CST Batch Contact Equilibrium Testing of TCCR Tank 10H Batch 1 and 1A Waste Supernate Samples

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EXECUTIVE SUMMARY

The Tank Closure Cesium Removal (TCCR) system uses ion exchange columns filled with crystalline silicotitanate media to process radioactive waste solutions for the removal of Cs-137. TCCR currently focuses on dissolving Savannah River Site (SRS) Tank 10H waste (primarily sodium saltcake solids) within the tank followed by at-tank ion exchange column treatment. Equilibrium batch contact tests conducted in the SRNL Shielded Cells laboratory and associated analyses indicated that both the Tank 10H Batch 1 (pre-production) and 1A (production) waste supernates are unique solutions for which CST cesium removal performance is lower than predicted by ZAM modeling [1]. Cesium distribution coefficients (K_d), percent removal, and CST loading data for the TCCR production supernate batch are provided in Table ES-1. ZAM-based cesium loading predictions are compared to the observed loading for the production batch in Figure ES-1, where significantly lower performance was observed than predicted by the model. Even lower cesium loading results (versus ZAM) were observed previously for the in-tank "teabag" batch contact samples [2, 3].

OLI Modeling indicates that the Batch 1 solution is supersaturated in aluminum and calcium and the Batch 1A solution is supersaturated in calcium and iron. Aluminum, calcium, and iron removal from solution were observed previously for the Batch 1 teabag CST samples [2] and calcium and iron removal were observed for the Batch 1A teabag CST samples [3]. Analysis of the laboratory Tank 10H equilibrium batch contact solutions prior to and after CST contact revealed complete calcium removal (within the measurement detection limit) from the waste during testing. In addition, indication of calcium and iron precipitation was observed during Tank 10H sample storage in the Shielded Cells under ambient conditions prior to batch contact testing. Calcium removal by CST has been observed previously, but the impact on cesium ion exchange in this waste composition is unknown. It appears that preparing waste supernate by the dissolution of Tank 10H salt using SRS well water and addition of caustic reagent (Batch 1A only) resulted in the formation of unstable, supersaturated solutions.

Further work is needed to examine the removal of Alkaline Earth metals and their potential impact on cesium removal. Future saltcake dissolution efforts should focus on avoiding supersaturated waste streams and targeting waste production in a more typical concentration range near 5 M Na^+. It would be beneficial to develop the ZAM isotherm model or an alternative model to more adequately cover low sodium and low hydroxide streams over a range of temperatures. Given the observation of low cesium loading with teabag contacts, more controlled laboratory batch contact test conditions where filtered solutions can be used are recommended as a supplemental method in combination with evaluations of solution supersaturation.

Table ES-1. Cesium Equilibrium Distribution Coefficients, % Removal, and Loading for CST and TCCR Tank 10H Process Supernate (Batch 1A) at 38 °C.

Sample Description	Initial Cs-137 (dpm/mL)	Final Cs-137 (dpm/mL)	Cs^+ K_d (mL/g)[a]	Cs^+ % Removal	mmol Cs^+/g CST[a,b]
December Surface #1	4.85E+07	2.89E+06	1926	94.0	1.30E-03
December Surface #2		2.85E+06	1961	94.1	1.31E-03
December Surface #3		2.86E+06	1956	94.1	1.31E-03
Average		---	1948	94.1	1.31E-03
%RSD	0.7	---	1.0	0.05	0.2

[a] dry CST mass basis

[b] cesium loading corresponds to total of all isotopes; total [Cs^+]: 1.14E-05 M [4]

