Preliminary Determination of the Impact of Alkaline Earth Metals on Crystalline Silicotitanate

Kathryn M. Taylor-Pashow
Thong Hang
Daniel J. McCabe
January 2020
SRNL-STI-2019-00678, Revision 0

DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

Keywords: *decontamination, Crystalline Silicotitanate, Tank Closure Cesium Removal*

Retention: *Permanent*

Preliminary Determination of the Impact of Alkaline Earth Metals on Crystalline Silicotitanate

Kathryn M. Taylor-Pashow
Thong Hang
Daniel J. McCabe

January 2020

Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

Savannah River National Laboratory®
OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

REVIEWS AND APPROVALS

AUTHORS:

Kathryn M. Taylor-Pashow, Seperation Sciences & Engineering Date

Thong Hang, Environmental Modeling Date

Daniel J. McCabe, Materials Science & Engineering Date

TECHNICAL REVIEW:

William D. King, Seperation Sciences & Engineering, Reviewed experimental per E7 2.60 Date

L. L. Hamm, Threat Assessments, Reviewed modeling per E7 2.60 Date

APPROVAL:

Boyd Wiedenman, Manager Date
Seperation Sciences & Engineering

Samuel Fink, Director, Chemical Processing Sciences Date

Eric Freed, SRR, Engineering Date

EXECUTIVE SUMMARY

Savannah River Remediation (SRR) recently deployed the Tank Closure Cesium Removal (TCCR) system which utilizes an ion exchange process to remove ^{137}Cs from tank waste supernate. In TCCR, salt solution is filtered and then passed through ion exchange columns containing crystalline silicotitanate (CST) media, commercially known as UOP IONSIV™ R9120-B[a], which is highly selective for removing cesium. The current process focuses on dissolving salt in Savannah River Site (SRS) Tank 10H, followed by processing in the TCCR skid located near the tank. Prior to processing each batch of waste generated in Tank 10H, the projected maximum cesium loading on the CST is determined using an in-tank batch contact equilibrium test. This involves placing a small amount (~0.1 g) of CST in a "teabag" device and submerging it in the tank waste for a period of 10 days. Results from those earlier teabag tests had indicated much lower cesium loading than predicted by the equilibrium sorption model (ZAM). There are numerous possible explanations for this result; however, based on the observed loadings of Ca (and other metals) on the CST from the teabag tests, it was hypothesized that competition from these other ions may be limiting the cesium loadings.

Strontium is a known competitor for ion exchange sites on CST and can decrease the absorption of cesium. Since strontium was known to absorb onto CST, it was conjectured that perhaps calcium (another akaline earth metal) was also absorbing and causing decreased cesium removal. This testing was designed to examine the impact of competition from alkaline earth metals, Ca, Sr, and Ba, on Cs removal by CST under various conditions. It was also important to understand their absorption behavior because the absorbed ^{90}Sr can contribute to the radioactive source term on spent CST and ^{137m}Ba is a radioactive daughter isotope of the absorbed ^{137}Cs that could leach during operation. A simulant of the TCCR Batch 1A waste supernate was prepared in an attempt to replicate the previous radioactive waste results as closely as possible, and testing was performed using it with and without added calcium. Testing was also performed with a simplified SRS average simulant both with and without added alkaline earths. The composition of the SRS Average simulant was adjusted, removing divalent anions and fluoride, to increase the solubility of the alkaline earths to levels comparable to the Cs concentration so their influence could be evaluated. A modified SRS average simulant was prepared and successfully spiked with Sr and Ba at concentrations sufficient for testing. Calcium was found to not be sufficiently soluble in the modified SRS average simulants and it was determined that the composition necessary to dissolve sufficient Ca deviated too far from actual waste compositions to provide a reasonable comparison.

Results of the testing showed that the alkaline earths were thorougly removed by the CST, resulting in high distribution coefficients (K_d); however, their presence had minimal impact on the Cs removal under these conditions (i.e., simulant testing with and without the presence of alkaline earths). This minimal influence was consistent with the magnitude predicted by the ZAM modeling for these compositions. In general, the measured cesium K_d values were lower (8-36%) than predicted by ZAM, particularly for the TCCR Batch 1A composition, even without added alkaline earth metals. It is not yet known if these lower K_d values are low due to some chemical interferance or if ZAM is overpredicting absorption under these conditions. However, the K_d results from the actual Batch 1A and simulant testing samples, with and without Ca, were very

---

[a] IONSIV is a trademark of Honeywell UOP, Des Plaines, IL, U.S.A.; R9140-B, R0120-B, and IE-911 are engineered forms of CST.

similar, with the simulant ~5% below the radioactive sample. A summary of the measured K_d values as well as ZAM modeling predictions is provided in Table ES-1.

Table ES-1. ZAM Calculated versus Measured Distribution Coefficients

Simulant	Phase Ratio[a]	Temp °C	Cs^+ K_d (mL/g)	ZAM[b] Prediction (mL/g)	AE[c] K_d	ZAM[b] AE Prediction (mL/g)
TCCR 1A	124:1	38	1832	2859	NA	NA
TCCR 1A	122:1	25	3253	4077	NA	NA
TCCR 1A with Ca	123:1	38	1887	2859[d]	> 233	1.17E5[d]
SRS Sim No Div/F	122:1	25	1091	1229	NA	NA
SRS Sim No Div/F	122:1	25	1132	1229	NA	NA
SRS Sim No Div/F w/ Sr	123:1	25	1031	1205	16440	7664
SRS Sim No Div/F w/ Ba	123:1	25	1028	1229	16950	NA

a. dry weight basis of engineered media; b. assumes binder dilution factor of 0.68; c. AE = Alkaline Earth; d. Calculated using Sr as a substitute for Ca in the ZAM model.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AE	alkaline earth
AMP	Ammonium MolybdoPhosphate
CST	Crystalline Silicotitanate
DOE	Department of Energy
g	gram
h	hour
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
IX	ion exchange
K_d	Distribution Coefficient
L	Liter
mg	milligram
mL	milliliter
OLI	OLI Thermodynamic Model
rpm	revolutions per minute
RSD	relative standard deviation
Sim	Simulant
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
Std. Dev.	standard deviation
TCCR	Tank Closure Cesium Removal
TGA	Thermal Gravimetric Analysis
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
ZAM	ZAM (Zheng, Anthony, and Miller) Isotherm Model

1.0 Introduction

In 2019, Savannah River Remediation (SRR) deployed the Tank Closure Cesium Removal (TCCR) system using an ion exchange (IX) process to remove radioactive ^{137}Cs from tank waste supernate. In TCCR, salt solution is filtered and then passes through IX columns containing crystalline silicotitanate (CST) media, commercially known as UOP IONSIV™ R9120-B[a], which is highly selective for removing cesium. The current process focuses on dissolving salt in Savannah River Site (SRS) Tank 10H, followed by processing in the TCCR skid located near the tank. Four TCCR columns were constructed, loaded with CST, and installed in a modular skid unit and placed near SRS Tank 10H. Schedules are currently under development for the installation of additional CST columns to process waste from other SRS tanks following the completion of the Tank 10H campaign.

Measurements of the projected maximum cesium loading on CST media from SRS Tank 10H waste supernate were conducted prior to processing using a "teabag" method [1]. The method involved placing a small amount of CST media (~0.1 g) in a screen holder and submerging it into radioactive supernate in Tank 10H for 10 days under nearly stagnant conditions. The teabag containing the CST was retrieved from the tank, the CST was digested, and the resulting solution was then analyzed. Results indicated much lower cesium loading than expected. The loading was about 33% of the expected value compared to the ZAM model. There are numerous possible explanations for this result. However, one unexpected observation was that calcium was also loaded onto the CST, exceeding the loading of total cesium by nearly an order of magnitude on a mole-per-gram basis. Additional studies and observations were identified to determine the cause of the low cesium loading and the removal of calcium.

A second unexpected observation was that the cesium loading of the batch of CST used in the TCCR columns initially appeared to be lower than previous batches when using the Tank 10 Batch 1A tank samples [2], as shown in Table 1-1. Although the distribution coefficient (K_d) values are very high versus typical tank waste, especially for 38 °C, the sodium and potassium ion concentrations were very low, which should have caused an increase in the cesium loading. The subsequent modeling with ZAM indicated a correction factor was needed to adjust the results to match the isotherm. Conversely, samples of the same batch of CST exhibited normal cesium removal behavior with SRS Average simulant, as shown in Table 1-2 [3]. Comparison of the simulant results to the predicted value from the ZAM computer model indicates a binder dilution factor of 0.76, which is in the normal range.[b] Both TCCR field teabag data [1] and standard laboratory CST batch contact tests [2] with Tank 10H samples unexpectedly also indicated removal of calcium and iron from the waste supernate by CST. It is suspected that the "lower apparent capacity" and unexpected removal of calcium and iron are related. In addition, there was evidence of calcium and iron precipitation during sample storage in the Shielded Cells at ambient temperature [2], indicating that the tank sample was unstable towards precipitation, either due to supersaturation or elevated tank temperature. As shown in Table 1-3, the calcium concentration in the Batch 1A sample decreased during the batch contact with CST.

---

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

[b] A binder dilution factor is invoked because the ZAM model was developed for the CST powder, and the IONSIV R9120-B contains an inert binder to form the engineered bead, which requires a "dilution factor" to adjust the isotherm calculated by ZAM.

