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Temperature Effect of Cesium Exchange onto Crystalline Silicotitanate in AP-107 and AP-105 Hanford Tank Wastes and Two Simulants

June 2021

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EL Campbell
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Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Pacific Northwest National Laboratory
Richland, Washington 99354

Summary

Washington River Protection Solutions, LLC (WRPS) is charged with the development of the Tank Side Cesium Removal (TSCR) system to process Hanford tank waste supernates in preparation for vitrification. In addition to a filtration step, TSCR will remove cesium (Cs) using ion exchange columns filled with crystalline silicotitanate (CST) ion exchange media. CST is produced by Honeywell UOP, LLC. The documented safety analysis (DSA) developed for the TSCR system limits a single column loading to 141,600 Ci ^{137}Cs. Given a ^{137}Cs isotopic mass fraction of 20% and the planned CST bed size of 596 L (157.5 gal) in a TSCR column, this equates to 0.10 mmole Cs per g CST (Cs distribution coefficient, K_d, 1400 mL/g). Factors that influence Cs uptake by CST include (but are not limited to) (1) CST production (lot-to-lot variations), (2) contact temperature, (3) contact duration, (4) competitors in the tank waste feed, (5) anionic composition of the tank waste feed, and (6) the ^{137}Cs isotopic mass fraction (differs slightly among tank wastes and decreases with time).

Recent testing using Hanford tank waste simulants has shown that bounding the worst-case matrix and test conditions to maximize Cs (^{137}Cs) exchange onto CST will exceed the DSA limit.[1] Therefore, actual tank waste testing was desirable to better determine if the DSA limit will be challenged under expected process conditions. Previous batch contact testing of AP-107 and AP-105 tank wastes with CST to develop Cs isotherms was conducted at ~30 °C (ambient hot cell temperature), which is higher than the expected 16 °C process temperature at TSCR. Therefore, a series of batch contact tests was conducted with these matrices to better assess Cs loading onto CST and to provide data to support modeling efforts at the expected process temperature.

To reduce the radiation dose to personnel, AP-107 and AP-105 tank wastes were first processed through CST ion exchange beds to strip ^{137}Cs (and Cs) allowing the matrices to be contact-handled during testing. Cs isotherms were then developed for each tank waste matrix at four different temperatures (12.7, 15.9, 21.0, and 34.5 °C). A Baseline simulant[2] and Simple simulant (4.6 M $NaNO_3$ and 1.0 M NaOH) were similarly processed at three different temperatures (12.7, 21.0, and 34.5 °C) to develop additional fundamental modeling data. From the isotherms and the equilibrium Cs concentrations, the Cs loading in terms of Q (mmoles Cs/g CST) and K_d (mL/g) were determined. Table S.1 provides a summary of the Q and K_d values for each matrix and temperature. All matrices resulted in a linear decrease of Cs loading with increasing temperature in the temperature range tested. Only AP-107 tank waste processing at 12.7 °C exceeded the DSA limit. The Baseline simulant processed at 12.7 °C reached the DSA limit.

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[1] Fiskum SK, EL Campbell, JL George, RA Peterson, and TT Trang-Le. 2021. *Maximum Cs-137 Curie Loading onto Crystalline Silicotitanate for the Documented Safety Analysis of the Tank Side Cesium Removal Platform*. PNNL-30976, Rev. 0; RPT-DSA-001, Rev. 0. Pacific Northwest National Laboratory, Richland, WA.
[2] Russell RL, PP Schonewill, and CA Burns. 2017. *Simulant Development for LAWPS Testing*. PNNL-26165, Rev. 0; RPT-LPIST-001, Rev. 0. Pacific Northwest National Laboratory, Richland, WA.

Table S.1 Summary K_d and Q Values with CST Lot 2002009604

Matrix Equilibrium Cs Concentration	Process Temperature (°C)	K_d (mL/g)	Q (mmoles/g)
AP-107 tank waste 6.91×10^{-5} M Cs[a]	12.7	1500	0.104
	15.9	1255	0.0868
	21.0	1143	0.0790
	30[b]	905[b]	0.0626[b]
	34.5	678	0.0469
AP-105 tank waste 5.65×10^{-5} M Cs[c]	12.7	1237	0.0699
	15.9	1029	0.0582
	21.0	960	0.543
	30[d]	743[d]	0.0420[d]
	34.5	521	0.0294
Baseline simulant 6.91×10^{-5} M Cs	12.7	1434	0.0991
	21.0	1165	0.0805
	34.5	648	0.0448
Simple simulant 6.91×10^{-5} M Cs	12.7	1200	0.0830
	21.0	861	0.0595
	34.5	482	0.0333

(a) AP-107 Cs concentration, ^{137}Cs reference date March 2019.

(b) Derived from data in Fiskum SK, AM Rovira, HA Colburn, AM Carney, and RA Peterson. 2019. *Cesium Ion Exchange Testing Using a Three-Column System with Crystalline Silicotitanate and Hanford Tank Waste 241-AP-107*. PNNL-28958, Rev. 0; RPT-DFTP-013, Rev. 0. Pacific Northwest National Laboratory, Richland, WA.

(c) AP-105 Cs concentration, ^{137}Cs reference date February 2021.

(d) Derived from data in Fiskum SK, AM Westesen, AM Carney, TT Trang-Le, and RA Peterson. 2021. *Ion Exchange Processing of AP-105 Hanford Tank Waste through Crystalline Silicotitanate in a Staged 2- then 3-Column System.* PNNL-30712, Rev. 0; RPT-DFTP-025, Rev. 0. Pacific Northwest National Laboratory, Richland, WA.

Acknowledgements

The authors thank Renee Russell for conducting the technical review of numerous calculation files, test data packages, and this report. The authors also thank Bill Dey for the quality reviews of the calculation files and this report and Matt Wilburn for his technical editing contribution to this report.

Acronyms and Abbreviations

CST	crystalline silicotitanate
DSA	documented safety analysis
GEA	gamma energy analysis
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
R&D	research and development
TSCR	Tank Side Cesium Removal
WRPS	Washington River Protection Solutions, LLC
WWFTP	WRPS Waste Form Testing Program

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1.0 Introduction

The Tank Side Cesium Removal (TSCR) system, under development by Washington River Protection Solutions, LLC (WRPS), will remove cesium from Hanford tank waste supernate. The treated supernate will eventually be sent to the Low-Activity Waste Facility at the Hanford Waste Treatment and Immobilization Plant for vitrification. The TSCR system uses a non-elutable ion exchange medium, crystalline silicotitanate (CST) produced by Honeywell UOP, LLC (Des Plaines, IL) under the product name IONSIV™ R9140-B.[1] The TSCR system processing will implement a lead-lag-polish column operational format. Each column will contain 596 L (157.5 gal) of CST media with a 234-cm (92-inch) bed height (Siewert 2019). Each column is annular (void center) to promote passive cooling.

The TSCR documented safety analysis (DSA) established a maximum 141,600 Ci ^{137}Cs column loading limit onto a single column (Anderson 2020). This corresponds to 238 Ci ^{137}Cs per kg CST and 0.10 mole Cs per kg CST (Fiskum et al. 2021a). Factors that influence the loading of Cs onto CST include, but are not limited to, CST production lot (different production lots behave differently), TSCR processing temperature, contact time with CST, ^{137}Cs isotopic mass fraction, matrix effects, and competitors in the tank waste feed.

Zheng et al. (1996) showed that CST Cs capacity decreased as contact temperature increased. Most Hanford tank waste testing through a small-column format and batch contacts has been conducted at hot-cell temperature, nominally 25 to 30 °C (Fiskum et al. 2019a, 2021b; Rovira et al. 2018). However, processing through the TSCR system is expected to be conducted closer to the Hanford tank waste temperature of 16 to 20 °C. Figure 1.1 shows the temperature profile of the Hanford AP-107 tank waste for the past year; the temperature averaged 17.8 °C with a range of 16.6 to 20.1 °C. Thus, testing to date may under-predict the total ^{137}Cs loading onto the CST in the TSCR system. Furthermore, limited tank waste feed volumes have been made available for column testing, and 50% Cs breakthrough has only been achieved with AP-107 and AP-105 tank waste (Fiskum et al. 2019a, 2021b).