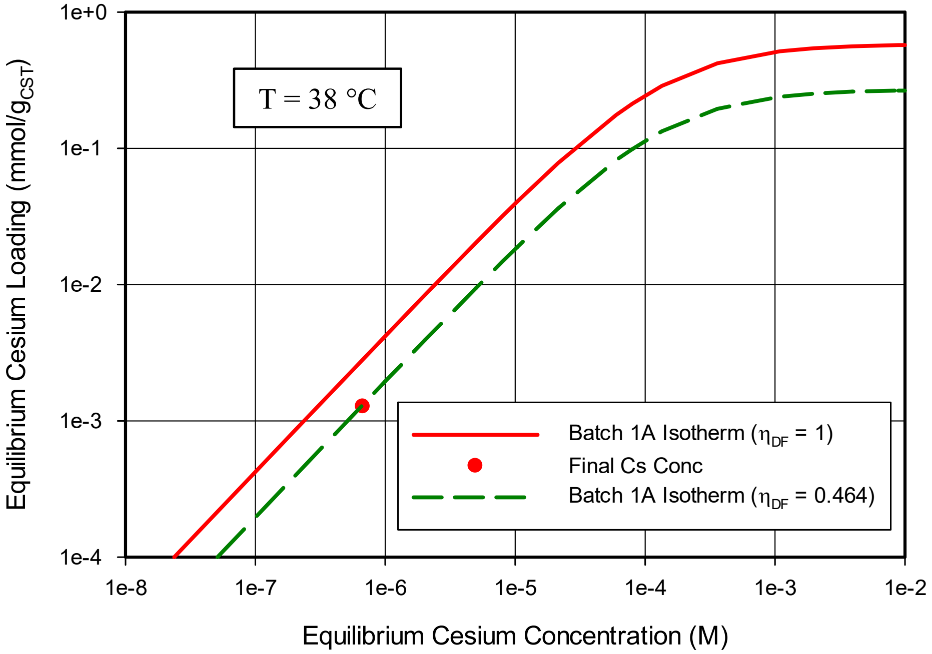

Figure ES-1 ZAM Model Prediction versus Batch Contact Result for the TCCR Tank 10H Process Supernate (Batch 1A).

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

CST	Crystalline Silicotitanate
DOE	Department of Energy
dpm	Disentegrations per minute
ELN	Electronic Laboratory Notebook
g	Gram
ICP-ES	Inductively Coupled Plasma - Emission Spectroscopy
K_d	Distribution Coefficient
mL	Milliliter
OLI	OLI Thermodynamic Model
PVDF	Polyvinyldifluoride
RPM	Revolutions per Minute
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TCCR	Tank Closure Cesium Removal
TGA	Thermal Gravimetric Analysis
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
ZAM	ZAM Isotherm Model

1.0 Introduction

Near the beginning of calendar year 2019, Savannah River Remediation (SRR) deployed the Tank Closure Cesium Removal (TCCR) system using an ion exchange process to remove radioactive cesium from waste supernate. In TCCR, filtered radioactive salt solution passes through ion exchange columns containing crystalline silicotitanate (CST) media, commercially known as UOP IONSIV™ R9120-B[a] (formerly called IE-911), to remove cesium. TCCR currently focuses on dissolving Savannah River Site (SRS) Tank 10H waste (primarily sodium saltcake solids) within the tank followed by at-tank ion exchange column treatment. Four TCCR columns were prepared, loaded with CST, and installed at SRS. Measurements of the projected maximum cesium loading on CST media from this waste supernate were conducted prior to TCCR processing using a "teabag" approach which involved contacting a small amount of CST solids (~0.1 g) with the large volume (>175,000 gallons) of Tank 10H radioactive waste supernate over a 10 day period. Cesium loading on the CST media within the teabags was 63-65% lower than ZAM isotherm model predictions for the waste compositions tested [2, 3]. To explore the difference, traditional CST batch contact tests were conducted at the Savannah River National Laboratory (SRNL) under controlled conditions using three Tank 10H waste supernate samples collected prior to and after the addition of NaOH reagent. The cesium equilibrium loading data from these tests are compared to the teabag results and ZAM model predictions.

1.1 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Manual E7, Procedure 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. The work was performed following the applicable TTQAP, Technical Task and Quality Assurance Plan [5]. The Technical Task Request (TTR) associated with this work [6] indicates that portions of this work are Safety Significant, but that the testing reported herein and the supporting modeling are for production support rather than technical baseline and are not Safety Significant (see section entitled "Clarification of Safety Significant Tasks"). The software packages used as part of this work scope must comply with 1Q, QAP 20-1 Software Quality Assurance, E7, Section 5.0 and Software Engineering and Control, Applicable provisions of Section 5.4, Procedure 2.31, E7 Manual. Data are recorded in the Electronic Laboratory Notebook (ELN) system as notebook/experiment number A2341-00117-11.

The OLI Studio™ is an acquired software that meets the commercial grade definition criteria in accordance with Manual E7 Procedure 3.46 and is accepted from the vendor by verifying the parts identifiers are correct. Dedication of the commercial grade software in accordance with Manual E7, Procedure 5.07 is not required for the OLI software, which was classified as Level D [7]. Therefore, OLI calculations meet the production support needs specified for this task in the TTR. All the activities related to the verification and validation of the OLI software database and the resulting models were documented in accordance with Manual E7 Procedure 5.40, Software Testing, Acceptance and Turnover.

SRNL was provided with two executable files (i.e., "CSTIEXV4.EXE" and "Cstiexv5.exe") of the ZAM program running on the PC platform. Version "Cstiexv5" includes some improvement to better account for strontium effects. It is however numerically less stable than version

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

"CSTIEXV4". ZAM was developed to function under MS Windows XP and older versions of Windows. For newer Windows version (e.g., Windows 7, Windows 10), emulators are required to provide XP functionalities for ZAM to run. Without emulators, ZAM will not run in Windows versions newer than Windows XP. ZAM is currently classified as Level D software [8] and ZAM calculations meet the production support needs specified for this task in the TTR. The functional requirements placed on ZAM Versions 4 and 5 were verified and validated [9].

