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Initial Testing of Alkaline Earth Metal Ion Absorption on Crystalline Silicotitanate – 20440

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ABSTRACT

The Tank Closure Cesium Removal process at the Savannah River Site (SRS) has processed aqueous tank waste using the inorganic ion exchange media IONSIV™ R9120-B[a] (which is also known as Crystalline Silicotitanate (CST)). Saltcake in Tank 10H at SRS was dissolved and processed through filters and ion exchange columns. The primary purpose of the process is to remove Cs-137 from the aqueous waste so that it can be disposed as low level waste. It is known that this inorganic media also absorbs strontium from solution, and that strontium competes with cesium ions for absorption sites. The strontium ion is actually more strongly absorbed than the cesium ion from typical tank waste. However, strontium is typically present in low concentrations so does not normally cause a significant impact. Strontium is present as both non-radioactive isotopes and the radioactive Sr-90 isotope; with the non-radioactive isotopes being much more abundant. Although the total strontium solubility is usually much lower than cesium, some tank waste compositions can have a high enough soluble strontium concentration to decrease the cesium absorption. Relatedly, some testing at SRS suggested that another alkaline earth metal, calcium, may also absorb onto CST and may decrease cesium absorption. Barium is also an important species in treatment of tank waste, but is also usually present at low concentrations. However, after the Cs-137 is absorbed onto CST, it emits a beta particle and converts to Ba-137m, which then decays to non-radioactive Ba-137 by emission of a gamma ray. If the Ba-137m were to desorb quickly, it could impact the dose rate in down-stream equipment. In order to understand the impact of these alkaline earth metals on CST, SRNL performed testing using simulants of SRS tank waste that contain soluble barium, strontium, and calcium. Testing examined both removal of the alkaline earth metals and their impact on removal of cesium. Testing involved first developing realistic waste simulant formulations and dissolving the alkaline earth metals to high enough concentrations to potentially impact the Cs absorption. Once the formulations were developed and prepared, computer modeling was used to calculate the expected Cs absorption behavior to determine if the alkaline earth metals impact the performance. Measurements of the alkaline earth metals absorption by the media is also important for disposition of spent media because of the added radionuclide inventory from the Sr-90. These initial tests are examining the general impact and will be used to determine if further testing or measurements are needed.

INTRODUCTION

In 2019, Savannah River Remediation (SRR) deployed the Tank Closure Cesium Removal (TCCR) system using an ion exchange (IX) process to remove radioactive Cs-137 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. Four TCCR columns were constructed, loaded with CST, and installed in a modular skid unit and installed at the SRS. 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. The method involved placing a

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[a] IONSIV is a trademark of Honeywell UOP, Inc. Des Plaines, Illinois, USA

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 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 10H Batch 1A tank samples in laboratory testing [1]. The subsequent modeling with the ZAM isotherm model indicated a correction factor was needed to adjust the results to the isotherm. Conversely, samples of the same batch of CST exhibited normal cesium removal behavior with SRS Average simulant [2], indicating that the batch exhibited normal performance when tested with routine simulant. Comparison of those 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] However, both TCCR field teabag data and standard laboratory CST batch contact tests [1] 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 [1], indicating that the tank sample was unstable towards precipitation, either due to supersaturation or cooling after sampling from the tank which had elevated temperature.

Another alkaline earth metal, strontium, is a known competitor for ion exchange sites on CST [3] and was thought to 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 Sr-90, 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 Cs-137 absorbs onto the CST, it decays via beta emission to Ba-137m, which then quickly emits a gamma ray to decay to Ba-137. In theory, if immediately after conversion the Ba-137m 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 Cs-137 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 Ba-137m leaching out could create a hazardous situation. It is therefore important to understand the chemistry of barium absorption/retention on CST.

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. Historical data from the characterization several SRS waste tanks shows the concentration of alkaline earths in the waste is highly variable, and in some cases is in the same molar range as the cesium

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[b] A binder dilution factor is invoked because the ZAM model was created 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.

concentrations [4]. The speciation that causes 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 of the historical data, 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 impact the cesium absorption onto CST even if it was a strong competitor for binding sites. In order to produce a simulant that could dissolve alkaline earth metals, the OLIStudio software was used to first get an idea of 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. This composition was then 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 OLIStudio software were then prepared in the laboratory and were 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 impact of the alkaline earth metals on cesium loading and determined the distribution coefficients for the alkaline earth metals on CST.

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 was 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 average SRS supernate simulant as a "control". The tests with the simulant of Batch 1A attempted to replicate the previous actual waste testing as closely as possible, with and without the calcium to determine its impact. Tests using SRS simulants containing strontium were performed to quantify the absorption and the impact 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.