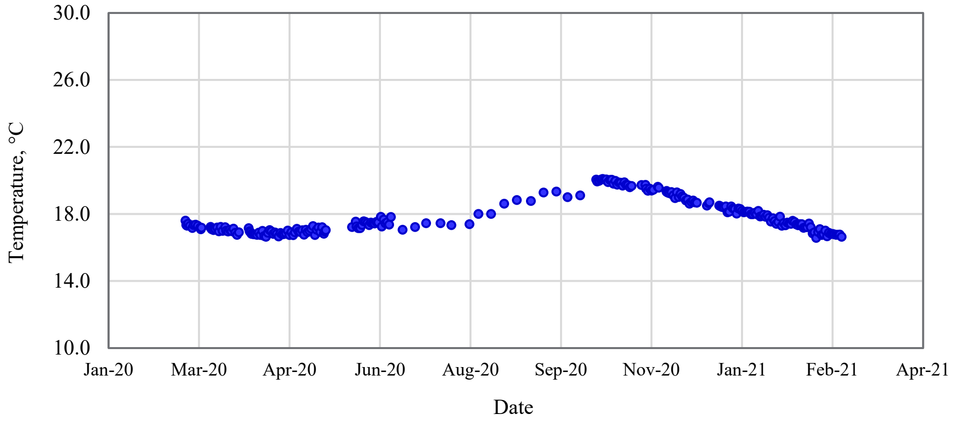

Figure Notes: Data collected from AP107-WST-TI-044 sensor.
Data downloaded from Tank Waste Information Network System on April 1, 2021.

Figure 1.1. AP-107 Tank Waste Temperatures from March 2, 2020 to February 28, 2021

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[1] CST is a Nb-substituted silicotitanate formulated by staff at Texas A&M University and Sandia National Laboratories and then manufactured in an engineered spherical form (Braun et al. 1996). Its chemical and physical properties, column dynamics, temperature tolerance, and radiation tolerance were previously described in a literature review (Pease et al. 2019).

Fiskum et al. (2021a) showed that the ^{137}Cs loading limit (per the DSA) would be exceeded based on relatively simple simulants formulated to provide bounding conditions for Cs loading onto CST. Therefore, emphasis turned to evaluation of actual tank wastes at bounding contact temperatures: 16 °C target including a lower limit of 13 °C to encompass measurement conservatisms.

This report describes the batch contact testing of AP-107 and AP-105 tank wastes at four temperatures (targets 13, 16, 21, and 35 °C) to establish Cs isotherms and Cs loading at the equilibrium feed Cs concentration, and to evaluate Cs thermodynamics. Two simulants, the Baseline simulant (5.6 M Na, Russell et al. 2017) and a Simple simulant (4.6 M $NaNO_3$ and 1.0 M NaOH), were similarly tested at three temperatures (targets 13, 21, and 35 °C).

2.0 Quality Assurance

All research and development (R&D) work at Pacific Northwest National Laboratory (PNNL) is performed in accordance with PNNL's Laboratory-Level Quality Management Program, which is based on a graded application of NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications* (ASME 2000), to R&D activities. To ensure that all client quality assurance (QA) expectations were addressed, the QA controls of the PNNL's WRPS Waste Form Testing Program (WWFTP) QA program were also implemented for this work. The WWFTP QA program implements the requirements of NQA-1-2008, *Quality Assurance Requirements for Nuclear Facility Applications* (ASME 2008), and NQA-1a-2009, *Addenda to ASME NQA-1-2008* (ASME 2009), and consists of the WWFTP Quality Assurance Plan (QA-WWFTP-001) and associated QA-NSLW-numbered procedures that provide detailed instructions for implementing NQA-1 requirements for R&D work.

The work described in this report was assigned the technology level "Applied Research" and was planned, performed, documented, and reported in accordance with procedure QA-NSLW-1102, *Scientific Investigation for Applied Research*. All staff members contributing to the work received proper technical and QA training prior to performing quality-affecting work.

3.0 Tank Waste and Simulant Preparations and Compositions

This section describes tank waste pretreatments prior to batch contacts, tank waste compositions, and simulant formulations and compositions. All work was conducted according to a test plan prepared by PNNL staff and approved by WRPS.[1]

3.1 AP-107 Tank Waste

WRPS staff collected supernate from tank AP-107 from near the bottom of the supernate layer in two sampling campaigns. Eighteen samples (~250 mL each) were collected on November 18, 2020, and another eighteen samples (~250 mL each) were collected on December 13, 2020. All samples were provided to PNNL for testing. At PNNL, the first samples collected from each sampling event (7AP-20-16 and 7AP-20-33) were combined and then passed through a single 10-mL CST bed at ~1.7 bed volumes per hour.[2] The intent was to remove sufficient ^{137}Cs such that the tank waste sample could be contact-handled and processed in a temperature-controlled chamber. After processing, a total of 476 mL of Cs-removed AP-107 was available for batch contact testing. The AP-107 product density was determined with a 10-mL volumetric flask to be 1.281 g/mL (at 20 °C). A 1-mL aliquot of untreated AP-107 tank waste was added back to the AP-107 effluent to provide enough ^{137}Cs concentration to effectively measure by gamma energy analysis (GEA), pre- and post-batch contacting. The final Cs concentration in the Cs-depleted AP-107 feed was ~0.022 µg/mL, calculated from the measured ^{137}Cs concentration (0.368 µCi/mL, reference date February 4, 2021), the ^{137}Cs specific activity (86.9 Ci/g), and the ^{137}Cs mass fraction of 19.2 wt%. The total Cs concentration in this AP-107 matrix (1.6×10^{-7} M) was much lower than the Cs concentrations to be spiked into the matrix (see Section 4.3) to develop the isotherms.

The remaining 34 samples of AP-107 tank waste collected in 2020 were composited to support TSCR system unit operations testing at 16 °C process temperature. A nominal 60-mL aliquot was collected from this AP-107 tank waste composite to support an additional comparative batch contact test at hot cell temperature, ~28 °C. This aliquot was processed as received, i.e., it was not processed through filtration to remove suspended solids or ion exchange to remove Cs (and other miscellaneous components such as Sr and Pb) before testing.

Note that the previous batch contact testing used for comparison herein was conducted with AP-107 tank waste that was collected in December 2018; its composition was previously reported (Fiskum et al. 2019a). The December 2018 AP-107 sample had been collected from a higher elevation in the AP-107 tank and its density was 1.266 g/mL (23 °C). The higher density of the November/December 2020 sample collection indicated that it was a bit saltier, i.e., slightly higher in cation and anion concentrations.

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[1] Westesen. 2020. TP-DFTP-099, Rev. 0.0. *FY21 Cesium Ion Exchange Testing with AP-107 Tank Waste with Crystalline Silicotitanate*. Pacific Northwest National Laboratory, Richland WA. Not publicly available.

[2] Processing was conducted according to PNNL Test Instruction TI-DFTP-109, *Isotherm Batch Contact Testing of Cs onto Crystalline Silicotitanate in AP-107 Tank Waste Matrix at Four Temperatures* (not publicly available) with -30 mesh sieve cut of CST from lot 2002009604. Implemented January through March 2021.

3.2 AP-105 Tank Waste

AP-105 tank waste sample collection and initial processing (dilution from 8.72 M Na to 5.92 M Na and filtration) were previously described (Allred et al. 2020). The diluted and filtered AP-105 tank waste sample was processed to remove Cs in a small-scale column operation as previously described (Fiskum et al. 2021b). An aliquot from one of the effluent fractions (Effluent-9) was used to support batch contact testing. The AP-105 ion exchange effluent composition was previously reported (Fiskum et al. 2021b). The residual Cs concentration in solution was ~0.0095 µg/mL based on the ^{137}Cs concentration, 0.149 µCi/mL, the ^{137}Cs specific activity, and the Cs mass fraction of 18.1 wt%. The total Cs concentration in this AP-105 matrix (7.1×10^{-8} M) was much lower than the Cs concentrations to be spiked into the matrix (see Section 4.3) to develop the isotherms.

3.3 Simulant Preparations

The Baseline simulant was formulated and created as previously described (Russell et al. 2017). However, sodium oxalate was omitted from the formulation to mitigate solids precipitation and Cs was omitted such that it could be added later to specific aliquots. The Simple simulant was formulated to contain only two compounds, $NaNO_3$ and NaOH, with no potential competitor cations other than Na.

The simulants were prepared with American Chemical Society reagent grade materials shown in Table 3.1 and according to a test instruction.[1] Component masses were measured into 500-mL volumetric flasks containing part of the requisite deionized water. Table 3.2 shows the added salt quantities and order of addition. The addition of Na_2CO_3 was conducted while swirling the volumetric flask to the extent practical to minimize clumping. After all salts were added and dissolved, the solutions were brought to volume with deionized water. Solution densities were measured in the preparation volumetric flasks at room temperature, ~20 °C (see Table 3.2). Each prepared solution was passed through a 0.45-micron pore size nylon filter.