2.0 Experimental Methods and Modeling Approach

2.1 CST Media Pretreatment

CST media from batch IONSIV R9120-B, Lot #2099000034, Mat. #8103701-556, Sub-sample from CUA #125953-A which had been pretreated as described in a previous report [10] was used for equilibrium testing. Thermal Gravimetric Analysis (TGA) was conducted on the pretreated CST to determine whether the media water content had changed during storage. Heating duplicate sub-samples of CST to a temperature of ~410 ºC revealed that the combined percentages of both physisorbed and chemisorbed water for these samples were 18.23 and 18.36% (upper bound in measurement uncertainty 0.8 wt. %). This gives an average value of 18.30%, which corresponds to a water mass correction factor (f-factor) of 0.8177 to convert the CST masses used in testing to a dry mass basis. The f-factor correction determined just after pretreatment for the same CST sample (approximately 1 year earlier) was 0.8186 [10].

2.2 Tank 10H Supernate Samples

Three Tank 10H dissolved salt samples were used for cesium batch contact equilibrium testing. Batch 1 supernate samples were collected after SRS well water was added to Tank 10H. Duplicate surface samples (HTF-10-18-104 and -105) and a single variable depth sample (HTF-10-18-111) of Tank 10H Batch 1 supernate were received at SRNL in November of 2018 [4]. The surface samples were composited prior to analysis. These surface and variable depth samples contained 2.0 M Na^+. Duplicate samples of Tank 10H Batch 1A supernate (HTF-10-18-118 and -119) were received at SRNL in December of 2018 which were subsequently composited for analysis [2]. Batch 1A supernate contained 3.8 M Na^+, due to the addition NaOH reagent to the supernate inside the waste tank. Previously reported characterization results for the Tank 10H supernate samples are summarized in Table 1.

2.3 CST Batch Contact Testing

Triplicate 10 mL sub-samples of the Tank 10H Batch 1 surface composite and Batch 1A surface composite samples were filtered (0.45 μm PVDF) and used for equilibrium batch contact testing with 0.1 g samples (~0.082 g after water content correction) of CST media. Single sub-samples of unfiltered Batch 1 surface and filtered Batch 1 variable depth samples were also tested for comparison. A ThermoScientific Incubator Shaker unit with a temperature controlled air atmosphere and an orbital agitation motion was installed in the Shielded Cells and the equilibrium tests were completed using an agitation rate of 150 rpm. The supernate and CST test samples were placed in 60 mL polyethylene bottles, transferred to the shaker oven, and continuously agitated for 5 contact days at 38 °C. Previous testing indicated that 4 contact days is sufficient to achieve cesium loading equilibrium [10]. At test completion, individual samples were removed from the shaker, filtered through 0.45 μm syringe filters, and submitted for Cs-137 (gamma) analysis with no dilution. Separate filtered sub-samples of each Tank 10H batch contact feed solution were also placed in 60 mL bottles, agitated in the shaker oven alongside the batch contact test samples (no CST contact), filtered again, and submitted for analysis. CST and Tank 10H supernate masses for individual samples during equilibrium batch contact testing are provided in Table 2.

Table 1. Reported Composition Data for the Tank 10H Samples.

Ion	November Surface (HTF-10-18-104 and 105)[a]	November Variable Depth (HTF-10-18-111)[a]	December Surface (HTF-10-18-118 and 119)[b]
	Molarity		
Na^+	2.02	2.03	3.79
K^+	1.84E-3	2.11E-3	2.21E-3
Ca^{2+}	9.48E-5	<7.52E-5	7.14E-5
Fe^{3+}	<2.67E-5	2.26E-5	4.99E-5
Free OH^-	0.235	NM	1.82
NO_3^-	0.714	NM	0.727
CO_3^{2-}	0.292	NM	0.322
SO_4^{2-}	0.131	NM	0.174
NO_2^-	7.43E-2	NM	7.55E-2
$Al(OH)_4^-$	4.13E-2	4.71E-2	4.22E-2
Br^-	<3.72E-3	NM	<3.76E-3
$C_2O_4^{2-}$	<3.38E-3	NM	4.27E-3
F^-	<1.56E-2	NM	<1.58E-3
Cl^-	<8.39E-3	NM	6.60E-3
CHO_2^-	<6.60E-3	NM	<6.68E-4
PO_4^{3-}	<3.13E-3	NM	<3.17E-4
Total Cs^+	1.17E-5	NM	1.15E-5
	dpm/mL		
Cs-137	4.98E+07	NM	4.87E7

[a] reference [4]
[b] reference [2]

Table 2. Tank 10H Supernate CST Equilibrium Batch Contact Sample Mass and Volume Data.