Table 1-1. TCCR Batch 1A Batch Contact Test Results at 38 °C (from King, SRNL-STI-2019-00150 [2])

Tank 10 Sample	$[Na^+]$ (M)	$[K^+]$ (M)	Initial ^{137}Cs (pCi/mL)	Final ^{137}Cs (pCi/mL)	Cs K_d[a] (mL/g)	Cs % removed	Cs loading (mmol/g)
Nov. '18 Surface (Batch 1)	2.02	1.84E-3	2.23E7	6.64E5	3991	97.0	1.39E-3
Dec. '18 Surface (Batch 1A[b])	3.79	2.21E-3	2.18E7	1.29E6	1948	94.1	1.31E-3

[a] Dry basis. [b] Batch 1A was prepared with the addition of NaOH to Batch 1 in Tank 10H.

Table 1-2. Cesium Loading with CST (R9120-B) and SRS Average Simulant (23 °C) (from King, SRNL-STI-2018-00277 [3])

Simulant ID (days)	Initial Total Cs (M)	Initial Cs-137 (dpm/mL)	Final Cs-137 (dpm/mL)	K_d* (mL/g)	% Cs removed	Measured Cs Loading (mmol/g)
B (13)	1.35E-4	2.12E6	1.38E5	1701	93.5	1.49E-2

*Dry basis

Table 1-3. ICP-OES Analysis Results Prior to and After CST Batch Contacts for Tank 10H Samples (from King, SRNL-STI-2019-00150 [2])

Metal	Tank 10H Batch 1			Tank 10H Batch 1A		
	Initial (M)	Final (M)	Final/Initial (%)	Initial (M)	Final (M)	Final/Initial (%)
Al	4.2E-2	4.1E-2	99	4.4E-2	4.4E-2	101
Ca	4.5E-5	<8.7E-6	<19	3.8E-5	<8.7E-6	<23

Another alkaline earth metal, strontium, is a known competitor for ion exchange sites on CST [4] and can decrease the absorption of cesium. In the alkaline solutions, some portion of the strontium is present as the monovalent cation, $SrOH^+$, which is believed to be the species that is absorbed by the CST. Additionally, some of the strontium that is soluble in the aqueous waste is present as ^{90}Sr, which also absorbs onto the CST, contributing radioactive inventory which causes increased dose and thermal load. Since strontium was known to absorb onto CST, it was conjectured that perhaps calcium was also absorbing and causing decreased cesium removal.

Barium is another alkaline earth metal that can be present in tank waste supernate in low concentrations. It is also important to CST chemistry because after the ^{137}Cs absorbs onto the CST, it decays via beta emission to ^{137m}Ba, which then quickly emits a gamma ray to decay to ^{137}Ba. If immediately after conversion the ^{137m}Ba were to be released from the CST, it could exit the column before emitting the gamma ray, causing a high dose rate from the liquid in down-stream equipment. Note that the inventory of ^{137}Cs on a loaded column can be extremely high, since the CST concentrates the cesium by ~1000X or more compared to the aqueous waste, so even a small amount of the ^{137m}Ba leaching could pose a hazardous situation. It is therefore important to understand the chemistry of barium absorption/retention on CST.

To perform these tests, it was first necessary to examine historical data to gain information about the range of alkaline earth metal ion solubility in actual SRS waste to determine if it is expected to have an impact if other tanks are processed. Several tank waste supernate samples were characterized by SRNL [5], and these results are shown in Table 1-4. The measurements were made on either unfiltered or filtered samples, with varying filter pore sizes. Also, some of the samples were pretreated with ammonium molybdophosphate (AMP) to remove ^{137}Cs so that subsamples could be handled in radiohoods, permitting use of more concentrated liquids to improve the detection limits. Clearly, the concentrations of the alkaline earth metals are highly variable. The reason for the variability is not clear, but a cursory comparison to the divalent anion concentration in the original report does not appear to be the cause. Also, the concentrations of alkaline earth metals are in the same molar range as cesium concentrations. The total cesium concentration was not reported, but the ^{137}Cs was 3.47E8 – 1.7E9 pCi/mL. Using an estimated 33% isotopic ratio of ^{137}Cs to total cesium, this is 12-58 mg/L (9.03E-5 - 4.36E-4 M) of total Cs; which is in a comparable molar range to the alkaline earth metals.

Most SRS tank wastes contain some amount of soluble divalent anions, such as carbonate, sulfate, and oxalate These divalent anions typically cause the divalent alkaline earth metals to have very low solubility. The data shown in Table 1-4 indicates that the solubility of the alkaline earth metals is comparable to the cesium concentration, but the speciation associated with this solubility has not been investigated. Nonetheless, it was necessary to produce a tank waste simulant that could dissolve a *reasonable* amount of alkaline earth metals. For this testing, a reasonable solubility was considered to be within the range shown in Table 1-4, and near the molar concentration of cesium. The reason for this latter criterion is because if the alkaline earth metal solubility is only a small fraction of the cesium concentration, it would not be present in sufficient amounts to influence the cesium absorption onto CST even if it was a strong competitor for binding sites. To produce a simulant that could dissolve alkaline earth metals, the OLI Studio software was used to identify a target composition that was soluble for major constituents, such as aluminum, and had good solubility of the three alkaline earth metals. The "baseline" composition used for the target composition was the simplified SRS Average simulant [6]. This composition was modified to reduce or eliminate anions that decrease the alkaline earth solubility so that their impact on cesium removal could be quantified. The compositions indicated by the OLI Studio software were then prepared in the laboratory. The simulants were then spiked with the alkaline earth metal salts in an attempt to dissolve them. If the alkaline earth metal did not dissolve, additional formulations were prepared and spiked. Once the solutions were prepared, and the alkaline earth metals shown sufficiently soluble, standard (agitated) batch contact tests were conducted. Tests evaluated the influence of the alkaline earth metals on cesium loading and determined the distribution coefficients for the alkaline earth metals on CST. Testing on removal of iron is deferred at this time because it is more likely that Ca is the key actor in this behavior, based on previous knowledge that another alkaline earth element (strontium) is well known to interfere with absorption of Cs onto ion exchange sites.

Table 1-4. Concentration of Alkaline Earth Metals in SRS Tank Waste Supernate Samples (from Stallings, et.al. [5])

Species	Filter (treatment)	Units	Average						
			Tank 13	Tank 30	Tank 37	Tank 39	Tank 45	Tank 46	Tank 49
Ba	unfiltered	mg/L	11.10	< 9.96	9.85	< 8.22	< 9.58	< 9.23	7.51
		M	8.08E-5	< 7.25E-5	7.17E-5	< 5.99E-5	< 6.98E-5	< 6.72E-5	5.47E-5
Ba	0.45 µm (No AMP)	mg/L	-	6.56	-	-	-	3.18	-
		M	-	4.78E-5	-	-	-	2.32E-5	-
Ba	0.45 µm (AMP)	mg/L	4.84	1.66	2.64	1.35	2.64	0.68	2.06
		M	3.52E-5	1.21E-5	1.92E-5	9.83E-6	1.92E-5	4.95E-6	1.50E-5
Ba	0.1 µ (AMP)	mg/L	4.61	1.11	2.44	1.17	1.35	0.43	1.76
		M	3.36E-5	8.08E-6	1.78E-5	8.52E-6	9.83E-6	3.13E-6	1.28E-5
Ba	0.02 µm (AMP)	mg/L	4.38	0.88	3.06	0.92	1.75	0.37	1.45
		M	3.19E-5	6.41E-6	2.23E-5	6.70E-6	1.27E-5	2.69E-06	1.06E-5
Ca	unfiltered	mg/L	21.80	< 301	< 12.9	< 248	< 290	< 279	< 12.6
		M	5.44E-04	< 7.51E-03	< 3.22E-04	< 6.19E-03	< 7.24E-03	< 6.96E-03	< 3.14E-04
Ca	0.45 µm (No AMP)	mg/L	-	150.0	-	-	-	9.73	-
		M	-	3.74E-03	-	-	-	2.43E-04	-
Ca	0.45 µm (AMP)	mg/L	9.09	27.10	8.40	48.20	25.80	13.40	10.30
		M	2.27E-04	6.76E-04	2.10E-04	1.20E-03	6.44E-04	3.34E-04	2.57E-04
Ca	0.1 µm (AMP)	mg/L	15.30	73.20	17.50	42.90	52.20	31.60	17.70
		M	3.82E-04	1.83E-03	4.37E-04	1.07E-03	1.30E-03	7.88E-04	4.42E-04
Ca	0.02 µm (AMP)	mg/L	23.70	35.80	19.00	41.40	32.50	23.60	17.80
		M	5.91E-04	8.93E-04	4.74E-04	1.03E-03	8.11E-04	5.89E-04	4.44E-04
Sr	unfiltered	mg/L	9.54	< 66.4	< 8.60	< 54.8	< 63.9	< 61.5	< 8.42
		M	1.09E-04	< 7.58E-04	< 9.82E-05	< 6.25E-04	< 7.29E-04	< 7.02E-04	< 9.61E-05
Sr	0.45 µm (No AMP)	mg/L	-	35.30	-	-	-	< 4.38	-
		M	-	4.03E-04	-	-	-	5.00E-5	-
Sr	0.45 µm (AMP)	mg/L	4.05	5.44	3.64	10.90	6.22	3.93	4.27
		M	4.62E-05	6.21E-05	4.15E-05	1.24E-04	7.10E-05	4.49E-05	4.87E-05
Sr	0.1 µm (AMP)	mg/L	5.27	17.00	5.90	11.10	12.30	7.84	5.90
		M	6.01E-05	1.94E-04	6.73E-05	1.27E-04	1.40E-04	8.95E-05	6.73E-05
Sr	0.02 µm (AMP)	mg/L	7.43	8.70	5.94	9.85	8.38	6.07	5.59
		M	8.48E-05	9.93E-05	6.78E-05	1.12E-04	9.56E-05	6.93E-05	6.38E-05
Species			**Average concentration**						
[Na+]	unfiltered	M	6.16	5.86	6.83	6.77	6.07	5.29	6.98
Cs-137	0.45 µm (No AMP)	(pCi/mL)	1.54E+09	8.27E+08	1.70E+09	6.73E+08	3.47E+08	5.07E+08	7.95E+08