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 OLIStudio 9.6. The initial composition input to the model was the SRS Average Simulant. That formulation, shown in Table I, has been used for multiple tests with CST [5]. OLI predicts that 38% of the aluminum precipitates as gibbsite, 98% of the silicon precipitates as cancrinite, and 90% of the oxalate precipitates as natroxalate. It is known that this SRS Average 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. Because of this, the final actual 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 I. SRS Average Simulant Composition

Chemical	Concentration (M)	OLI predicted % soluble (solid species)
NaOH	3.16	100
$Al(NO_3)_3 \cdot 9H_2O$	0.310	62 (gibbsite)
KNO_3	0.015	100
$CsNO_3$	1.39E-04	100
$NaNO_3$	1.195	100
$NaNO_2$	0.520	100
$Na_2CO_3 \cdot H_2O$	0.160	100
Na_2SO_4	0.150	100
NaCl	0.025	100
NaF	0.032	100
$Na_2HPO_4 \cdot 7H_2O$	0.010	100
$Na_2C_2O_4$	0.008	10 (natroxalate)
$Na_2SiO_3 \cdot 9H_2O$	0.004	2 (cancrinite)
$Na_2MoO_4 \cdot 2H_2O$	1.98E-04	100

ZAM Modeling

Modeling of the absorption of cations on CST was performed using the ZAM (Zheng, Anthony, and Miller) model developed at Texas A&M University. The techniques and methodologies have been previously reported in detail [6].

TCCR Batch 1A Simulant Formulation

The target simulant formulation for the TCCR Batch 1A is shown in Table II. The composition is the same as that used in prior ZAM modeling [6]. 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 actually 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 impact on ionic strength it has a weak impact 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 actually be prepared from laboratory chemicals.

TABLE II. 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

DESCRIPTION OF METHODS

Simulant Preparation

The simulants were prepared by dissolving standard 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 [7]. 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.

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 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.

CST Media

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 [2], was not further optimized for the tested feeds.

Thermal Gravimetric Analysis (TGA) was conducted on each CST batch in duplicate to determine the water content. The thermal analysis involved heating sub-samples of CST at a rate of 5 °C per minute to 400 °C and holding the sample at that temperature for 240 minutes followed by a second heating period up to 700 °C. Mass loss profiles versus temperature during thermal analysis are provided in a previous report [7]. The total mass loss was determined as the sum of several successive mass losses believed to be associated with both physisorbed and chemisorbed water loss. Mass loss data for each CST sample up to 400 ºC is summarized and average F-factor (water content correction) values are provided in Table III.

TABLE III. CST F-factor (Dry Mass Correction Factor) Data.

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

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 to target phase ratios of ~100 or ~30. 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.

RESULTS AND DISCUSSION

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 that were similar to the SRS Average composition, but which would have 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 gave an indication of which anions should be removed in order to increase the solubility of alkaline earth metals. The target concentrations used for the modeling were 25 mg/L for Ca, 17 mg/L for Ba, and 10 mg/L for Sr. These concentrations were estimated to be reasonably within the ranges of this historical tank waste characterization data [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.

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 were at or well below the expected analysis limits and were below the concentration of Cs and so would not be sufficient to impact its absorption on CST. Because of these observations, all of the divalent anions and fluoride were removed from the simulant formulation in an attempt to create a simulant with higher alkaline earth metal solubility.

In order 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 IV. Despite the name used for this mixture, note that the moderate pH formulation does contain sulfate, a divalent anion, but this was found to not cause precipitation problems.

TABLE IV. 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 V. 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 used in the strontium and barium absorption testing with CST.

TABLE V. 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 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 and the target composition is shown in Table IV. Additional sodium nitrate, sodium sulfate, and sodium chloride were added to the formulation to compensate for the lower hydroxide and aluminate concentrations. The OLI calculated solubility of Ca in this simulant was 11 mg/L, 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.