Table 3.1. Reagents Used for Simulant Preparation

Compound	MW (g/mole)	Manufacturer	Product Number	Lot Number	Assay (%)
$Al(NO_3)_3\cdot 9H_2O$	375.1	Sigma-Aldrich	237973-500g	BCBR0256V	99.9
$NaNO_3$	85.00	Alpha Aesar	14493	Q16F033	99.60
KCl	74.6	Sigma-Aldrich	746436-500G	SLBR9127V	99.9
$Na_3PO_4\cdot 12H_2O$	380.1	Fisher	S377-500	126469	100.8
Na_2SO_4	142.0	Sigma-Aldrich	239313-500g	SLBN9500V	99.7
50% NaOH	40.00	Sigma Aldrich	72064-500	BCBZ4353	50.0
Na_2CO_3	105.99	Sigma Aldrich	222321-500g	MKCM9200	99.54
$NaNO_2$	69.00	Sigma-Aldrich	237213-2.5kg	MKBV1410V	100.1
$CsNO_3$	194.9	Johnson and Matthey	14440	015016	99.99

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[1] Fiskum SK. 2021. TI-DFTP-111, *Isotherm Batch Contact Testing of Cs onto Crystalline Silicotitanate in AP-105 Tank Waste, Baseline Simulant, and Simple Simulant at Multiple Temperatures*. Pacific Northwest National Laboratory, Richland, WA. Not publicly available. Implemented February-March 2021.

Table 3.2. Component Masses for Baseline and Simple Simulant Preparations

Compound	Baseline Simulant (g / 0.5 L)	Simple Simulant (g / 0.5 L)
Water	To volume	To volume
$Al(NO_3)_3·9H_2O$	31.16	0
$NaNO_3$	54.50	195.60
KCl	4.55	0
$Na_3PO_4·12H_2O$	8.21	0
Na_2SO_4	4.69	0
50% NaOH	82.96	40.04
Na_2CO_3	24.75	0
$NaNO_2$	35.19	0
Density (g/mL)	1.254	1.270

3.4 Matrix Composition Summary

Table 3.3 provides the major component concentrations for the two tank wastes and the calculated component concentrations for the simulants. The AP-107 tank waste effluent composition was assumed from results reported by Fiskum et al. 2019a (for cations) and Rovira et al. 2018 (for anions). Because these components were not measured on the AP-107 sample collected in November/December 2020 and processed in 2021, they must be considered approximate. The AP-105 tank waste composition was measured and reported on a composite effluent sample that was expected to represent Effluent-9 reasonably well (Fiskum et al. 2021b). Note that other minor and trace components are present in the tank wastes; Table 3.3 is intended to provide only the higher-concentration components with comparison to the simulants.

Table 3.3. Tank Waste and Simulant Compositions

Matrix>>	AP-107	AP-105(a)	Baseline Sim.	Simple Sim.
Ion	Molarity			
Al as $Al(OH)_4^-$	3.61E-1(b)	5.23E-1	1.66E-1	--
NO_3^-	1.85E+0(c)	1.89E+0	1.78E+0	4.58E+0
K^+	1.15E-1(b)	1.02E-1	1.22E-1	--
PO_4^{3-}	1.61E-2(c)	8.72E-3	4.32E-2	--
SO_4^{2-}	1.92E-2(c)	2.44E-2	6.59E-2	--
free OH^-	1.01E+0(c)	1.24E+0	1.41E+0	1.00E+0
CO_3^{2-}	6.65E-1(b)	4.72E-1	4.65E-1	--
NO_2^-	1.14E+0(c)	1.38E+0	1.02E+0	--
Na^+	5.71E-1(b)	6.00E+0	5.56E+0	5.58E+0
Cl^-	6.40E-2(c)	1.10E-1	1.22E-1	--

(a) Fiskum et al. 2021b
(b) Fiskum et al. 2019a
(c) Rovira et al. 2018

A 380-mL aliquot was collected from each simulant and traced with ^{137}Cs. The traced simulants were used as stock solutions for testing. No tracer additions were required for the tank wastes; sufficient ^{137}Cs concentrations were present to trace Cs uptake.

4.0 Experimental

This section describes the CST and pretreatment, F-factor determination, experimental conditions to conduct batch contact testing, and calculation approach.

4.1 CST Sample and Pretreatment

CST is manufactured by Honeywell UOP, LLC as IONSIV™. WRPS purchased CST product R9140-B,[1] 18 × 50 mesh, lot number 2002009604. PNNL received a sample from WRPS on September 20, 2018 for testing. Delivery and initial subsampling were described previously (Fiskum et al. 2019b).

Batch contact testing was conducted on the full particle size distribution of CST. A 34.5-g aliquot of the as-received CST was collected and rinsed with ~100 mL of 0.1 M NaOH three times to remove colloidal fines. The CST was then rinsed once with 80 mL of deionized water to remove the salt solution. The rinsed CST was set aside to dry at ambient (~20 °C) temperature for 13 days, at which point it essentially reached constant mass. Before subsampling, the CST was mixed by hand-tumbling the container.

4.2 F-Factor

The F-factor (dry CST mass per sampled CST mass) was determined after heating CST at two temperatures: 105 °C and 427 °C. The F-factor samples were collected in duplicate each time a CST sample set was collected for a batch contact experiment. The F-factor duplicate pair collection bracketed batch contact sample collection. F-factors samples masses ranged from 0.3 to 0.6 g of CST.

For the 105 °C processing, CST was placed in a glass vial and then placed into an Isotemp vacuum oven (Fisher Scientific Model 280A) set to 105 °C. The vial was periodically removed from the oven and allowed to cool until the glass threads were cool to the touch but the main vial body was still warm. Then the vial was capped and cooled completely, and the gross mass was measured. The net mass of CST was calculated. Typically, mass measures were collected every 4 to 12 h until the mass change was <0.5% between successive drying-weighing events. One set of F-factor samples was left in the oven for a 70-h duration and resulted in a lower-than-expected F-factor value (0.8743), which was only 3% higher than the value established at 427 °C heating. This lower F-factor applied to results generated for the 13 °C and 21 °C testing with AP-105 tank waste, Baseline simulant, and Simple simulant.

For the 427 °C processing, CST was placed in a tared stainless-steel crucible. The crucible was transferred into a Thermoline furnace (Fisher Scientific Model FB1415) that was preheated to 427 °C. After 4 h, the crucible was removed from the furnace and cooled in a desiccator containing moisture-indicating Drierite desiccant. Then the gross mass was measured and net CST mass was calculated. Fiskum et al. (2021a) and King et al. (2018) showed that no further mass losses were achieved after heating CST to 427 °C.

4.3 Batch Contact Testing

Aliquots (2 mL) from each matrix (tank wastes and ^{137}Cs-spiked simulants) were collected to determine the initial ^{137}Cs concentrations. Appropriately sized bottles were spiked with either 0.750 M or 0.0848 M $CsNO_3$ solutions (exact volumes determined by masses transferred divided by solution densities). Cesium

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[1] Product R9140-B is provided in the sodium form and did not require conversion from the hydrogen form to the sodium form prior to testing.

spike volumes were small relative to the test matrix volume to minimize matrix alteration from dilution. For the three lowest spike concentrations (linear part of the isotherm), spike volumes accounted for <0.5% of the matrix volume; for the highest spike concentration (highest end of the isotherm), the spike volume represented 2.2% of the matrix volume. Aliquots of the various test matrices were added to the containers with the $CsNO_3$ spike solution. Four stock Cs concentrations were prepared in this manner for each of the four matrices. Added matrix volumes were determined based on the masses transferred divided by the appropriate solution densities. The in-cell testing with AP-107 tank waste was conducted similarly except only two (instead of four) Cs concentration spikes were prepared.

Nominal 0.075-g (dry mass basis) aliquots of CST were measured into 20-mL vials (actual masses measured to nearest 0.0001 g). The CST masses were corrected per the F-factor mass measured at 105 °C. Then a nominal 15-mL stock solution aliquot was added; the exact solution volume transferred was determined from net solution mass and density. The ~5-mL headspace in this configuration allowed for significant fluid motion, assuring good mixing. The solution volume-to-CST mass phase ratios ranged from 183 to 223.

Figure 4.1 provides an example process flowchart with AP-107 tank waste showing (1) $CsNO_3$ addition to the containers (dark blue ellipses), (2) the AP-107 tank waste added to these bottles, and (3) subdivision of the Cs-spiked AP-107 into duplicate vials pre-loaded with CST for the contact testing at the specified temperature. The AP-105 tank waste, Baseline simulant, and Simple simulant were similarly processed. Each test was conducted in duplicate. See Appendix A for specific CST masses and matrix volumes. Table 4.1 provides the initial Cs concentration achieved for each batch contact test condition. The 13 and 21 °C test temperature sample sets were processed first and in parallel. The 16 and 35 °C test sample sets were sequentially processed after the first set. This allowed for minimal CST contact time with the matrix at temperatures other than the target temperature.