Modeling of the expected absorption of cesium on CST was performed using the ZAM model. Although experimental data exists on the cesium absorption on CST with SRS Average simulant, none exists with the modified simulant formulations developed for this task. The ZAM model includes the competition from strontium in the calculations, but not barium or calcium. Modeling was performed using formulations both with and without the strontium.

The objective of this task is to provide an initial measurement of the absorption of alkaline earth metals and to measure their impact on absorption of cesium on CST. Non-radioactive CST batch contact tests were conducted using both modified SRS supernate simulants containing the alkaline earth metals and a TCCR Tank 10H Batch 1A simulant, along with an SRS Average supernate simulant as a "control". The tests with the simulant of Batch 1A attempted to replicate the previous radioactive waste testing as closely as possible, with and without the calcium to determine its influence. Tests using SRS simulants containing strontium were performed to quantify the absorption and the influence on cesium removal. Tests were performed with CST and simulant solutions containing soluble barium to quantify the behavior of retaining Ba after the radiolytic decay of cesium.

1.1 OLI modeling

To develop a simulant of SRS tank supernate that would have higher solubility of alkaline earth metals, modeling of the aqueous compositions was performed using OLI Studio 9.6. The initial composition input to the model was the SRS Average simulant. That formulation, shown in

Table 1-5, has been used for multiple tests with CST [6]. OLI predicts that 38% of the aluminum precipitates as gibbsite, 97% of the silicon precipitates as cancrinite, and 90% of the oxalate precipitates as natroxalate. It is known that this formulation can be produced and is almost completely soluble; but is unstable. In particular, the concentration of silica used in this formulation is known to be problematic, and has been found to cause precipitated solids in testing for both previous CST work and solvent extraction [7]. Because of this, the final formulation used for this testing did not add any silica. In the baseline composition, the oxalate appears to only partially dissolve in the simulant when it is prepared. However, since it is a divalent anion and can precipitate with divalent alkaline earth metals, it was also excluded from these test formulations. Similarly, the divalent anion molybdate is not significant to this testing, and was excluded. The aluminum does not precipitate as long as the formulation protocol is followed, but the solution is likely supersaturated. This possible supersaturation of aluminum has not been problematic in prior testing. This basic composition was then used in the OLI model to calculate a modified composition that would have higher alkaline earth metal solubility.

Table 1-5. SRS Average Simulant Composition

Chemical	Concentration (M)
NaOH	3.16
$Al(NO_3)_3 \cdot 9H_2O$	0.310
KNO_3	0.015
$CsNO_3$	1.39E-04
$NaNO_3$	1.195
$NaNO_2$	0.520
$Na_2CO_3 \cdot H_2O$	0.160
Na_2SO_4	0.150
NaCl	0.025
NaF	0.032
$Na_2HPO_4 \cdot 7H_2O$	0.010
$Na_2C_2O_4$	0.008
$Na_2SiO_3 \cdot 9H_2O$	0.004
$Na_2MoO_4 \cdot 2H_2O$	1.98E-04

1.2 ZAM Modeling

Modeling of the absorption of cations on CST was performed using the ZAM model. The techniques and methodologies have been previously reported in detail [8], and will not be repeated here.

1.3 TCCR Batch 1A Simulant Formulation

The target simulant formulation for the TCCR Batch 1A is shown in Table 1-6. The composition is the same as that used in prior ZAM modeling [8]. That composition was based on the analysis of the Batch 1A sample. Since the analysis of the Batch 1A sample was based on multiple measurements, each with their own variability, it was necessary to adjust the anions or cations to achieve charge balance and create a formulation that could be prepared from lab chemicals. Since CST is a cation exchanger, it was believed most important to maintain the total cation concentration, so the sodium, potassium, and cesium concentrations were fixed to those values obtained from the analysis. Summing the anions as measured in the radioactive sample showed that there was a shortage of anions, so an anion had to be selected to achieve charge balance. Since Cs absorption on CST is dependent on pH, the hydroxide concentration was fixed at the measured amount. Conversely, since the chloride ion has a relatively weak influence on ionic strength it has a weak infuence on Cs absorption, so was selected to charge balance the composition. The final mixture of cations and anions was then manipulated to create a formulation that could be prepared from laboratory chemicals.

Table 1-6. TCCR Batch 1A Simulant Formulation

Chemical	Concentration (g/L)	Concentration (M)
NaOH	79.55	1.99
$Al(NO_3)_3 \cdot 9H_2O$	15.8	4.22E-2
KNO_3	0.223	2.21E-3
$CsNO_3$	0.0022	1.13E-5
$NaNO_3$	50.81	0.727
$NaNO_2$	5.21	7.55E-2
$Na_2CO_3 \cdot H_2O$	39.93	0.322
Na_2SO_4	24.7	0.174
NaCl	7.42	0.127
$Na_2C_2O_4$	0.57	4.27E-3

2.0 Experimental Procedure

2.1 Simulant Preparation

The simulants were prepared by dissolving laboratory grade chemicals into deionized water. The formulations were initially prepared without addition of the alkaline earth metals. All solutions were almost clear with only traces of insoluble solids. All simulants were filtered after stirring at least 12 hours. A sample of SRS Average simulant was not prepared specifically for this work but was instead obtained from another test program [9]. Samples of the filtered simulants were analyzed for cesium by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). Metals were analyzed by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES), anions were measured by Ion Chromatography, and hydroxide by titration.

2.2 Simulant Spiking with Alkaline Earth Metals

After the simulants were prepared, the alkaline earth metal nitrate salts were added individually to subsamples of the solution. The mixtures were stirred to dissolve the alkaline earth salts. If the salts did not quickly dissolve, the solutions were heated to 60 °C on a stirrer hotplate. The solutions were then filtered at ambient temperature and analyzed for the alkaline earth metal ion concentration. The strontium and barium were analyzed by ICP-MS and the calcium was analyzed by ICP-OES.

2.3 CST Media Pretreatment

All testing in this program was performed with a sample of the CST that was the major portion of the material used in the TCCR columns. It was from production batch IONSIV R9120-B, Lot #2099000034 (Mat. #8103701-556, Sub-sample from CUA #125953-A) which had undergone the laboratory pretreatment method as described in previous reports [3].

2.4 CST Water Content Determination

Thermal Gravimetric Analysis (TGA) was conducted on each CST batch in duplicate to determine the water content. The thermal analysis involved heating sub-samples of CST at a rate 5 °C per minute to 400 °C and holding the sample at that temperature for 240 minutes followed by a second heating period to 700 °C. Mass loss profiles versus temperature during thermal analysis are provided in a previous report [10]. The total mass loss was determined as the sum of several successive mass losses believed to be associated with both physisorbed and chemisorbed water loss. Mass loss data for each CST sample up to 410 ºC is summarized and average F-factor (water content correction) values are provided in Table 2-1.

2.5 CST Batch Contact Testing

To perform the CST batch contacts tests, duplicate 10 mL (or 6 mL) sub-samples of the filtered simulants were mixed with 0.1 g (or 0.2 g) samples of CST media (hydrated CST mass basis). The simulant and CST test samples were placed in 60-mL polyethylene bottles. The mixtures were placed in a New Brunswick Scientific Innova 42 Incubator Shaker unit with a temperature controlled air atmosphere and an orbital agitation motion at a rate of 150 rpm. The mixtures were continuously agitated for four or eight contact days at either 25 or 38 °C. The oven display temperature was manually monitored and recorded periodically throughout testing and was checked with a calibrated thermometer. At test completion, individual samples were removed from the shaker, filtered through 0.45-µm syringe filters, and submitted for analysis. To prepare "blanks" for comparison, separate filtered sub-samples of each simulant solution were also placed in 60-mL bottles, agitated in the shaker oven along with the batch contact test samples (no CST contact), filtered, and submitted for analysis. CST and simulant masses for individual samples during equilibrium batch contact testing are provided in Appendix A.