Tank Sample ID#	Sample Description	CST (g)[a]	Tank 10H (g)	Tank 10H (mL)[b]
HTF-10-18-104 and 105	November Surface #1	0.0998	10.896	10.01
	November Surface #2	0.1004	10.894	10.00
	November Surface #3	0.1002	10.896	10.01
	November Surface unfiltered	0.1001	10.907	10.02
HTF-10-18-111	November VD	0.1004	11.022	10.01
HTF-10-18-118 and 119	December Surface #1	0.1002	11.645	10.00
	December Surface #2	0.0998	11.632	9.99
	December Surface #3	0.0998	11.644	10.00

[a] reference state mass basis; multiply by 0.8177 to correct to dry state mass basis

[b] liquid sample densities (g/mL): November Surface – 1.089 [2], November VD – 1.101 [2], December Surface – 1.164 [4]

2.4 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 available [1].

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

3.0 Results and Discussion

3.1 CST Batch Contact Test Results

Based on the gamma scan results and the original total Cs analysis reported previously [2, 4], cesium distribution coefficients (K_d; Equation 1), % removal (Equation 2), and loading (mmol Cs^+/g CST; Equation 3) values were calculated for each test sample. Results are provided in Table 3. Initial Cs-137 concentrations for the Tank 10H samples were similar to results reported previously (Table 1). Cesium loading results were very consistent between replicate samples for both the November and December Tank 10H surface samples (<6% RSD for K_d data). More effective cesium removal was observed with the November Surface sample (averages: Cs^+ K_d 3991 mL/g, 97.0% Cs^+ removal, 1.39E-3 mmol Cs^+/g CST) relative to the December Surface sample (averages: K_d 1948 mL/g, 94.1% removal, 1.31E-3 mmol Cs^+/g CST) due to the addition of NaOH reagent and the fact that Na^+ directly competes with Cs^+ for sorption sites. Similar results were observed for filtered and unfiltered November Surface samples. Slightly lower cesium removal was observed for the November Variable Depth sample (Cs^+ K_d = 3474 mL/g, 96.6% Cs^+ removal) than the November Surface sample. This result is outside of the 95% confidence interval of the triplicate November Surface Sample results. This difference may due to variability in the experiment or analysis, but could also be attributable to the slightly higher potassium concentration in the variable depth sample (see Table 1).

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

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

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

where,

K_d - distribution coefficient, (ml/g) on a dry mass basis

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

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

V - liquid-phase volume, (ml)

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

F - mass correction factor for CST water content, and

Q - total Cs^+ loading.

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

Table 3. Cesium Equilibrium Distribution Coefficients, % Removal, and Loading for CST and Tank 10H Supernates at 38 °C.

Sample Description	Initial Cs-137 (dpm/mL)	Final Cs-137 (dpm/mL)	Cs^+ K_d (mL/g)[a]	Cs^+ % Removal	mmol Cs^+/g CST[a,b]
November Surface #1	4.95E+07	1.40E+06	4211	97.2	1.40E-03
November Surface #2		1.56E+06	3744	96.8	1.39E-03
November Surface #3		1.46E+06	4017	97.0	1.39E-03
Average		---	3991	97.0	1.39E-03
%RSD	0.7	---	5.9	0.2	0.5
November Surface <u>unfiltered</u>	4.95E+07	1.46E+06	4025	97.0	1.39E-03
November VD	4.45E+07	1.51E+06	3474	96.6	---
December Surface #1	4.85E+07	2.89E+06	1926	94.0	1.30E-03
December Surface #2		2.85E+06	1961	94.1	1.31E-03
December Surface #3		2.86E+06	1956	94.1	1.31E-03
Average		---	1948	94.1	1.31E-03
%RSD	0.7	---	1.0	0.05	0.2

[a] dry CST mass basis

[b] cesium loading corresponds to total of all isotopes; total [Cs^+]: November Surface – 1.17E-05 M [2], December Surface – 1.14E-05 M [4]

The Tank 10H batch contact solutions were analyzed by ICP-ES following CST contact and filtration. Separate Tank 10H sub-samples which were not contacted with CST but were exposed to agitation and filtration were also analyzed for comparison. Analysis results are provided in Table 4 for aluminum, calcium, and iron. Within measurement limitations, calcium was completely removed from the supernate samples during CST contact, while aluminum concentrations were unchanged. The calcium concentrations in the Tank 10H solutions used for batch contact testing were approximately 50% of the concentrations reported previously [2, 3] for the as-received samples (Batch 1 Ca: 9.5E-05 M; Batch 1A Ca: 7.1E-05 M) analyzed several weeks earlier. The Tank 10H Batch 1A solution used for equilibrium testing also contained no detectable iron (<2.7E-5 M), indicating that the iron had decreased by >50% relative to the as-received sample (5.0E-5 M Fe) due to precipitation during storage [3]. The temperature of the samples during storage was not monitored or controlled during this time period, but is believed to have ranged from 15-20 ºC. The Tank 10H samples were filtered prior to batch contact testing, except for the sample identified as unfiltered. It is unknown whether calcium precipitation/fouling, or ion exchange, or both phenomena may have occurred during testing. The as-received Tank 10H process sample (Batch 1A) was unstable toward calcium and iron precipitation, although calcium ion exchange may have also occurred. CST ion exchange is well-known to occur with strontium, another divalent alkaline earth metal.