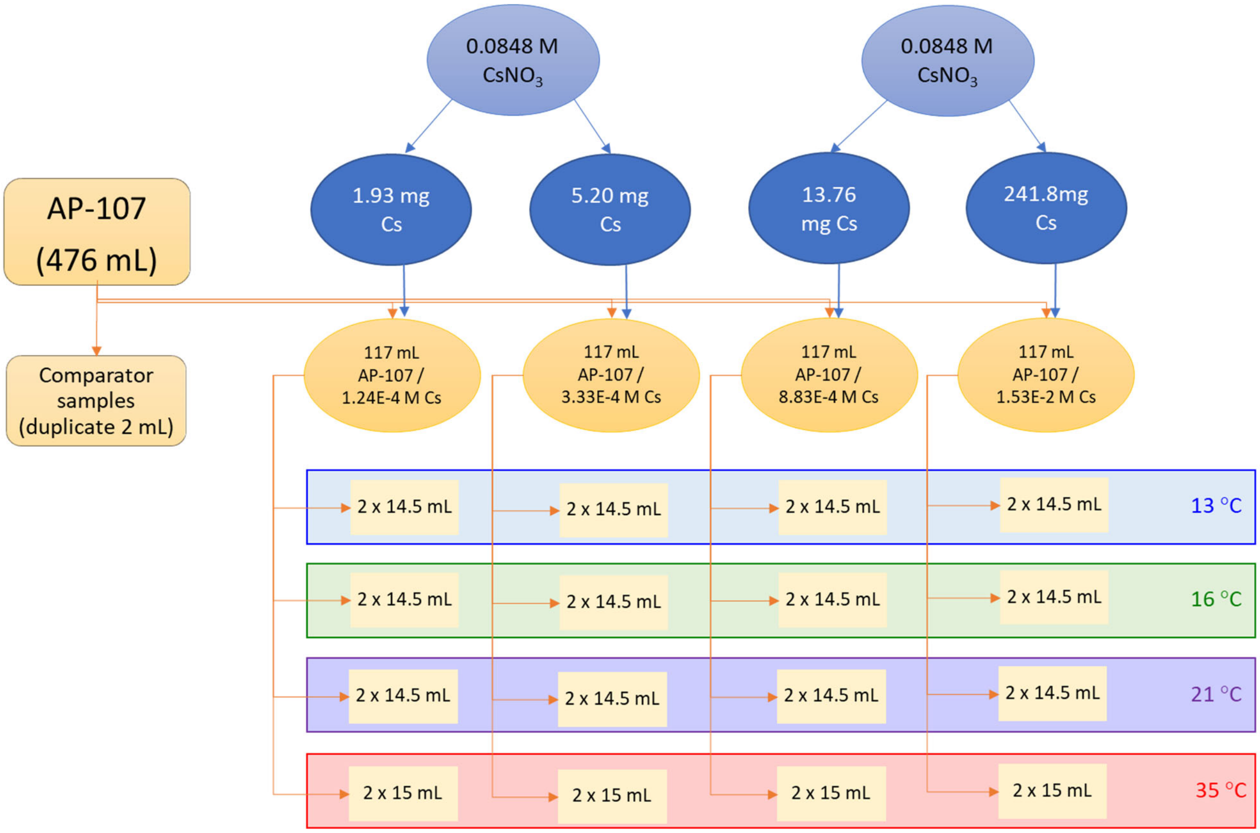

Figure 4.1. AP-107 Spiking and Aliquoting (prototypic)

Table 4.1. Initial Cesium Molarity in the Batch Contact Test Solutions

AP-107	AP-105	Baseline Simulant	Simple Simulant	AP-107 Neat
1.24E-4	1.28E-4	1.34E-4	1.32E-4	--
3.33E-4	3.36E-4	3.44E-4	3.34E-4	3.58E-4
8.83E-4	8.84E-4	8.91E-4	8.78E-4	1.05E-3
1.53E-2	1.61E-2	1.58E-2	1.57E-2	--

The 21 °C test samples were contacted on a Cole-Parmer (Vernon Hills, Illinois) large orbital shaker with a 16-mm orbit set to 240 rpm. The 13, 16, and 35 °C test samples were sequentially contacted in a Benchmark (Sayreville, New Jersey) Incu-Shaker™ 10LR refrigerated/heated orbital shaker with 19-mm orbit set to 200 rpm. The hot cell testing with neat[1] AP-107 tank waste was conducted with a Thermo LP vortex mixer set to ~400 rpm. The small size and mass of the Thermo LP vortex mixer was amenable to constraints in the hot cell.

Vials of water were co-located with each sample set; their temperatures were measured periodically during the contact period with a type K thermocouple (weekend measurements were excluded). The water samples served as temperature sentinels for each sample set. Samples were mixed for ~238 h. The hot cell test with neat AP-107 was contacted for 214 h and its temperature was only checked once at the end of the test period. Figure 4.2 and Figure 4.3 show the measured test temperatures of the benchtop tests as a function of contact time. The error bars represent the Type K thermocouple measurement uncertainty of

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[1] This sample was processed as pulled from the AP-107 tank, with no initial Cs removal.

2.2 °C. The dashed lines represent the ±2.2 °C expected tolerance relative to the target temperature. Table 4.2 provides the weighted mean of the measured temperatures.

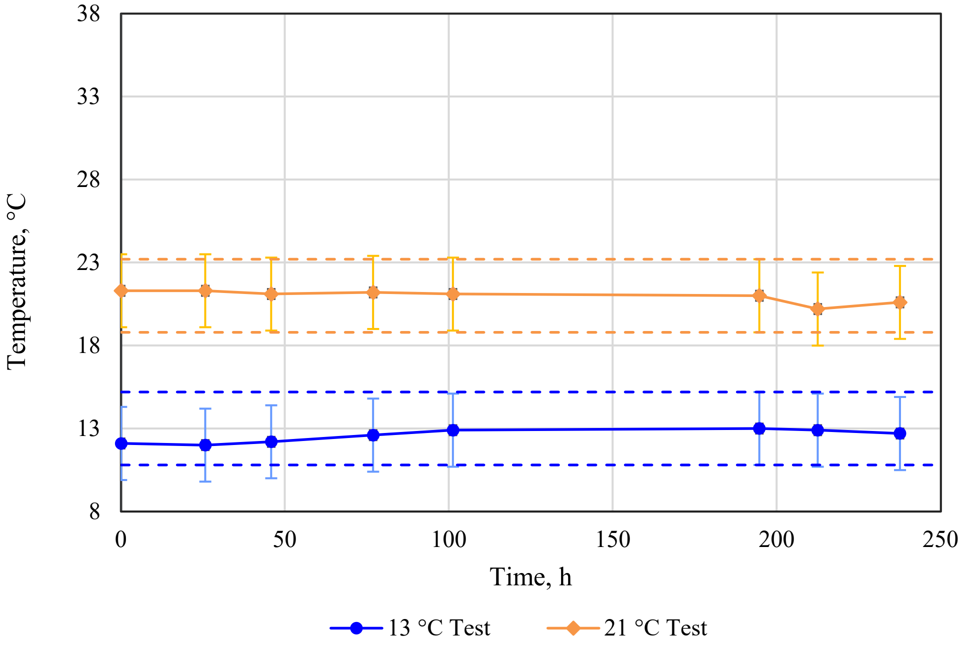

Figure 4.2. Temperature Profiles during Testing at 13 °C and 21 °C Targets

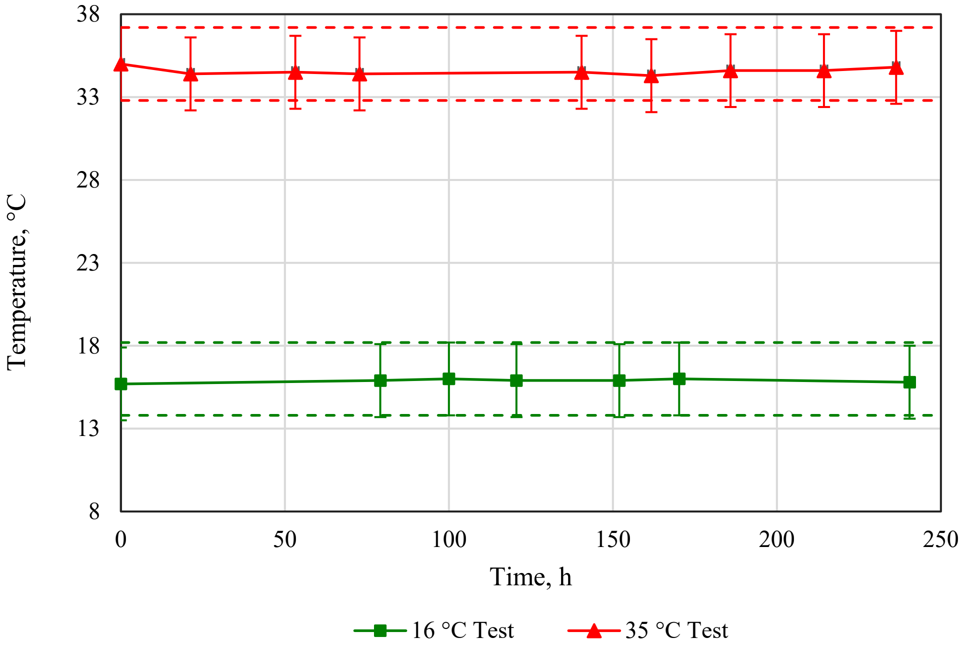

Figure 4.3. Temperature Profiles during Testing at 16 °C and 35 °C Targets

Table 4.2. Average Contact Temperature

Target Temperature (°C)	Weighted Mean Temperature (°C)
13	12.7
16	15.9
21	21.0
35	34.5

To mitigate the possibility of temperature-driven changes to Cs exchange with increasing (or decreasing) sample temperature during post-contact activities, samples were removed in pairs from the incubator for final processing. The remaining samples stayed at process temperature and agitation conditions until ready for handling. The CST settled quickly; a nominal 2-mL solution aliquot was collected and filtered through a 0.45-micron pore size nylon syringe filter. The filtrate was collected in a clean vial for GEA.