Table 2-1. CST F-factor (Dry Mass Correction Factor) Data. [10]

CST Batch/Sample[a]	Sample	Mass Loss at 410 °C
LP R9120-B	A	18.530
	B	18.572
Average Mass Loss		18.551
Mass Loss %RSD		0.2%
F-factor		0.814

[a] LP = lab-pretreated Lot 209900034

2.6 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2 [11]. Results are recorded in Electronic Laboratory Notebook #E7518-00211 [12]. This report documents completion of Task 4.3 and 4.11 in the Task Technical and Quality Assurance Plan SRNL-RP-2019-00350, Rev. 1 [13]. However, due to the inability to dissolve sufficient calcium in the simulant to perform some of the testing, the calcium testing in the modified SRS average composition was not performed. The Technical Task Request (TTR) associated with this work [14] requested a functional classification of Safety Class; and this was met through technical review of this report by design verification. As described in the TTQAP [13], the OLI and ZAM modeling are for Production Support purposes only (see section 9.5 of the TTQAP entitled "Clarification of Safety Class Functional Classification"). The software packages used as part of this work scope must comply with 1Q, QAP 20-1 Software Quality Assurance, E7, Section 5.0 and Software Engineering and Control, Applicable provisions of Section 5.4, Procedure 2.31, E7 Manual.

OLI modeling is controlled under Software Quality Assurance Plan X-SQP-A-00001, Rev. 0 [15]. The ZAM Isotherm Model code is purchased commercial software developed at Texas A&M University by Z. Zheng, R. G. Anthony, and J. E. Miller designed to simulate ion-exchange equilibria of electrolytic solutions and CST solids. The ZAM model is currently classified as Level D software [16] and ZAM calculations meet the Production Support needs specified for this task in the TTR. The functional requirements placed on ZAM were verified and validated. [17]

3.0 Results and Discussion

3.1 OLI modeling

As discussed above, the SRS Average simulant formulation was used for OLI modeling. The objective of this work was to develop simulant formulations similar to the SRS Average composition, but with higher solubility of the alkaline earth ions. Initially, this modeling focused on predicting the solubility of the alkaline earth ions and on identifying which species were likely to precipitate when the alkaline earth salts were added. This approach gave an indication of which anions should be removed to increase the solubility of alkaline earth metals. The target concentrations used for the modeling are shown in Table 3-1. These concentrations were judged to be reasonably within the ranges indicated in Table 1-4, with the exception of higher barium. A higher barium concentration was targeted so that it was high enough above the analysis detection limits to enable measurement of a distribution coefficient.

Table 3-1. Alkaline Earth Spike Concentrations used in OLI modeling

Chemical	Target Concentration (M)	Target Concentration* (mg/L)
$Ca(NO_3)_2 \cdot 4H_2O$	6.27E-04	25
$Ba(NO_3)_2$	1.22E-04	17
$Sr(NO_3)_2$	1.13E-04	10

*Of the metal ion.

As expected with the SRS Average simulant, the divalent anions were predicted by the model to cause precipitation of the divalent alkaline earth cations. Barium was predicted to precipitate as the sulfate and strontium as the carbonate. OLI also predicted that calcium would precipitate as the mixed salt, fluorapatite, $Ca_5F(PO_4)_3$. To avoid fluorapatite formation, a subsequent calculation was performed that excluded phosphate; however, the calcium was predicted to still precipitate but this time as fluorite, CaF_2. The alkaline earth solubilities (Table 3-2) were at or well below the expected analysis limits, and were below the concentration of Cs and so would not be sufficient to assess its influence on absorption on CST. Because of these observations, all of the divalent anions and fluoride were removed from the simulant formulation in an attempt to prepare a simulant with higher alkaline earth metal solubility.

Table 3-2. OLI Predicted Solubility of Alkaline Earth Metals in SRS Average Simulant

Metal ion	**Solubility (M)**
Ba	1.8E-5 (2.5 mg/L)
Sr	1.0E-6 (0.088 mg/L)
Ca	2.1E-8 (8.4E-4 mg/L)

To keep the test comparable to prior testing with SRS Average simulant, the sodium ion concentration was maintained at 5.6 M, and the pH (free OH^-) and aluminate ion concentrations were also kept constant. To compensate for the absence of divalent anions and fluoride, it was necessary to add other monovalent anions to the formulation. The first formulation used sodium nitrate as the additive. The "SRS Simulant without Divalents/Fluoride" was developed and is shown in Table 3-3.

Table 3-3. SRS Tank Waste Simulant Formulations

Chemical	**SRS Avg (M)**	**SRS Sim. w/o Divalents/F (M)**	**SRS Sim. w/o Divalents/F Moderate pH (M)**
NaOH	3.16	3.16	1
$Al(NO_3)_3{\cdot}9H_2O$	0.310	0.310	0.050
KNO_3	0.015	0.015	0.015
$CsNO_3$	1.39E-04	1.39E-04	1.39E-04
$NaNO_3$	1.195	1.891	2.577
$NaNO_2$	0.520	0.520	0.520
$Na_2CO_3{\cdot}H_2O$	0.160	0.000	0.000
Na_2SO_4	0.150	0.000	0.300
NaCl	0.025	0.025	0.900
NaF	0.032	0.000	0.000
$Na_2HPO_4{\cdot}7H_2O$	0.010	0.000	0.000
$Na_2C_2O_4$	0.008	0.000	0.000
$Na_2SiO_3{\cdot}9H_2O$	0.004	0.000	0.000
$Na_2MoO_4{\cdot}2H_2O$	1.98E-04	0.00E+00	0.00E+00
Total Na	5.60	5.60	5.60
Total Nitrate	2.140	2.837	2.743
Free OH	1.92	1.92	0.80
Total Chloride	0.025	0.025	0.900

The second step in the modeling was to check the solubility of the divalent alkaline earth metals in the modified SRS simulant. This calculation was performed to project the solubility of the alkaline earth metal ions in the simulant without divalents and fluoride. Results are shown in Table 3-4. Solubility of the barium and strontium were well above the amount needed for testing, but the calcium solubility was still lower than desired to obtain good absorption data. This formulation was targeted for preparation and use in the strontium and barium absorption testing with CST.

Table 3-4. OLI Predicted Solubility of Alkaline Earth Metals in SRS Simulant without Divalents or Fluoride

Metal ion	Solubility (M)
Ba	>1.0E-2
Sr	>1.0E-2
Ca	6.1E-5 (2.4 mg/L)

In the simulant without divalents or fluoride, the calcium was predicted to have low solubility due to formation of portlandite, $Ca(OH)_2$. This suggested that reducing the free hydroxide concentration may improve the solubility of calcium. A survey of the solubility of calcium species versus pH was completed using OLI, and is shown in Figure 3-1. This suggests that this solution with a pH of ~13.9 should dissolve ~11 mg/L of calcium. Further, the predominant species is the monovalent $CaOH^+$ cation which would be expected to most directly compete with the monovalent cesium ion for binding sites on CST. These calculations led to developing another simulant that was tailored to use for calcium testing. That simulant also excluded all divalent anions except sulfate, and decreased the free hydroxide concentration. Because the composition had lower free hydroxide, it was also necessary to decrease the aluminum concentration to prevent precipitation of gibbsite. The resulting formulation, “SRS simulant without Divalents/Fluoride Moderate pH” was developed. Additional sodium nitrate, sodium sulfate, and sodium chloride were added to the formulation to compensate for the lower hydroxide and aluminate concentrations. Despite the name for this simulant, it did contain the divalent sulfate anion, but this was calculated to not cause precipitation problems. The OLI calculated solubility of Ca in this simulant is shown in Table 3-5, and the limiting species was still portlandite. Since this concentration of calcium was nearly twice the concentration of cesium in the simulant, this formulation was targeted for preparation and testing.