Aluminum, calcium, and iron removal were also observed during in-tank teabag contacts with Tank 10H Batch 1 supernate while calcium and iron removal were observed with Batch 1A [2, 3].

Calcium and iron loadings for the Tank 10H Batch 1A CST teabag sample were higher than the cesium loading (5.6E-02 mmol Ca/g CST, 2.1E-02 mmol Fe/g CST, versus ≥9.0E-03 mmol Cs/g CST). Precipitation/fouling or competitive ion exchange involving these metals may have reduced the cesium loading for the teabag samples.

Table 4. ICP-ES Analysis Results Prior to and After CST Batch Contacts for Tank 10H Samples

Metal	Tank 10H Batch 1			Tank 10H Batch 1A		
	Initial (M)[a]	Final (M)	Final/Initial (%)	Initial (M)[a]	Final (M)	Final/Initial (%)
Al	4.2E-02	4.1E-02	99	4.4E-02	4.4E-02	101
Ca	4.5E-05	<8.7E-06	<19	3.8E-05	<8.7E-06	<23
Fe	<2.7E-05	<2.7E-05	---	<2.7E-05	<2.7E-05	---

[a] initial represents liquid concentrations from filtered Tank 10H samples which were agitated alongside the batch contact samples in the shaker oven

3.2 OLI Thermodynamic Modeling of the Tank 10H Waste Compositions

The Tank 10H Batch 1 and 1A supernate compositions were evaluated using the OLI thermodynamic model and it was discovered that the solutions are expected to be unstable toward precipitation. The adjusted, ionically balanced OLI input compositions (based on the reported compositions in Table 1) used for each supernate solution are provided in Table 5. Note that chloride anion is used for charge balance in these calculations since previous analyses have indicated that the chloride concentration minimally impacts cesium loading on CST [9, 11]. As shown in Table 6, Batch 1 supernate was predicted to be supersaturated in both aluminum and calcium at 38 °C (near the Tank 10H temperature). Approximately 41% of the Al and 74% of the Ca were predicted to precipitate from this solution. Batch 1A supernate was predicted to be supersaturated in calcium. The aluminum in the Batch 1A solution was predicted to be soluble, presumably because of the added caustic reagent. Conversely, approximately 31% of the Ca was predicted to precipitate from the Batch 1A solution. These results are consistent with the observation of both aluminum and calcium loading on the teabag CST for Batch 1 solution [2] but only calcium loading on the teabag CST for the Batch 1A solution [3]. The results are also consistent with the observation of calcium precipitation for these solutions after aging in the Shielded Cells, where the temperature was lower than the reported tank temperature. For Batch 1A supernate, iron was included in the OLI input and most of the iron was predicted to precipitate from solution. As discussed above, iron precipitation was observed from the Batch 1A sample during storage in the Shielded Cells.

Table 5. Adjusted Ionically Balanced Tank 10H Input Compositions Used for OLI Modeling.

Ion	Batch 1	Batch 1A
Na^+	2.019	3.790
NO_3^-	0.714	0.727
CO_3^{2-}	0.292	0.322
Free OH-	0.235	1.820
SO_4^{2-}	0.131	0.174
Cl^-	0.111[a]	0.127[a]
NO_2^-	0.074	0.075
$Al(OH)_4^-$	0.041	0.042
$C_2O_4^{2-}$	---	4.270E-03
K^+	1.839E-03	2.210E-03
Cs^+	1.173E-05	1.131E-05
Ca^{2+}	9.475E-05	7.140E-05
Fe^{3+}	---	4.990E-05
Sr^{2+}	1.36E-07	2.096E-07
$Sr(OH)^+$	3.047E-08	---

[a] chloride added as a spectator ion for charge balance

Table 6. OLI Thermodynamic Model Output for Tank 10H Solutions at 38 °C.

Tank 10 H Sample	% Al Precipitation	% Ca Precipitation	% Fe Precipitation
Batch 1	40.7	73.9	--[a]
Batch 1A	0.0	30.8	95.4

[a] iron not included as a component for Batch 1

3.3 ZAM Isotherm Modeling of the Batch Contact Tests

The ZAM Isotherm Model was used to predict cesium equilibrium loading on CST media during batch contact testing with Tank 10H Batches 1 and 1A supernate samples. A dilution factor is used to account for the contribution of binder materials to the mass of engineered CST media. Recent studies indicated that the dilution factor for the TCCR R9120-B CST media is near 0.68 [10]. This factor is used to correct the mass of engineered CST to a powder CST mass. Conversely, a dilution factor of "1" would mean no correction for binder dilution (i.e., the same as powder CST mass). As shown in Figure 1, the final cesium concentration observed for Tank 10H Batch 1 did not fall on the equilibrium isotherm predicted for powder-form CST, as expected. A correction factor of 0.53 was applied to the equilibrium isotherm to match the experimental results. This correction exceeds that for the correction factor used in previous testing (0.68) and indicates that CST cesium removal performance is lower than expected, though not as low as was observed for the teabag, which required a correction factor of 0.35 [2]. As shown in Figure 2, a correction factor of 0.46 was required to adjust the predictions to match the experimental results for Tank