The ^{137}Cs was measured in the pre- and post-contacted solutions[1] using GEA, and the measured ^{137}Cs fractionation was used to determine the total Cs exchange. Analysis and data reduction were conducted using the methods previously reported (Fiskum et al. 2019a). The isotherm data were fitted to a Freundlich/Langmuir hybrid equilibrium fit (Hamm et al. 2002).

The ^{137}Cs in each sample was analyzed using a high-purity lithium-drifted germanium gamma detector. Comparator samples were prepared from aliquots collected from the starting feed matrix and measured identically to the post-contacted samples. Sample count time was adjusted to achieve an overall statistical count uncertainty of <1%.

The batch distribution coefficients were calculated according to Eq. (4.1).

$$\frac{(A_0 - A_1)}{A_1} \times \frac{V}{M \times F} = K_d \tag{4.1}$$

where A_0 = initial ^{137}Cs concentration (µCi/mL)
A_1 = final (equilibrium) ^{137}Cs concentration (µCi/mL)
V = volume of the batch contact liquid (mL)
M = measured mass of CST (g)
F = F-factor, mass of the 105 °C dried CST divided by the mass of the undried CST
K_d = batch-distribution coefficient (mL/g)

Final (equilibrium) Cs concentrations (C_{Eq}) were calculated relative to the tracer recovered in the contacted samples (A_1) and the initial metal concentration (C_0) according to Eq. (4.2).

$$C_0 \times \left(\frac{A_1}{A_0}\right) = C_{Eq} \tag{4.2}$$

where C_0 = initial Cs concentration in solution (µg/mL or M)
C_{Eq} = equilibrium Cs concentration in solution (µg/mL or M)

---

[1] Both the primary and the duplicate samples from tank waste processing were measured; the primary simulant samples were measured by GEA; the duplicate sample was analyzed if the primary result appeared to be anomalous.

The equilibrium Cs concentrations loaded onto the CST (Q in units of mmoles Cs per gram of dry CST mass) were calculated according to Eq. (4.3).

$$\frac{C_0 \times V \times \left(1 - \frac{A_1}{A_0}\right)}{M \times F \times 1000 \times FW} = Q \tag{4.3}$$

where Q = equilibrium Cs concentration in the CST (mmole/g CST)
1000 = conversion factor to convert µg to mg
FW = Cs formula weight

5.0 Results

This section provides the K_d and isotherm curves for the AP-107 and AP-105 tank wastes and Baseline and Simple simulants at each of the process test temperatures. Input data supporting the various isotherms and figures are provided in Appendix A.

5.1 K_d and Isotherm Results

Figure 5.1, Figure 5.2, Figure 5.3, and Figure 5.4 show the K_d dependence on Cs concentration for the various matrices, as applicable, at 13, 16, 21, and 35 °C, respectively. The lower three Cs concentrations showed minimal K_d variation at a given process temperature. Examination of all figures shows that increasing contact temperature resulted in decreasing K_d values.