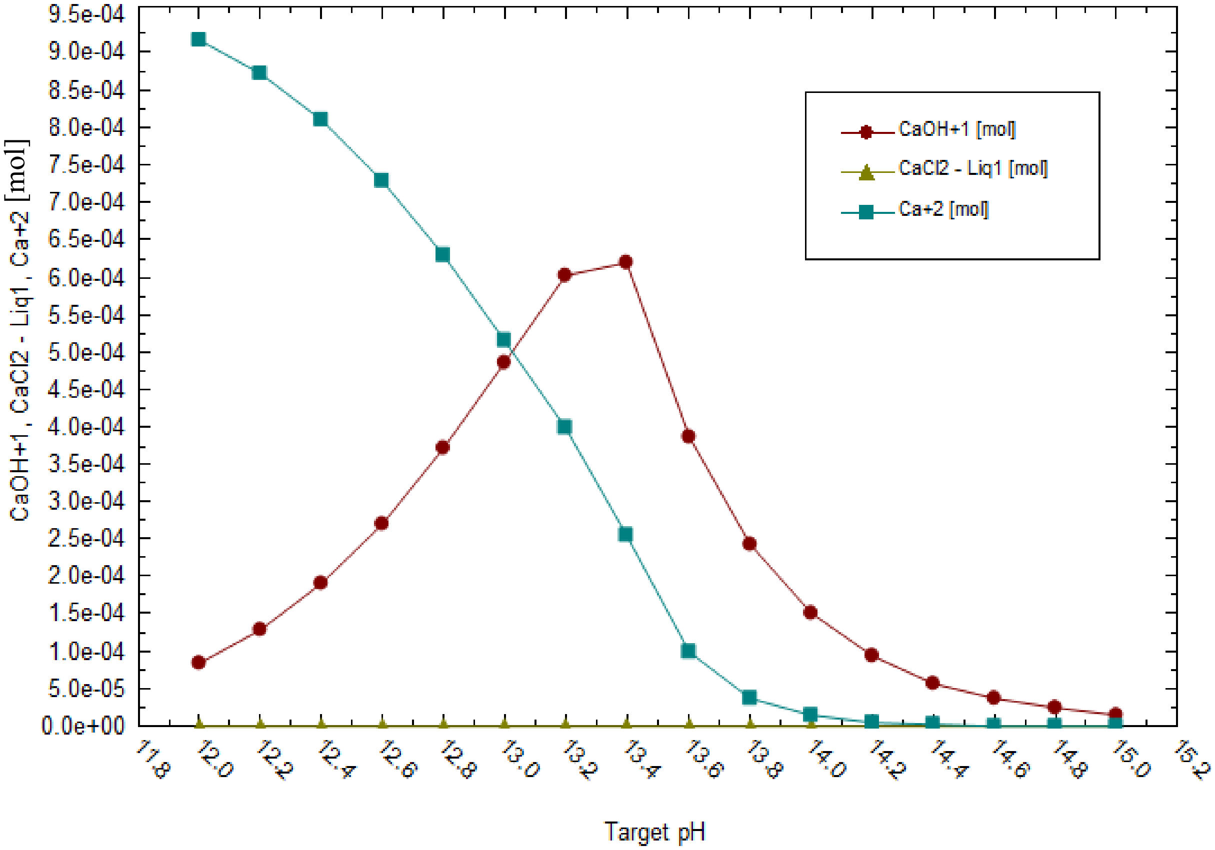

Figure 3-1. OLI model results for calcium solubility versus pH in SRS Simulant without Divalents or Fluoride

Table 3-5. OLI Predicted Solubility of Calcium in SRS Simulant without Divalents or Fluoride; Moderate pH

Metal ion	Solubility (M)
Ca	2.7E-4 (11 mg/L)

3.2 Simulant Analysis

Analytical results of the simulants used for these tests are shown in Table 3-6. The results represent analysis of duplicate samples.

Table 3-6. Simulant Filtrate Analysis Results

Species	SRS Avg (M)	Std. Dev.[a]	SRS Sim. w/o Divalents/ F (M)	Std. Dev.[a]	SRS Sim. w/o Divalents/F Moderate pH (M)	Std. Dev.[a]	TCCR Batch 1A (M)	Std. Dev.[a]
Al	0.334	2.36E-3	0.340	8.58E-3	0.0484	1.88E-3	0.0457	2.81E-3
Cs	4.35E-5	1.31E-6	1.37E-4	7.29E-7	1.38E-4	6.82E-9	1.02E-5	4.58E-8
K	0.0152	5.43E-4	< 0.019	n/a	0.0165	4.67E-4	< 0.019	n/a
Na	5.55	3.08E-2	5.42	0.109	5.85	0.190	3.52	7.83E-2
Free OH	1.82	2.83E-2	1.89	n/a	0.740	4.24E-3	1.70	n/a
NO_3^-	2.13	2.28E-2	2.97	n/a	2.90	6.84E-2	0.706	n/a
SO_4^{-2}	0.148	2.21E-3	-	-	0.316	8.83E-3	0.155	n/a
NO_2^-	0.514	1.54E-3	0.537	n/a	0.559	1.23E-2	0.0726	n/a
oxalate	5.79E-3	4.02E-5	-	-	-	-	< 5.68E-3	n/a
F^-	0.0168	1.12E-4	-	-	-	-	-	-
Cl^-	0.0242	7.98E-5	0.025	n/a	0.948	1.99E-2	0.122	n/a
PO_4^{-3}	7.07E-3	3.05E-4	-	-	-	-	-	-
CO_3^{-2}	0.166	8.33E-4	-	-	-	-	0.350	n/a
Density (g/mL)	1.253	n/a	1.255	n/a	1.257	n/a	1.165	n/a

[a]Standard deviation of the average of 2 measured values.
n/a = not applicable because of single measurement or less than detection limit
– = not added

The simulants were then spiked with calcium nitrate, barium nitrate, or strontium nitrate in the amounts shown in Table 3-2. The barium appeared to completely dissolve in the SRS Simulant without Divalents or Fluoride almost immediately. The strontium did not immediately dissolve and was therefore heated to 60 °C for two hours. Upon cooling the solution appeared clear indicating the strontium had dissolved. The calcium solution was cloudy and so was heated to 60 °C for 15 total hours. After stirring and cooling to room temperature, the solution was still cloudy, indicating that the calcium had either not dissolved or perhaps dissolved but then reprecipitated as another species. All spiked simulants were filtered through a 0.45-micron filter prior to analysis. Results of the analysis of the filtered samples are shown in Table 3-7.

Table 3-7. Alkaline Earth Metal Analysis Results

Species	SRS Sim. w/o Divalents/F (mg/L)	Std. Dev.
Ca	<1.27	n/a
Sr	7.81	3.82E-2
Ba	18.2	0.117

Since the calcium was not sufficiently soluble in this simulant, the alternate formulation was prepared that excluded most of the divalents or fluoride and was lower in hydroxide concentration. The calcium nitrate was mixed with the simulant at 60 °C for 12 hours, but the solution was still cloudy. The simulant was cooled to room temperature, filtered, and a sample was analyzed for calcium concentration. Results are shown in Table 3-8.

Table 3-8. Calcium Analysis Results

Species	SRS Sim. w/o Divalents/F Moderate pH (mg/L)	Std. Dev.
Ca	<0.17	n/a

Because the calcium was not sufficiently soluble, two other approaches were taken to try to increase the solubility. First, calcium nitrate was added a second time to the same batch of simulant. This was to address possible trace amounts of carbonate that could have been present in the simulant that was limiting the solubility. After the second addition of calcium nitrate, the mixture was stirred at room temperature for approximately 3 days followed by filtration. Second, a fresh batch of the simulant was prepared using well water from H-area tank farm instead of deionized water. The well water initially contained 15 mg/L of soluble calcium [18]. No additional calcium nitrate was added to this batch of simulant and it was not heated. The simulant samples were filtered and analyzed for calcium. Results of the analyses are shown in Table 3-9.

Table 3-9. Calcium Analysis Results for Second Preparations

Species	SRS Sim. w/o Divalents/F Moderate pH (mg/L)			
	Second strike	Std. Dev.	Well water preparation	Std. Dev.
Ca	0.743	0.131	0.89	0.0156

Since no formulation could be prepared that had soluble calcium that was in the range needed to be competitive with cesium, further testing was not performed. Although formulation of a simulant with a lower free hydroxide content would likely exhibit a higher calcium solubility, it was judged too unlike tank waste compositions to be a good comparison.

3.3 Distribution Coefficient Results

After contacting the simulants with CST, the samples were filtered and analyzed for cesium concentration, as well as barium, strontium, and calcium, as applicable. Based on the analysis results and the original total Cs analysis, cesium distribution coefficients (K_d; Equation 1), and loading (mmol Cs^+/g CST; Equation 3) values were calculated for each test sample.

$$K_d = [(C_i/C_f)-1][V/mF] \qquad \text{(Equation 1)}$$

where K_d – sorption phasic 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 hydrated reference state mass, (g), and
F – F-Factor for mass correction of CST water content.

The last grouping of terms in Equation 1 is typically referred to as the phase ratio of a given batch contact experiment expressed as:

$$\phi = V/mF \qquad \text{(Equation 2)}$$

where ϕ – phase ratio, (mL/g) and usually stated on a dry mass basis. The Cs loading can then be computed from the above values by:

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

where Q – Total Cs loading on CST, (mmol/g) and usually stated on a dry mass basis. Loading also must designate the form of CST being tested (i.e., either in powdered-form or engineered-form).

A sample of SRS Average simulant was tested with this batch of CST at 25 °C as a comparison point to prior data. The calculated distribution coefficient is shown in Table 3-10. This value is slightly lower than ZAM modeling predicts, at 1582 mL/g, but is within the range of experimental and analysis variability. Similarly, this batch of CST exhibited a measured K_d of 1701 mL/g, when measured previously at 23 °C and using a different batch of simulant [3].

Table 3-10. Distribution Coefficient Calculation Results with SRS Average Simulant at 25 °C

Simulant	**Phase Ratio**[a]	**Initial [Cs] (mg/L)**	**Final [Cs] (mg/L)**	**Cs^+ K_d (mL/g)**	**ZAM**[b] **Prediction (mL/g)**	**Cs^+ % Removal**	**mmol Cs^+/g CST**[c]
SRS Average	122:1	5.71	0.455	1414	1582	92.0	4.8E-3

a. Dry Basis
b. Assumes binder dilution factor = 0.68
c. Dry basis of engineered material

3.4 Batch 1A Simulant Testing

As discussed above, a simulant of the TCCR Batch 1A was prepared and tested with CST. The testing was to examine the cause of the lower-than-expected distribution coefficient obtained from testing with the radioactive tank waste sample. That testing had been performed at 38 °C. The simulant was tested with and without added calcium. Tests were performed with two different phase ratios to obtain two points on the isotherm. Results are shown in Table 3-11. The measured K_d with added Ca, 1887 mL/g, is comparable to that measured with the Tank 10 Batch 1A radioactive sample, which was 1948 mL/g [2]. The measured K_d in the Batch 1A simulant without added Ca was similar, 1832 mL/g, indicating that Ca did not have an influence on Cs removal under these conditions.

