 0.68. The total cesium capacity term is only a function of which batch of powder-form material is being considered and is set to 0.58 mmole Cs^+ /gCST. With the dilution factor and the total cesium capacity set, the above equation contains only one free parameter (beta) that needs to be specified. The beta parameter varies slightly over a particular isotherm and as such an average value is generally employed. For each unique isotherm presented in the various figures of this report an average beta factor was computed and its values are listed in Table B-1 below.

Table B-1. ZAM Beta Values.

Sample	Temperature (°C)	Figure	Beta
Average SRS Simulant	23	3-3	2.352E-4
As-Received Tank 10H Surface	30	3-6, 3-7	1.162E-4
Tank 10H Surface Mod 1	30	3-6	1.265E-4
Tank 10H Surface Mod 2	30		1.502E-4
Tank 10H Surface Mod 3	30	3-7	1.624E-4
Tank 10H Surface Mod 4	30		1.479E-4
Tank 10H Surface Mod 5	30		1.766E-4
Tank 10H Surface Desorption Studies	30	3-10	1.502E-4
	80		5.000E-4
	90		6.132E-4
As-Received Tank 10H VD	30	3-8, 3-9	1.025E-4
Tank 10H VD Mod 1	30	3-8	1.225E-4
Tank 10H VD Mod 2	30		1.460E-4
Tank 10H VD Mod 3	30	3-9	1.528E-4
Tank 10H VD Mod 4	30		2.418E-4
Tank 10H VD Mod 5	30		2.410E-4
Tank 10H VD Desorption Studies	30	3-11	1.460E-4
	80		4.855E-4
	90		5.953E-4

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