10H Batch 1A supernate. Again, this correction exceeds that for the correction factor used in previous testing and indicates that CST cesium removal performance is lower than expected, though not as low as was observed for the teabag, which required a correction factor of 0.37 from the prediction for engineered form CST [3]. Since earlier testing indicated that this batch of R9120-B CST exhibits the normal correction factor of 0.68, these correction factors indicate that an unknown competing species or precipitate is limiting cesium ion exchange. Another possibility is that the ZAM model is not accurately predicting the equilibrium at elevated temperature, although recent ZAM predictions matched elevated temperature cesium batch contact data [10].

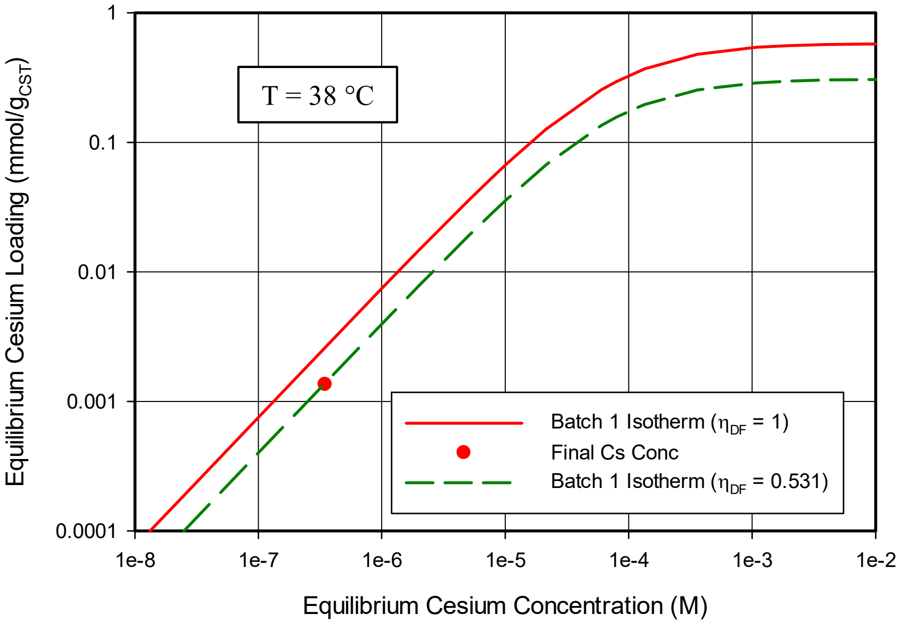

Figure 1. ZAM Model Prediction versus Batch Contact Result for the Tank 10H Batch 1 Supernate.

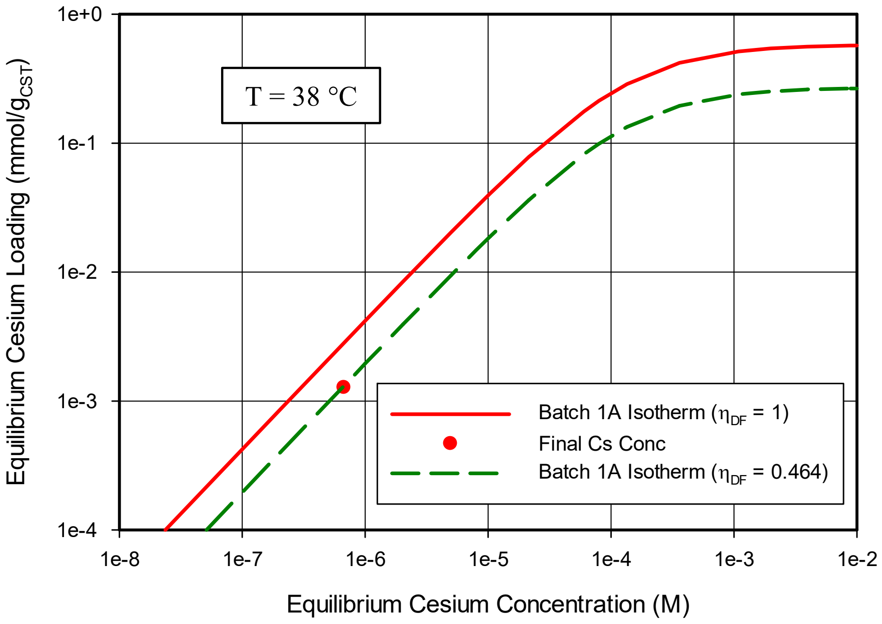

Figure 2. ZAM Model Prediction versus Batch Contact Result for the Tank 10H Batch 1A Supernate.