Table 3-11. Distribution Coefficient Calculation Results with Batch 1A Simulant

Simulant	Phase Ratio[a]	Temp. (°C)	Days	Initial[b] [Cs] (mg/L)	Final [Cs] (mg/L)	Cs^+ K_d (mL/g)	Initial[b] [Ca] (mg/L)	Final [Ca] (mg/L)	Ca K_d (mL/g)
TCCR 1A	124:1	38	4	1.35	0.084	1832	NA	NA	NA
TCCR 1A	37:1	38	4		0.028	1721	NA	NA	NA
TCCR 1A	122:1	25	8		0.046	3253	NA	NA	NA
TCCR 1A with Ca	123:1	38	4		0.083	1887	2.48	< 0.989	> 223
TCCR 1A with Ca	37:1	38	4		0.032	1535		< 0.989	> 67

a. Dry Basis
b. Values are the overall average of all analyses (control samples and initial characterization).

3.5 SRS Simulant Testing

As discussed above, a simulant of SRS tank supernate designed for increased alkaline earth solubility was prepared and tested with CST. The testing was to examine the influence of the strontium and calcium on the Cs absorption and to examine the retention of barium on the CST as the ^{137}Cs decays to ^{137m}Ba. Since the calcium did not dissolve in the simulants, that testing was not performed. The simulant was tested with and without added strontium and barium. All mixtures were agitated for four days or eight days at 25 °C. Tests were performed with two different phase ratios in order to obtain two points on the isotherm. Results are shown in Table 3-112.

The calculated K_d for the eight-day test with SRS simulant was only marginally higher than the four-day test, indicating that the samples were very near equilibrium after four days. Secondly, the results show that the addition of 7.92 mg/L of strontium did not influence the cesium removal and that the K_d for strontium was more than an order of magnitude higher than for cesium. Third, the barium behavior was very similar to strontium. The barium did not influence the K_d for cesium, and its K_d was nearly an order of magnitude higher than cesium. This indicates that the barium would likely be retained on the CST after the ^{137}Cs converts to ^{137m}Ba. Finally, using a phase ratio of ~120:1 or 37:1 resulted in nearly the same K_d value for cesium, indicating a linear isotherm in this range. It should be noted that although the cesium loading on CST appeared to be complete after 4 contact days, the alkaline earth loading increased between 4 and 8 days, indicating slower alkaline loading kinetics relative to cesium.

Table 3-12. Distribution Coefficient Calculation Results with SRS Simulant without Divalents or Fluoride at 25 °C

Simulant	Phase Ratio[a]	Days	Initial[b] [Cs] (mg/L)	Final [Cs] (mg/L)	Cs^+ K_d (mL/g)	Initial[b] [AE][c] (mg/L)	Final [AE] (mg/L)	AE K_d (mL/g)
SRS Sim w/o Div/F	122:1	4	18.2	1.84	1091	NA	NA	NA
SRS Sim w/o Div/F	37:1	4		0.61	1066	NA	NA	NA
SRS Sim w/o Div/F	122:1	8		1.77	1132	NA	NA	NA
SRS Sim w/o Div/F w/ Sr	123:1	4		1.94	1031	7.92	0.059	1.64E4
SRS Sim w/o Div/F w/ Sr	37:1	4		0.63	1028		0.016	1.85E4
SRS Sim w/o Div/F w/ Sr	123:1	8		1.80	1137		0.030	3.35E4
SRS Sim w/o Div/F w/ Ba	123:1	4		1.96	1028	18.2	0.13	1.70E4
SRS Sim w/o Div/F w/ Ba	37:1	4		0.62	1044		0.038	1.79E4
SRS Sim w/o Div/F w/ Ba	123:1	8		1.81	1107		0.061	3.62E4

a. Dry Basis
b. Values are the overall average of all analyses (control samples and initial characterization).
c. AE = alkaline earth metal

3.6 Comparison of Distribution Coefficients to ZAM

The ZAM model was used to calculate the expected distribution coefficients for the various simulants used in this testing. Those results are shown in Table 3-13. Also in Table 3-13 the optimized correction factors are given at which the ZAM results are equal to the test data. All optimized values are lower than the historical dilution factor value of 0.68, but the reason for the lower values has not been determined. For the TCCR 1A with Ca simulant at 38 °C, ZAM was used to calculate the K_d for strontium and this is shown in the "ZAM AE Prediction" column. Although this calculation is for strontium, the testing shown in the previous sections indicates that calcium and strontium exhibit comparable performance. The calculated value, 1.17E5 mL/g, is shown to give an indication of what the expected performance would be for strontium. Similarly, the ZAM model calculated the K_d for cesium using the same substitution of strontium for calcium.

All of the test results are slightly lower than the ZAM calculation results. Although the test results are generally within the experimental and analytical variability, all of the results show the same bias to lower K_d values. The reason for this offset is not known. It is possible that the ZAM model is over-predicting the cesium absorption under these conditions. The mixture excludes the divalent anions, and perhaps the ZAM calculation of activity coefficients is less accurate for this composition. Second, ZAM must account for the temperature increase, and limited testing has been done to examine its ability to do so.

Table 3-13. ZAM Calculated versus Measured Distribution Coefficients

Simulant	**Phase Ratio**[a]	**Temp °C**	**Cs^+ K_d (mL/g)**	**ZAM**[b] **K_d Prediction (mL/g)**	**Optimized Correction Factor**	**AE K_d**	**ZAM**[b] **AE K_d Prediction (mL/g)**
TCCR 1A	124:1	38	1832	2859	0.437	NA	NA
TCCR 1A	122:1	25	3253	4077	0.543	NA	NA
TCCR 1A with Ca	123:1	38	1887	2859	0.45	> 233	*1.17E5*
SRS Sim No Div/F	122:1	25	1091	1229	0.606	NA	NA
SRS Sim No Div/F	122:1	25	1132[c]	1229	0.629	NA	NA
SRS Sim No Div/F w/ Sr	123:1	25	1031	1205	0.588	16440	7664
SRS Sim No Div/F w/ Ba	123:1	25	1028	1229	0.573	16950	NA

a. Dry basis.
b. Assumes correction factor = 0.68
c. Results from 8-day batch contact test; all others are 4-day.

4.0 Conclusions

Utilizing OLI modeling, a modified SRS Average simulant formulation was developed that provided a composition that exhibited sufficient solubility of Sr and Ba to perform testing of the impact of alkaline earth metals. The increased solubility was achieved by removing the divalent anions, phosphate, and fluoride. In contrast, Ca could not be dissolved to a sufficient concentration in this modified SRS Average simulant, which the OLI software indicated was due to the precipitation of $Ca(OH)_2$. Consequently, an alternate simulant was developed with a lower pH (lower free $[OH^-]$); however, the calcium was still not sufficiently soluble. Further decreasing the pH would likely have resulted in a simulant with sufficient Ca solubility, but it was determined that composition deviated too far from radioactive waste compositions to provide a reasonable comparison. By contrast, a simulant of the TCCR Batch 1A composition was successfully prepared both with and without soluble Ca.

Batch contact testing was performed with the various simulant solutions and results of the testing showed that the alkaline earths were efficiently removed by the CST, resulting in high distribution coefficients (K_d); however, their presence had minimal influence on the Cs removal under these conditions. The minimal measured influence on Cs removal was consistent with that predicted by the ZAM modeling for these compositions. In general, the measured K_d values were (8-36%) lower than predicted by ZAM, particularly for the TCCR Batch 1A composition. The reason for theses lower values has not been determined, but may be due to a chemical interference or inaccurate projections by the ZAM model for these conditions of composition and temperature.

5.0 Future Work

Further testing is recommended to examine the influence of calcium. Since it is challenging to develop a simulant that will dissolve calcium, this is best done using tank waste samples. Samples of tank waste that contain soluble calcium either at or above the molar concentration of cesium have been identified previously, and could be used for this testing. Pre-striking a portion of the sample with monosodium titanate would remove the calcium but leave the cesium unaffected, and could be used for “with and without calcium” batch contact tests.

Further testing is also recommended to determine the cause of the lower than expected absorption of cesium with the batch of SRS Average simulant. It appears that this batch of simulant exhibited lower K_d values for both this test program and another [9], indicating that an interfering species is present.

Finally, further testing is recommended to determine if ZAM can accurately account for differences in anion composition and temperature.