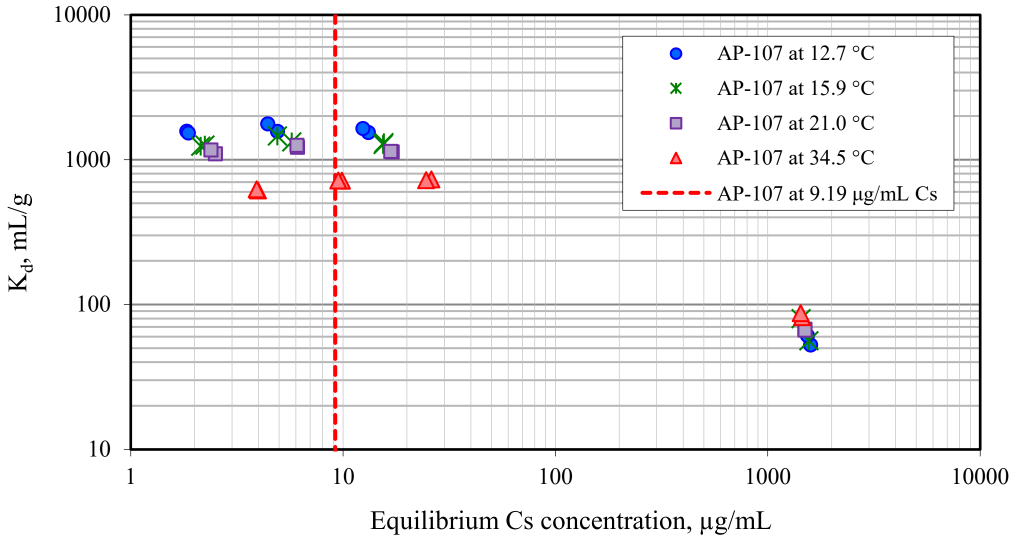

Figure 5.1. Cs K_d vs. Cs Concentration, AP-107 Tank Waste, Four Temperatures

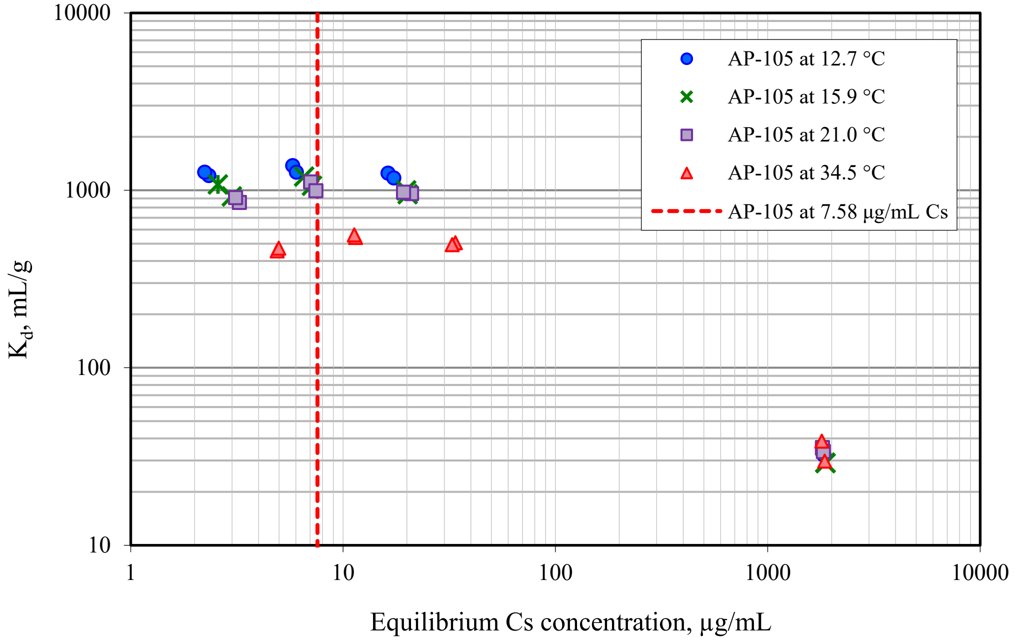

Figure 5.2. Cs K_d vs. Cs Concentration, AP-105 Tank Waste, Four Temperatures

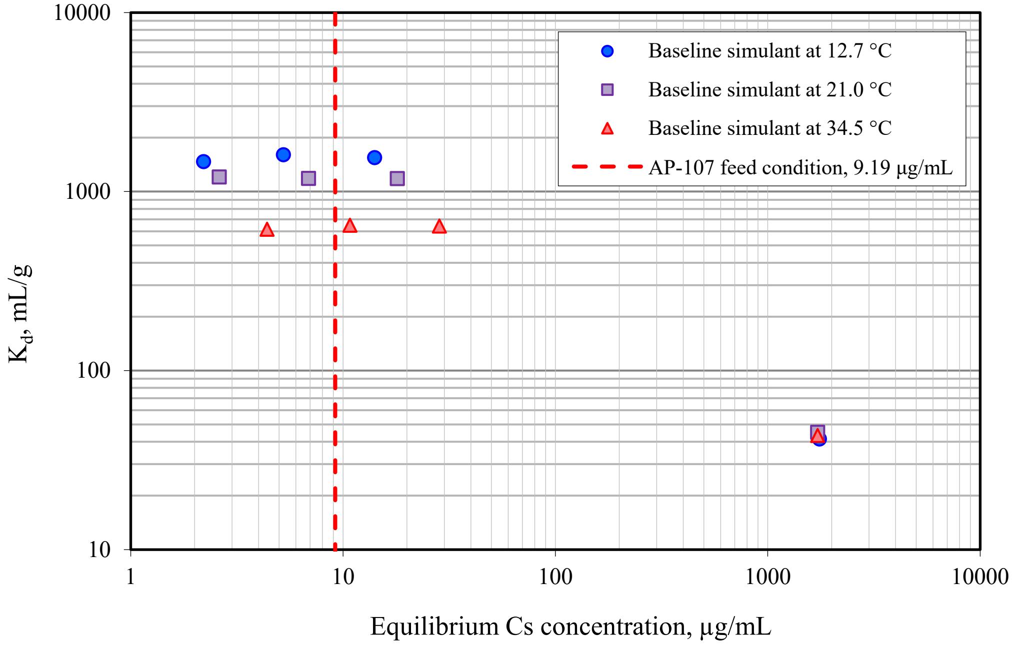

Figure 5.3. Cs K_d vs. Cs Concentration, Baseline Simulant, Three Temperatures

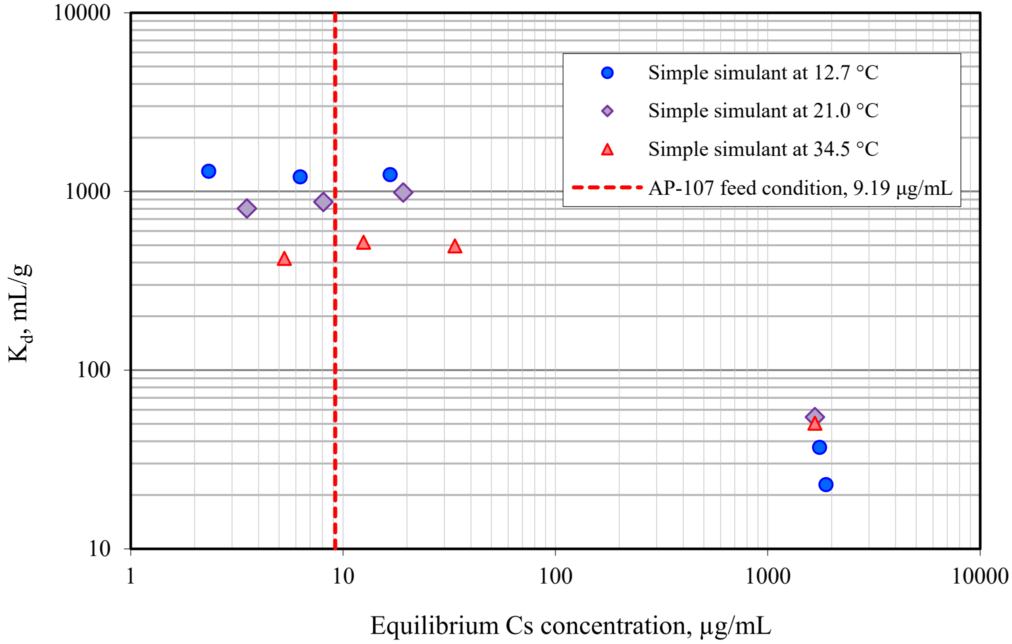

Figure 5.4. Cs K_d vs. Cs Concentration, Simple Simulant, Three Temperatures

Figure 5.5 through Figure 5.8 show the corresponding isotherms and Q (mmoles Cs/g dry CST) values versus Cs molarity for each test matrix and test temperature. Also provided are the curve fits to the Freundlich/Langmuir hybrid equilibrium model as given in Eq. (5.1) (Hamm et al. 2002). The AP-107 and AP-105 tank waste data (Figure 5.5, Figure 5.6) also include the isotherms and fits generated previously from testing in the hot cell at nominally 29 to 30 °C (Fiskum et al. 2019a and Fiskum et al. 2021b, respectively).

$$Q = \frac{\alpha_i \times [Cs]}{(\beta + [Cs])} \tag{5.1}$$

where [Cs] = equilibrium Cs concentration, mmoles/mL or M
Q = equilibrium Cs loading on the CST, mmole Cs per g CST
α_i = isotherm parameter constant (mmoles/g), equivalent to total capacity in the matrix
β = isotherm parameter constant (mmoles/mL or M), selectivity coefficient, dependent on matrix and temperature; the larger the value, the less selective the CST is for Cs (Hamm et al. 2002)

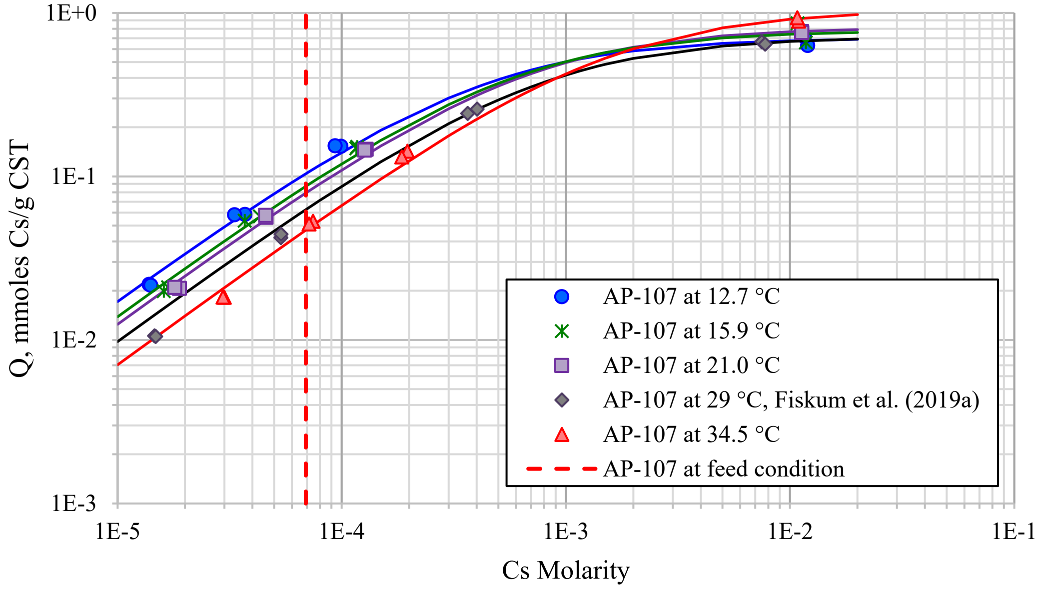

Figure 5.5. Q vs. Cs Equilibrium Concentration, AP-107 Tank Waste with Freundlich/Langmuir Hybrid Equilibrium Fits, Five Temperatures

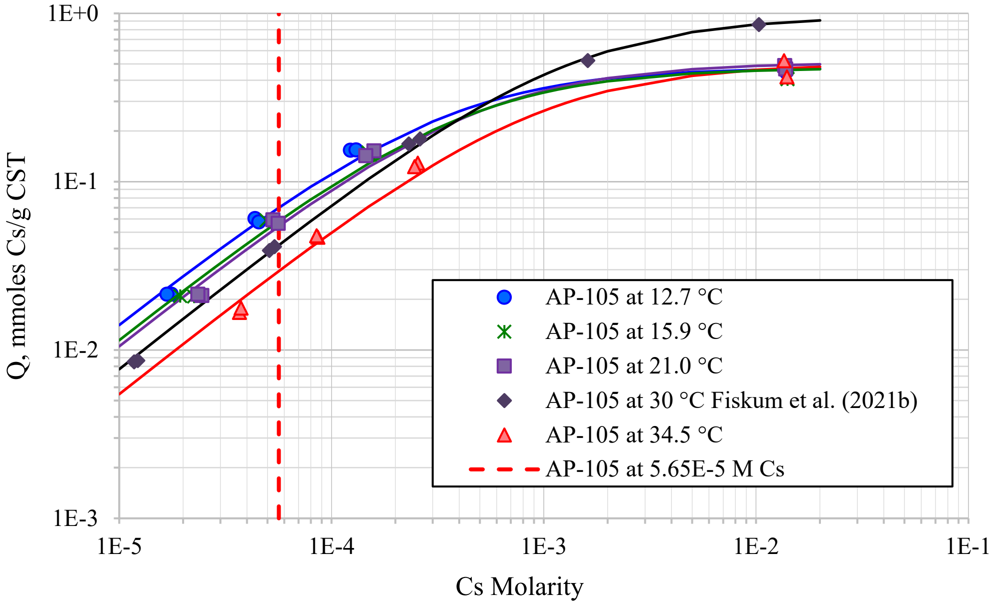

Figure 5.6. Q vs. Cs Equilibrium Concentration, AP-105 Tank Waste with Freundlich/Langmuir Hybrid Equilibrium Fits, Five Temperatures