3.4 Estimating Maximum Cesium Loading on CST from Tank 10H Batch Contact Data

As shown in Figures 1 and 2, a linear portion exists in the CST cesium loading isotherms across the concentration range from 1E-8 to 1E-5 M Cs^+ where the slope is constant. The distribution coefficient K_d (Equation 1) represents the slope of the isotherm. The average cesium K_d measured for the Batch 1A samples of 1948 mL/g where the final cesium concentation was 6.7E-7 M should therefore approximate the K_d value that would be observed if the equilibrium cesium concentration had been equal to that of the initial Batch 1A supernate (1.1E-5 M Cs^+). Similarly, the average cesium K_d measured for the Batch 1 samples of 3988 mL/g where the final and initial cesium concentations were 3.5E-7 M and 1.2E-5 M, respectively, was conducted within the linear range of the isotherm. Examination of numerous CST cesium loading isotherms for waste supernates indicated that the range of linearity in the concentration range does not vary greatly.

As discussed by Hamm [12] and shown in Equation 4, cesium loading on CST (Q_X) is the product of the cesium distribution coefficient (K_d^X) and the equilibrium (final) cesium concentration (C_f^X) for the solution. This equation can be used to calculate the cesium loading on CST for a given traditional batch contact test where the final cesium concentration is much lower than the feed concentration. As indicated in Equation 5, in the linear concentration range of the cesium isotherm the K_d is constant and distribution coefficients measured at lower equilibrium cesium concentrations (i.e., K_d^X) are equal to K_d^{FD}, the distribution coefficient at a final solution cesium concentration equal to the feed concentration. K_d^{FD} can be experimentally measured with some effort by spiking a sample of the waste supernate with sufficient cesium to produce the target equilibrium concentration at a given liquid:solid phase ratio. However, when operating in the linear concentration range of the isotherm, cesium spiking and direct measurement of K_d^{FD} is unnecessary since $K_d^X = K_d^{FD}$ (Equation 5). When this is the case, the maximum cesium loading of the feed solution on CST (Q_{FD}) can be calculated as the product of K_d^X and the original concentration of the waste feed solution (C^{FD}), as shown in Equation 6. Furthermore, since deviation from linearity in the upper end of the linear range is toward lower distribution coefficients, the loading calculated using K_d^X should be bounding and conservative.

$$Q_X = [K_d^X][C_f^X] \qquad \text{(Equation 4)}$$

$$K_d^X = K_d^{FD} \text{ (in linear concentration range of isotherm)} \qquad \text{(Equation 5)}$$

$$Q_{FD} = [K_d^{FD}][C^{FD}] = [K_d^X][C^{FD}] \qquad \text{(Equation 6)}$$

where,

Q_X	- total cesium loading in mmol/g dry CST for a given batch contact test X,
Q_{FD}	- maximum total cesium loading in mmol/g dry CST for the waste feed solution,
C_f^X	- equilibrium cesium concentration below the initial Tank 10H cesium concentration (such as would be observed in a traditional batch contact test with Tank 10H supernate),
C^{FD}	- equilibrium cesium concentration equal to the initial Tank 10H cesium feexdconcentration,
K_d^X	- cesium distribution coefficient in mL supernate/g dry CST at an equilibrium Cs concentration below the feed, and
K_d^{FD}	- cesium distribution coefficient in mL supernate/g dry CST at an equilibrium Cs concentration equal to the initial feed concentration.

Maximum cesium loading values on CST were calculated using Equation 6 for Tank 10H Batch 1 and 1A supernate solutions based on the measured distribution coefficients (K_d^X) and the previously reported cesium concentrations [2, 4]. The results are provided in Table 7. This calculational approach is an alternative method to the teabag approach for the generation of a bounding cesium loading value for CST and may be applicable to most supernate solutions that will be encountered during TCCR operations. The calculated bounding loading for the Batch 1A TCCR process sample based on the measured distribution coefficient was 42.9 Ci Cs-137/kg dry CST. For comparison, the CST loading predicted using the ZAM isotherm model with a correction factor of 0.68 was 62.5 Ci Cs-137/kg dry CST, while the measured loading for the teabag was 23.2 Ci Cs-137/kg dry CST [3]. As discussed above, lower cesium uptake was observed than predicted for both the laboratory batch contact tests and the in-tank teabag method. Reduced performance was presumably due to the presence of species which impact cesium ion exchange on CST by physical fouling of the porous media, by competitive ion exchange, or both mechanisms. Alternatively, poor prediction by ZAM at elevated temperature could lead to the difference between predicted and observed loading.

Table 7. Bounding CST Cesium Loading Predictions For Tank 10H Samples Based on Measured Distribution Coefficients.