6.0 References

1. Taylor-Pashow, K. M. L., Hang, T., and Nash, C. A. “Summary of Expedited Results from Samples Supporting Tank Closure Cesium Removal (TCCR) Batch 1A and Modeling Results for Cs Loading on CST”, SRNL-L3100-2019-00002, Rev. 2, February 2019.
2. King, W. D., Hamm, L. L., Hang, T., and Fondeur, F. F. “CST Batch Contact Equilibrium Testing of TCCR Tank 10H Batch 1 and 1A Waste Supernate Samples”, SRNL-STI-2019-00150, Rev. 0, April 2019.
3. King, W. D., Hamm, L. L., Coleman, C. J., Fondeur, F. F., Reboul, S. H. “Crystalline Silicotitanate (CST) Ion Exchange Media Performance Evaluations in SRS Average Supernate Simulant and Tank 10H Waste Solution to Support TCCR”, SRNL-STI-2018-00277, Rev. 0, June 2018.
4. Hamm, L. L., Hang, T., McCabe, D. J., King, W. D., “Preliminary Ion Exchange Modeling for Removal of Cesium from Hanford Waste Using Hydrous Crystalline Silicotitanate Material”, WSRC-TR-2001-00400, Rev. 0, July 2002.
5. Stallings, M.E., Barnes, M.J., Peters, T.B., Diprete, D.P., Fondeur, F.F., Hobbs, D.T., Fink, S.D., Characterization of Supernate Samples from High Level Waste Tanks 13H, 30H, 37H, 39H, 45F, 46F and 49H, WSRC-TR-2004-00386, Revision 2, June 15, 2005.
6. Walker, D. D. “Preparation of Simulated Waste Solutions”, WSRC-TR-99-00116, Rev. 0, April 1999.

7. Wilmarth, W. R., Hang, T., Mills, J. T., Dukes, V. H, Fink, S. D., “The Effect of Pretreatment, Superficial Velocity, and Presence of Organic Constituents on IONSIV® IE-911 Column Performance”, WSRC-TR-99-00313, August 1999.
8. Hang, T., Modeling Crystalline Silicotitanate Performance to Support TCCR Batch 1 and Batch 1A Operations, SRNL-STI-2019-00147, May, 2019.
9. King, W. D., Mathurin, L. E., Hang, T., Fondeur, F. F., “Cesium Removal Performance Comparisons of Crystalline Silicotitanate Media Batches with Savannah River Site Waste Simulant”, SRNL-STI-2019-00648, Rev. 0, October 2019.
10. King, W. D., Taylor-Pashow, K. M., Hang, T., Fondeur, F. F., “Characterization and CST Batch Contact Equilibrium Testing of Aged TCCR Tank 10H Batch 1A and 2 Process Supernate Samples”, SRNL-STI-2019-00623, Rev. 0, October 2019.
11. “Savannah River National Laboratory Technical Report Design Check Guidelines”, WSRC-IM-2002-00011, Rev. 2, August 2004.
12. Savannah River National Laboratory Electronic Laboratory Notebook #E7518-00211.
13. King, W. D., McCabe, D. J., Nash, C. A., “Task Technical and Quality Assurance Plan for CST Batch Contact and Column Testing to Support Tank Closure Cesium Removal Operations”, SRNL-RP-2019-00350. Rev. 1, July 2019.
14. Fellinger, T. L., “Research and Development (R&D) for Tank 9 Processing Through the Tank Closure Cesium Removal (TCCR) Unit”, X-TTR-H-00085, Rev. 0, May 2019.
15. Choi, A. S. “Software Quality Assurance Plan for OLI Platform Software Used at the Savannah River Site”, X-SQP-A-00001, Rev. 0, September 2019.
16. Tamburello, D. A., “Software Classification Document – ZAM”, B-SWCD-A-00598, May 2011.
17. Hamm, L. L., Hang, T., McCabe, D. J., and King, W. D. “Preliminary Ion Exchange Modeling for Removal of Cesium from Hanford Waste Using Hydrous Crystalline Silicotitanate Material”, WSRC-TR-2001-00400, July 2001.
18. Taylor-Pashow, K. M. L. “Summary of Analytical Results from Tank 11H Tank Closure Cesium Removal (TCCR) Post-Batch 2 Processing Sample”, SRNL-L3100-2019-00028, Rev. 0, August 2019.

Appendix A. Batch Contact Testing Experimental Details

Table A-1. Experimental Details for Batch Contact Tests with SRS Average Simulant

Test ID	SRS-AVG-1	SRS-AVG-2
Temperature (°C)	25	
Simulant	SRS Average (TCCR-2019-2)	
Measured Mass CST (g)	0.1001	0.1007
F-Factor Correct CST Mass (g)	0.0815	0.0820
Mass of Simulant (g)	12.5577	12.4924
Volume of Simulant (mL)	10.02	9.97
Phase Ratio (mL/g)	123	122
Contact Time (h)	196	196

Table A-2. Experimental Details for Batch Contact Tests with TCCR Batch 1A Simulant

Test ID	TCCR-Sim-11	TCCR-Sim-12	TCCR-Sim-14	TCCR-Sim-15	TCCR-Sim-16	TCCR-Sim-17
Temperature (°C)	25			38		
Simulant	TCCR Batch 1A Simulant					
Measured Mass CST (g)	0.1006	0.1003	0.0998	0.1002	0.1999	0.2007
F-Factor Correct CST Mass (g)	0.0819	0.0817	0.0813	0.0816	0.1628	0.1635
Mass of Simulant (g)	11.6763	11.6588	11.7231	11.7362	7.0091	7.0254
Volume of Simulant (mL)	10.02	10.01	10.06	10.07	6.02	6.03
Phase Ratio (mL/g)	122	123	124	123	37	37
Contact Time (h)	196	196	96	96	96	96

Table A-3. Experimental Details for Batch Contact Tests with Ca Spiked TCCR Batch 1A Simulant

Test ID	Ca-TCCR-Sim-6	Ca-TCCR-Sim-7	Ca-TCCR-Sim-8	Ca-TCCR-Sim-9
Temperature (°C)	38			
Simulant	Ca Spiked TCCR Batch 1A Simulant			
Measured Mass CST (g)	0.1002	0.0999	0.2000	0.1999
F-Factor Correct CST Mass (g)	0.0816	0.0814	0.1629	0.1628
Mass of Simulant (g)	11.6793	11.6969	7.0086	7.0265
Volume of Simulant (mL)	10.03	10.04	6.02	6.03
Phase Ratio (mL/g)	123	123	37	37
Contact Time (h)	96	96	96	96

Table A-4. Experimental Details for Batch Contact Tests with SRS Average Simulant without Divalents or Fluoride

Test ID	SRS Sim-0DVF-1	SRS Sim-0DVF-2	SRS Sim-0DVF-3	SRS Sim-0DVF-4	SRS Sim-0DVF-6	SRS Sim-0DVF-7
Temperature (°C)	25					
Simulant	SRS 5.6 M Na Simulant without divalents or fluoride					
Measured Mass CST (g)	0.1010	0.1008	0.2001	0.2001	0.1010	0.1002
F-Factor Correct CST Mass (g)	0.0823	0.0821	0.1630	0.1630	0.0823	0.0816
Mass of Simulant (g)	12.5649	12.5377	7.4627	7.4819	12.5780	12.5503
Volume of Simulant (mL)	10.02	9.99	5.95	5.96	10.03	10.00
Phase Ratio (mL/g)	122	122	36	37	122	123
Contact Time (h)	97	97	97	97	196	196

Table A-5. Experimental Details for Batch Contact Tests with Sr Spiked SRS Average Simulant without Divalents or Fluoride

Test ID	**Sr-SRS Sim-0DVF-1**	**Sr-SRS Sim-0DVF-2**	**Sr-SRS Sim-0DVF-3**	**Sr-SRS Sim-0DVF-4**	**Sr-SRS Sim-0DVF-6**	**Sr-SRS Sim-0DVF-7**
Temperature (°C)	25					
Simulant	Sr Spiked SRS 5.6 M Na Simulant without divalents or fluoride					
Measured Mass CST (g)	0.1001	0.0997	0.1999	0.1999	0.1001	0.1002
F-Factor Correct CST Mass (g)	0.0815	0.0812	0.1628	0.1628	0.0815	0.0816
Mass of Simulant (g)	12.5828	12.5453	7.5103	7.5050	12.6599	12.6045
Volume of Simulant (mL)	10.03	10.00	5.99	5.98	10.09	10.05
Phase Ratio (mL/g)	123	123	37	37	124	123
Contact Time (h)	97	97	97	97	196	196

Table A-6. Experimental Details for Batch Contact Tests with Ba Spiked SRS Average Simulant without Divalents or Fluoride

Test ID	**Ba-SRS Sim-0DVF-1**	**Ba-SRS Sim-0DVF-2**	**Ba-SRS Sim-0DVF-3**	**Ba-SRS Sim-0DVF-4**	**Ba-SRS Sim-0DVF-6**	**Ba-SRS Sim-0DVF-7**
Temperature (°C)	25					
Simulant	Ba Spiked SRS 5.6 M Na Simulant without divalents or fluoride					
Measured Mass CST (g)	0.0999	0.0999	0.1999	0.2006	0.0997	0.0997
F-Factor Correct CST Mass (g)	0.0814	0.0814	0.1628	0.1634	0.0812	0.0812
Mass of Simulant (g)	12.5729	12.5608	7.5112	7.4975	12.6036	12.5560
Volume of Simulant (mL)	10.02	10.01	5.99	5.98	10.05	10.01
Phase Ratio (mL/g)	123	123	37	37	124	123
Contact Time (h)	97	97	97	97	196	196

Appendix B. Analysis Results

Table B-1. Analysis Results for Batch Contact Tests with SRS Average Simulant

Test ID	SRS-AVG-1	SRS-AVG-2	SRS-AVG-3 (control/blank)
[Sr] (µg/L)	< 2.00E+00	< 2.00E+00	7.23E+01
[Cs] (µg/L)	4.62E+02	4.47E+02	5.71E+03
[Ba] (µg/L)	< 2.00E+00	< 2.00E+00	1.10E+02