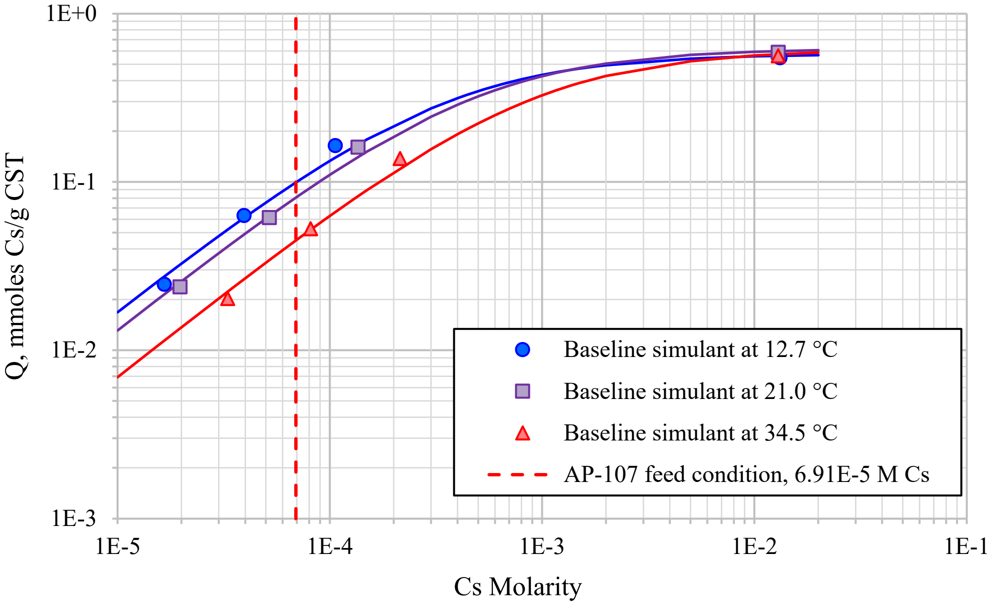

Figure 5.7. Q vs. Cs Equilibrium Concentration, Baseline Simulant with Freundlich/Langmuir Hybrid Equilibrium Fits, Three Temperatures

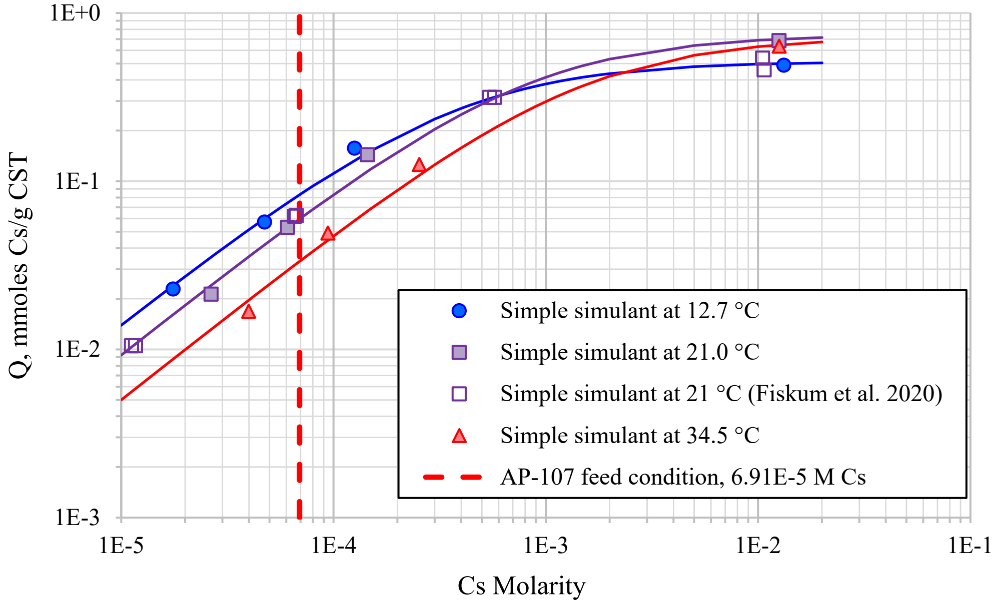

Figure 5.8. Q vs. Cs Equilibrium Concentration, Simple Simulant with Freundlich/Langmuir Hybrid Equilibrium Fits, Three Temperatures

The α_i and β parameters for the Freundlich/Langmuir hybrid equilibrium fits are summarized in Table 5.1. Data from previous testing with tank waste and Simple simulant are also provided for comparison. Examinations of the isotherm figures and Table 5.1 α_i values show that the isotherms generally converge at a common capacity, independent of contact temperature, with a few exceptions:

1. The AP-107 bench testing showed increasing capacity with increasing temperature; the hot cell processing on virgin tank waste did not fit this trend (see Figure 5.5 and Table 5.1).
2. The in-cell testing with AP-105 tank waste (Fiskum et al. 2021b) uniquely exceeded the Cs capacity measured during the bench testing on the Cs-decontaminated product Q = 0.97 mmoles Cs/g CST versus Q = ~0.49 mmoles Cs/g CST.

Figure 4.11 of Fiskum et al. (2020) showed that addition of Sr, Pb, and Ca to a Simple simulant test matrix increased the maximum Cs loading. This indicated that a synergistic effect between selected cations and Cs was at play. The synergistic interaction is not known, but one hypothesis is that selected cations optimize the crystal lattice opening to better incorporate Cs exchange. Processing through the ion exchange columns in-cell to remove Cs would have removed these synergistic constituents and thus eliminated this effect during the fume hood testing at multiple temperatures. However, any synergism as applied to improved Cs capacity in the AP-105 tank waste did not appear to be in play for the AP-107 tank waste.

Table 5.1. Freundlich/Langmuir Hybrid Equilibrium Model α_i and β Parameter Summary

Matrix	Process Temperature (°C)	α_i, (mmoles Cs/g CST)	β, (Cs M)	Reference
AP-107 Tank Waste	12.7	0.703	4.00E-4	Current testing
	15.9	0.782	5.53E-4	Current testing
	21.0	0.817	6.45E-4	Current testing
	30	0.72	7.25E-4	Fiskum et al. 2019a
	34.5	1.05	1.48E-3	Current testing
AP-105 Tank Waste	12.7	0.477	3.29E-4	Current testing
	15.9	0.475	4.05E-4	Current testing
	21.0	0.510	4.75E-4	Current testing
	30	0.97	1.24E-3	Fiskum et al. 2021b
	34.5	0.503	9.11E-4	Current testing
Baseline Simulant	12.7	0.576	3.32E-4	Current testing
	21.0	0.621	4.64E-4	Current testing
	34.5	0.613	8.76E-4	Current testing
Simple Simulant	12.7	0.515	3.60E-4	Current testing
	21.0	0.744	7.95E-4	Current testing
	21	0.54	5.29E-4	Fiskum et al. 2020
	34.5	0.722	1.43E-3	Current testing

In contrast, hot cell testing of tank waste exchange capacity at the *equilibrium* Cs feed condition aligned with the temperature trend established from the bench-scale tests based on visual examination of the isotherm (Figure 5.5 and Figure 5.6) and linear dependence of Cs exchange on temperature (Section 5.2).

5.2 Temperature Dependence on Cs Load Capacity

The Freundlich/Langmuir hybrid fit parameters were used to calculate Q at the equilibrium Cs molarity of 6.91×10^{-5} M (AP-107 tank waste feed condition) at each process temperature (inclusive of the Baseline and Simple simulants). Similarly, the Q values were calculated for AP-105 tank waste tests at the AP-105 equilibrium Cs molarity of 5.65×10^{-5} M. The K_d and Q values at the equilibrium Cs concentrations are summarized in Table 5.2. Two conditions were observed that would challenge the TSCR DSA (upper limit of Q = 0.10 mmoles Cs/ g CST and K_d = 1400 mL/g): AP-107 tank waste and Baseline simulant processing at 12.7 °C. Cs loading at all higher process temperatures and matrices was below the DSA limit. Figure 5.9 shows Q versus temperature curves for all test matrices. Excellent linearity was observed over the test range (12.7 to 34.5 °C) in all matrices. Simulant bounding matrix conditions maximizing Cs loading onto CST described by Fiskum et al. (2021a) exceeded the DSA. Therefore, actual waste testing results are recommended to guide adherence of TSCR system operations to the DSA.