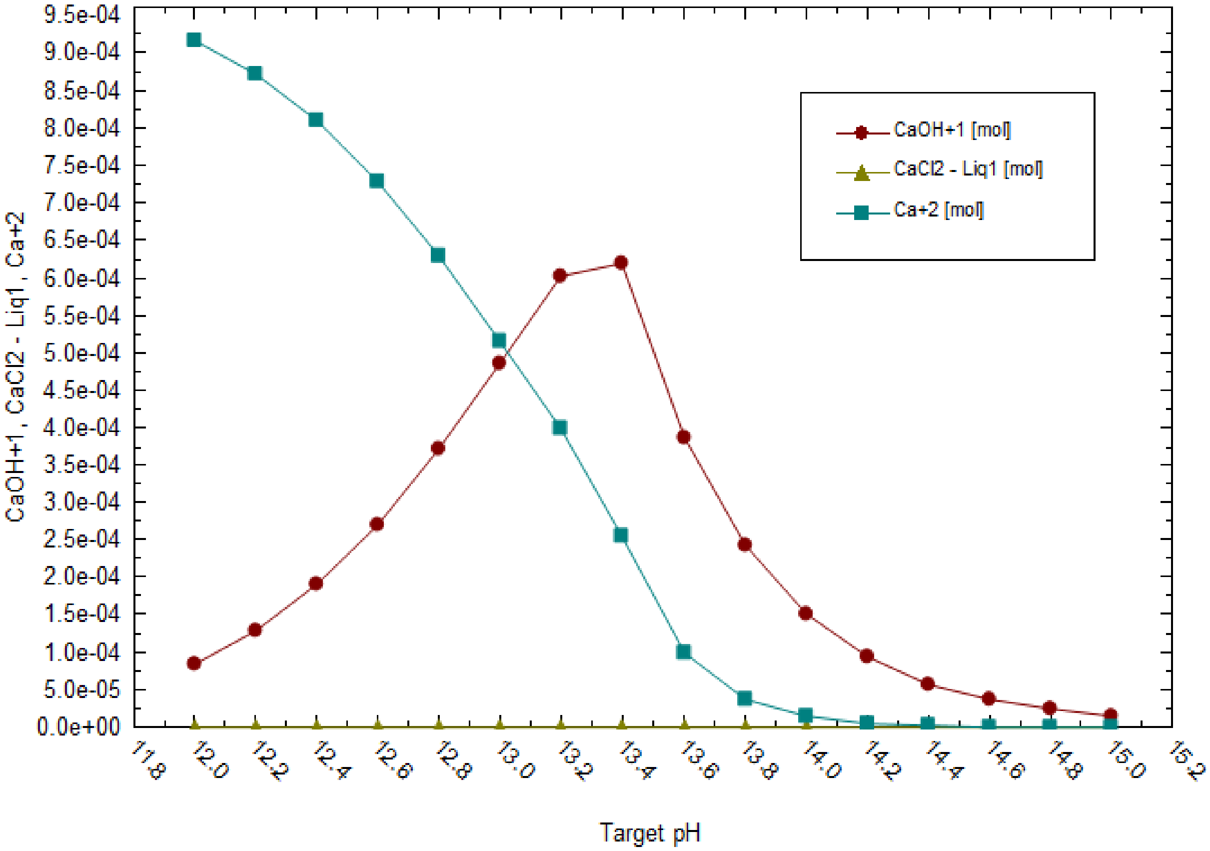

Figure 1. OLI model results for calcium solubility versus pH in SRS Simulant without Divalents or Fluoride.

Simulant Analysis

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

TABLE VI. 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 target amounts discussed above. 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 VII.

TABLE VII. 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 and fluoride and was lower hydroxide concentration. The calcium nitrate was mixed with the simulant at 60 °C for 12 hours, but the solution remained cloudy. The simulant was cooled to room temperature, filtered, and a sample was analyzed for calcium concentration. Results indicated a calcium concentration of < 0.17 mg/L.

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. 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 VIII.

TABLE VIII. 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.

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)
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:

$\phi = V/mF$ (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:

$Q = (C_i - C_f)V/mF$ (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 IX. 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 [2].

TABLE IX. 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.

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 actual 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 in order to obtain two points on the isotherm. Results are shown in Table X.

TABLE X. Distribution Coefficient Calculation Results with Batch 1A Simulant

Simulant	**Phase Ratio**[a]	**Temp. (°C)**	**Hours**	**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	96	1.35	0.084	1832	NA	NA	NA
TCCR 1A	37:1	38	96		0.028	1721	NA	NA	NA
TCCR 1A	122:1	25	196		0.046	3253	NA	NA	NA
TCCR 1A with Ca	123:1	38	96		0.083	1887	2.48	< 0.989	> 223
TCCR 1A with Ca	37:1	38	96		0.032	1535		< 0.989	> 67

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

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 impact of the strontium and calcium on the Cs absorption and to examine the retention of barium on the CST as the Cs-137 decays to Ba-137m. 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 XI.

The results show that the calculated K_d for the eight-day test with the modified 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 impact 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 impact 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 Cs-137 converts to Ba-137m. 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.

TABLE XI. 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

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 XII. 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. Note that the K_d for strontium is for the total strontium, and is not apportioned for the amount of $Sr(OH)^+$ in solution, which is believed to be the actual species that is absorbed by the CST. Also, some removal of strontium could be attributable to absorption onto the binder material rather than ion exchange in binding sites in CST.

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 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 XII. ZAM Calculated versus Measured Distribution Coefficients

Simulant	**Phase Ratio**[a]	**Temp (°C)**	**Cs^+ K_d (mL/g)**	**ZAM**[b] **Prediction (mL/g)**	**AE 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*	> 233	*1.17E5*
SRS Sim No Div/F	122:1	25	1091	1229	NA	NA
SRS Sim No Div/F	122:1	25	1132[c]	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 basis. [b] Assumes binder dilution factor = 0.68. [c] Results from 8-day batch contact tests; all others are 4-day.

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 actual 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 impact on the Cs removal under these conditions. The minimal measured impact on Cs removal was consistent with that predicted by the ZAM modeling for these compositions. In general, the measured K_d values were lower than predicted by ZAM, particularly for the TCCR Batch 1A composition. The reason for these 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.

Further testing is needed to examine the impact of calcium. Since it is challenging to develop a simulant that will dissolve calcium, this is best done using actual 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. Further testing is also recommended to determine if ZAM can accurately account for differences in anion composition and temperature.

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