Table B-2. Analysis Results for Batch Contact Tests with TCCR Batch 1A Simulant

Test ID	TCCR-Sim-11	TCCR-Sim-12	TCCR-Sim-13 (control/blank)	TCCR-Sim-14	TCCR-Sim-15	TCCR-Sim-16	TCCR-Sim-17	TCCR-Sim-18 (control/blank)
[Sr] (µg/L)	< 2.00E+00	< 2.00E+00	3.51E+01	< 1.00E+01	< 1.00E+01	< 1.00E+01	< 1.00E+01	9.47E+01
[Cs] (µg/L)	4.47E+01	4.72E+01	1.27E+03	8.32E+01	8.57E+01	1.46E+01	1.41E+01	1.36E+03
[Ba] (µg/L)	< 2.00E+00	< 2.00E+00	1.06E+02	1.70E+01	1.71E+01	< 1.00E+01	< 1.00E+01	1.37E+02

Table B-3. Analysis Results for Batch Contact Tests with Ca Spiked TCCR Batch 1A Simulant

Test ID	Ca-TCCR-Sim-6	Ca-TCCR-Sim-7	Ca-TCCR-Sim-8	Ca-TCCR-Sim-9	Ca-TCCR-Sim-10 (control/blank)
[Sr] (µg/L)	1.09E+01	< 1.00E+01	< 1.00E+01	< 1.00E+01	5.49E+01
[Cs] (µg/L)	6.79E+01	7.39E+01	1.40E+01	1.34E+01	1.36E+03
[Ba] (µg/L)	2.79E+01	< 1.00E+01	< 1.00E+01	< 1.00E+01	1.47E+02
[Ca] (mg/L)	< 0.989	< 0.989	< 0.989	< 0.989	2.78

Table B-4. Analysis Results for Batch Contact Tests with SRS Average Simulant without Divalents or Fluoride

Test ID	SRS Sim-0DVF-1	SRS Sim-0DVF-2	SRS Sim-0DVF-3	SRS Sim-0DVF-4	SRS Sim-0DVF-5 (control/blank)	SRS Sim-0DVF-6	SRS Sim-0DVF-7	SRS Sim-0DVF-8 (control/blank)
[Sr] (µg/L)	< 2.00E+00	< 2.00E+00	< 2.00E+00	< 2.00E+00	5.22E+01	< 2.00E+00	< 2.00E+00	4.88E+01
[Cs] (µg/L)	1.79E+03	1.89E+03	5.97E+02	6.18E+02	1.83E+04	1.71E+03	1.83E+03	1.82E+04
[Ba] (µg/L)	< 2.00E+00	< 2.00E+00	< 2.00E+00	< 2.00E+00	4.72E+02	< 2.00E+00	< 2.00E+00	4.60E+02

Table B-5. Analysis Results for Batch Contact Tests with Sr Spiked SRS Average Simulant without Divalents or Fluoride

Test ID	Sr-SRS Sim-0DVF-1	Sr-SRS Sim-0DVF-2	Sr-SRS Sim-0DVF-3	Sr-SRS Sim-0DVF-4	Sr-SRS Sim-0DVF-5 (control/blank)	Sr-SRS Sim-0DVF-6	Sr-SRS Sim-0DVF-7	Sr-SRS Sim-0DVF-8 (control/blank)
[Sr] (µg/L)	6.05E+01	5.74E+01	1.57E+01	1.57E+01	7.92E+03	3.06E+01	2.91E+01	8.14E+03
[Cs] (µg/L)	1.93E+03	1.95E+03	6.32E+02	6.23E+02	1.82E+04	1.81E+03	1.80E+03	1.84E+04
[Ba] (µg/L)	< 2.00E+00	< 2.00E+00	< 2.00E+00	< 2.00E+00	6.30E+02	< 2.00E+00	< 2.00E+00	6.08E+02

Table B-6. Analysis Results for Batch Contact Tests with Ba Spiked SRS Average Simulant without Divalents or Fluoride

Test ID	Ba-SRS Sim-0DVF-1	Ba-SRS Sim-0DVF-2	Ba-SRS Sim-0DVF-3	Ba-SRS Sim-0DVF-4	Ba-SRS Sim-0DVF-5 (control/blank)	Ba-SRS Sim-0DVF-6	Ba-SRS Sim-0DVF-7	Ba-SRS Sim-0DVF-8 (control/blank)
[Sr] (µg/L)	< 1.90E+01	< 1.90E+01	< 1.90E+01	< 1.90E+01	6.00E+01	< 2.00E+00	< 2.00E+00	5.16E+01
[Cs] (µg/L)	1.97E+03	1.96E+03	6.32E+02	6.12E+02	1.83E+04	1.76E+03	1.86E+03	1.80E+04
[Ba] (µg/L)	1.31E+02	1.34E+02	3.70E+01	3.82E+01	1.84E+04	6.04E+01	6.06E+01	1.78E+04

Appendix C. ZAM isotherm parameters.

Feed	**T (^{0}C)**	**η_{df}**	**C_T (mmol$_{Cs}$/g$_{CST}$)**	**ρ_{Bed} (g$_{CST}$/ml)**	**M_a**	**M_b**	**β**	**b**
TCCR Batch 1A	25	1	0.58	0.9892	1	1	9.6974E-5	1
TCCR Batch 1A	38	1	0.58	0.9892	1	1	1.3781E-4	1
TCCR Batch 1A w/o Sr	38	1	0.58	0.9892	1	1	1.3768E-4	1
SRS Avg w/o Divalents & F	25	1	0.58	0.9892	1	1	5.1373E-4	1
SRS Avg w/o Divalents, F, Sr	25	1	0.58	0.9892	1	1	3.0895E-4	1

Appendix D. Cesium and Alkaline Earth Loadings on CST.

Table D-1. Cesium and Calcium Loading from TCCR Batch 1A Simulant

Simulant	Phase Ratio[a]	Temp. (°C)	Days	Cs Loading (mmol/g_{CST})	Ca Loading (mmol/ g_{CST})
TCCR 1A	124:1	38	4	1.16E-03	NA
TCCR 1A	37:1	38	4	3.63E-04	NA
TCCR 1A	122:1	25	8	1.12E-03	NA
TCCR 1A with Ca	123:1	38	4	1.17E-03	> 5.50E-06
TCCR 1A with Ca	37:1	38	4	3.67E-04	> 1.65E-06

a. Dry Basis

Table D-2. Cesium and Alkaline Earth Loadings from SRS Simulant without Divalents or Fluoride at 25 °C

Simulant	Phase Ratio[a]	Days	Cs Loading (mmol/g_{CST})	AE[b] Loading (mmol/ g_{CST})
SRS Sim w/o Div/F	122:1	4	1.51E-02	NA
SRS Sim w/o Div/F	37:1	4	4.88E-03	NA
SRS Sim w/o Div/F	122:1	8	1.51E-02	NA
SRS Sim w/o Div/F w/ Sr	123:1	4	1.50E-02	1.10E-02
SRS Sim w/o Div/F w/ Sr	37:1	4	4.85E-03	3.32E-03
SRS Sim w/o Div/F w/ Sr	123:1	8	1.54E-02	1.14E-02
SRS Sim w/o Div/F w/ Ba	123:1	4	1.52E-02	1.64E-02
SRS Sim w/o Div/F w/ Ba	37:1	4	4.89E-03	4.91E-03
SRS Sim w/o Div/F w/ Ba	123:1	8	1.51E-02	1.59E-02

a. Dry Basis
b. AE = alkaline earth metal

Distribution:

alex.cozzi@srnl.doe.gov
david.crowley@srnl.doe.gov
a.fellinger@srnl.doe.gov
samuel.fink@srnl.doe.gov
connie.herman@srnl.doe.gov
Joseph.Manna@srnl.doe.gov
john.mayer@srnl.doe.gov
daniel.mccabe@srnl.doe.gov
Gregg.Morgan@srnl.doe.gov
frank.pennebaker@srnl.doe.gov
Amy.Ramsey@srnl.doe.gov
William.Ramsey@SRNL.DOE.gov
michael.stone@srnl.doe.gov
Boyd.Wiedenman@srnl.doe.gov
jeffrey.crenshaw@srs.gov
james.folk@srs.gov
tony.polk@srs.gov
patricia.suggs@srs.gov
celia.aponte@srs.gov
timothy.baughman@srs.gov
earl.brass@srs.gov
Richard.Edwards@srs.gov
Azikiwe.hooker@srs.gov
Thomas.Huff@srs.gov
Ryan.McNew@srs.gov
phillip.norris@srs.gov
Christine.Ridgeway@srs.gov
Azadeh.Samadi-Dezfouli@srs.gov
Christie.sudduth@srs.gov
Vijay.Jain@srs.gov
arthur.wiggins@srs.gov
terri.fellinger@srs.gov
eric.freed@srs.gov
john.occhipinti@srs.gov
john.iaukea@srs.gov
Aubrey.Silker@srs.gov
david02.martin@srs.gov
gregory.arthur@srs.gov
Alexander.Luzzatti@srs.gov
Rachel.Seeley@srs.gov
Records Administration (EDWS)