Tank 10H Sample	K_d^X (mL/g)[a]	Ci Cs-137/kg CST[b]	Cs-137 Mass %
Batch 1	3988	89.8	16.5 [2]
Batch 1A	1946	42.9	16.7 [3]

[a] K_d^X assumed equal to K_d^{FD}
[b] based on $Q_{FD} = [K_d^X][C^{FD}]$

3.5 Alkaline Earth and Iron Sorption on CST

Stontium, primarily as the species $SrOH^+$, is a known competitor of cesium for ion exchange sites on CST media [13, 14]. Strontium was not present above detectable levels in the Batch 1 and 1A feed solutions used for batch contact testing. In theory, other Alkaline Earth metal cations may also compete for sorption sites on CST. Fondeur, et. al. [15] evaluated the impact of calcium, barium, and magnesium on CST cesium removal performance using modified SRS average simulants (5.6 M Na^+, 1.9 M OH^-, 1E-4 M Cs^+). Calcium exhibited the highest solubility of the Alkaline Earth metals evaluated and the concentration in the simulant (5E-4 M) greatly exceeded the predicted solubility using OLI (2E-5 M). Calcium at this concentration decreased the cesium loading on CST powder (IE-910) by 12%, but no decrease in the cesium loading was observed with IE-911 CST. The authors concluded that the presence of calcium would not significantly affect cesium loading. Barium and magnesium added to the solubility limits in this simulant did not impact cesium loading on CST. Literature reports also indicate that some Ca is removed by the IE-911 CST from a Hanford tank waste simulant, but not much is removed by IE-910, suggesting that it is primarily the binder that was absorbing the Ca with that composition and batch of CST. [16]

During recent CST column studies conducted on Hanford Tank AP-107 waste, which contained a high calcium concentration and some iron (Na^+ = 5.5 M, OH^- = 1.0 M, Cs^+ = 6E-5 M, Ca = 9E-4 M, Fe = 3E-4 M), 49% of the calcium and 65% of the iron were removed from the solution by the CST [17]. A ZAM correction factor near 0.5 was used to match the experimental data and the same dilution factor was required for a similar test with a simple simulant sample which contained no added calcium [16, 18]. This suggests no impact on the cesium absorption by calcium, although there are irregularities in the results compared to most historical data and no analysis of calcium contaminant was reported for the simulant. A different dry CST mass basis was used in these tests than has traditionally been used at SRNL and it is believed that the low correction factor needed to make the computer model fit the PNNL data is associated with the mass basis difference rather than competitive ion exchange between cesium and other metals like calcium.

Other information on Alkaline Earth and iron sorption on CST is available in the literature [19, 20]. Ba, Mg, Sr, Ca, and Fe have been reported to load onto CST. Other than strontium, the degree to which ion exchange of these metals impacts cesium loading in these solutions is not known.

4.0 Conclusions

Equilibrium batch contact tests conducted in the SRNL Shielded Cells laboratory and associated analyses indicate that both the Tank 10H Batch 1 and 1A waste supernates are unique solutions for which CST cesium removal performance is lower than predicted by ZAM modeling. Even lower cesium loading results (versus ZAM) were observed previously for the in-tank teabag samples [1, 2]. OLI Modeling indicates that the Batch 1 solution is supersaturated in aluminum and calcium and the Batch 1A solution is supersaturated in calcium and iron. Aluminum, calcium, and iron removal from solution were observed previously for the Batch 1 teabag CST samples [2] and calcium and iron removal were observed for the Batch 1A teabag CST samples [3]. Analysis of the laboratory Tank 10H equilibrium batch contact solutions prior to and after CST contact revealed complete calcium removal (within the measurement detection limit) from the waste during testing. In addition, indication of calcium and iron precipitation was observed during Tank 10H sample storage in the Shielded Cells prior to batch contact testing. Calcium removal by CST has been observed previously, but the impact on cesium loading in this waste composition is unknown. It appears that preparing waste supernate by the dissolution of Tank 10H salt using SRS well water and addition of caustic reagent resulted in the formation of unstable, supersaturated solutions.

5.0 Recommendations

Further work is needed to examine the removal of secondary species (such as Alkaline Earth metals) and their potential impact on cesium removal. Future saltcake dissolution efforts should focus on avoiding supersaturated waste streams. If possible, it may also be advantageous to target the production of waste in a more typical concentration range near 5 M total sodium to maximize salt disposal and minimize CST use. It would also be beneficial to develop the ZAM isotherm model or an alternative model to more adequately cover waste compositions (such as low sodium and low hydroxide streams) outside of the current database that was tested historically, and over a range of temperatures. Given the observation of low cesium loading with teabag contacts, more controlled laboratory batch contact test conditions where filtered solutions can be used are recommended as a supplemental method in combination with evaluations of solution supersaturation. Other testing approaches to determine the maximum cesium loading such as batch contacts with cesium-spiked solutions, batch contacts varying the liquid to solid phase ratio, or high phase ratio batch contacts should also be considered.

6.0 References

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