Table 5.2. Summary K_d and Q Values for CST Lot 2002009604

Matrix Equilibrium Cs Concentration	Process Temperature (°C)	K_d (mL/g)[(a)]	Q, mmoles/g
AP-107 Tank Waste 6.91×10^{-5} M Cs[(b)]	12.7	1500	0.104
	15.9	1255	0.0868
	21.0	1143	0.0790
	30	905	0.0626
	34.5	678	0.0469
AP-105 Tank Waste 5.65×10^{-5} M Cs[(c)]	12.7	1237	0.0699
	15.9	1029	0.0582
	21.0	960	0.0543
	30	743	0.0420
	34.5	521	0.0294
Baseline Simulant 6.91×10^{-5} M Cs	12.7	1434	0.0991
	21.0	1165	0.0805
	34.5	648	0.0448
Simple Simulant 6.91×10^{-5} M Cs	12.7	1200	0.0830
	21.0	861	0.0595
	34.5	482	0.0333

(a) K_d calculated as follows: Q, mmoles/g, divided by equilibrium Cs concentration, mmoles/mL.
(b) AP-107 Cs concentration, reference date March 2019.
(c) AP-105 Cs concentration, reference date February 2021.

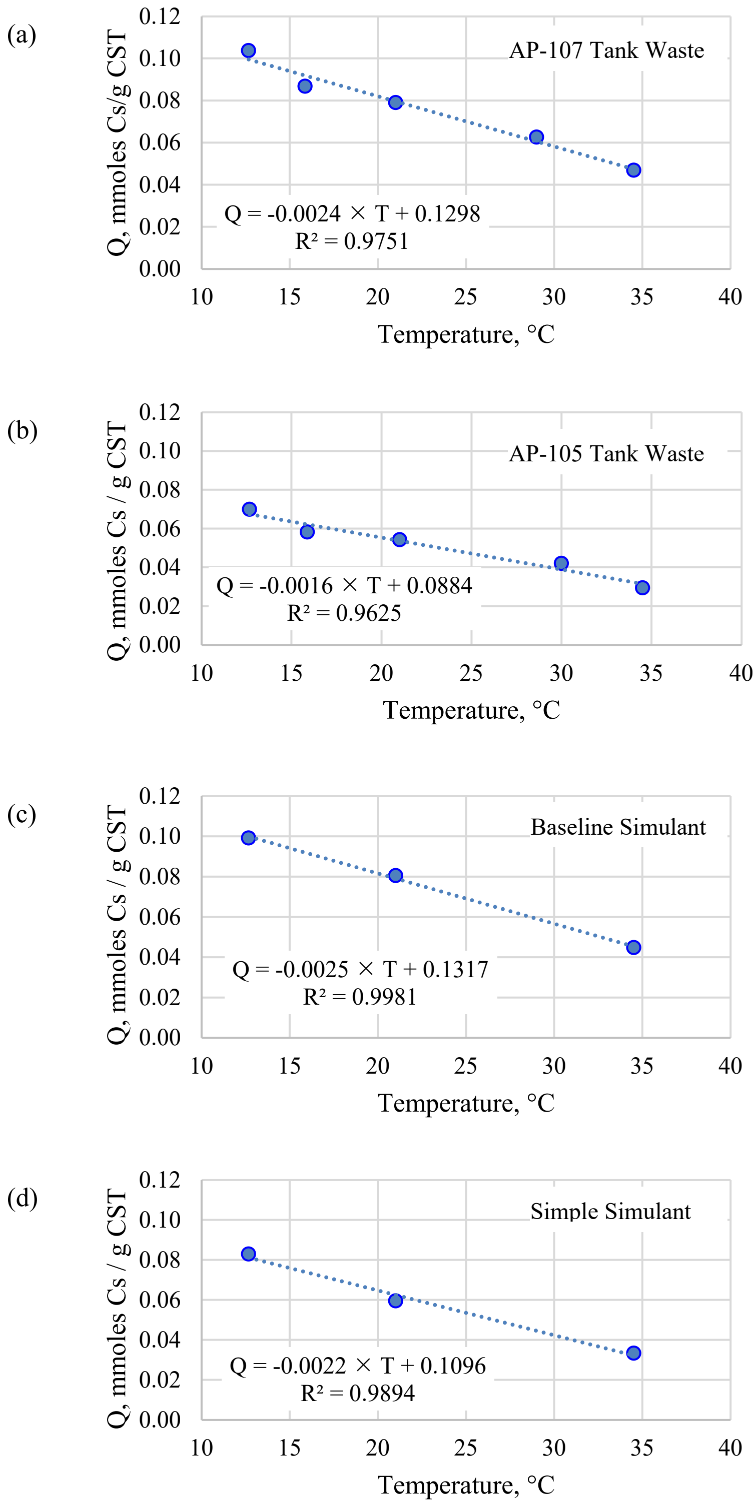

Figure 5.9. Q Dependence on Temperature for (a) AP-107 Tank Waste, (b) AP-105 Tank Waste, (c) Baseline Simulant, and (d) Simple Simulant

The activation energy (heat of reaction) for Cs exchange onto CST at 6.91×10^{-5} M Cs in the Simple simulant matrix (4.6 M $NaNO_3$ and 1.0 M NaOH) was determined using the data from Table 5.2 and application of the Arrhenius equation [Eq. (5.2)].

$$\ln(Q) = \frac{-E_a}{R} \times \frac{1}{T} + \ln(Q_{ref}) \qquad (5.2)$$

Figure 5.10 provides the graph of ln(Q) versus $\frac{1}{T}$ (where temperature, T, is expressed in Kelvins, K). The activation energy, E_a, was derived from the slope $\left(\frac{-E_a}{R}\right)$ where R is the universal gas constant (8.314 J/(K·mole). The activation energy for Cs exchange onto CST in the Simple simulant at a Cs concentration of 6.91×10^{-5} M was -3.07×10^4 J/mole (temperature range of 12.7 to 34.5 °C). Zheng et al. (1997) reported an activation energy of -2.18×10^4 J/mole for the reaction shown in Eq (5.3) using a similar matrix consisting of 5.1 M $NaNO_3$ and 0.6 M NaOH (presumably in the temperature range of 25 to 44 °C). The activation energy derived by this current work, -3.07×10^4 J/mole, was 41% lower than the Zheng-derived activation energy.

$$Cs^{+} + Na_3X \leftrightarrows Na_2CsX + Na^{+} \qquad (5.3)$$

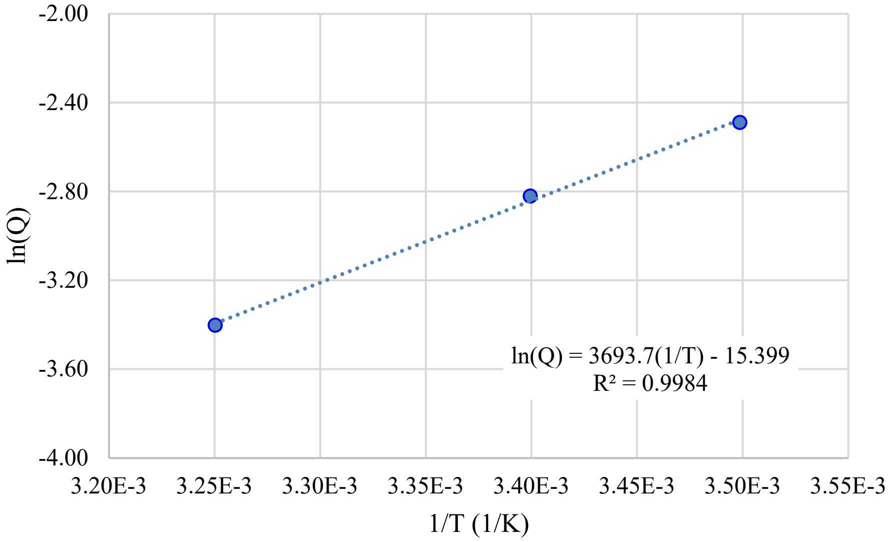

Figure 5.10. Graph of ln(Q) vs. 1/T for Simple Simulant (4.6 M $NaNO_3$ and 1.0 M NaOH)

5.3 Isotherm Comparison of AP-107 Tank Waste Pulled from Different Tank Depths

There was concern that the AP-107 tank waste collected in November/December 2020 may have differed chemically from the previous AP-107 sample collected in 2018 and that this difference could drive an unexpected shift in the Cs isotherm, voiding direct isotherm comparisons. The recent (November/ December 2020) AP-107 tank waste was collected close to the bottom of the supernate level and it had higher density, and thus expected higher salt concentration, than the earlier samples collected closer to the surface of the tank supernate (densities of 1.29 versus 1.26 g/mL, respectively). A limited batch contact study was conducted in-cell with the higher-density material, and results were compared to the previously generated isotherm (Fiskum et al. 2019a). Figure 5.11 overlays the higher-density AP-107 (2020 sample) isotherm results on the previous AP-107 (2018 sample) isotherm. Within the overall expected measurement uncertainties, there was no indication that the higher-density AP-107 pulled from deeper in the supernate layer impacted the established AP-107 Cs isotherm, and thus direct comparisons for Cs exchange between the two sample pulls are valid.

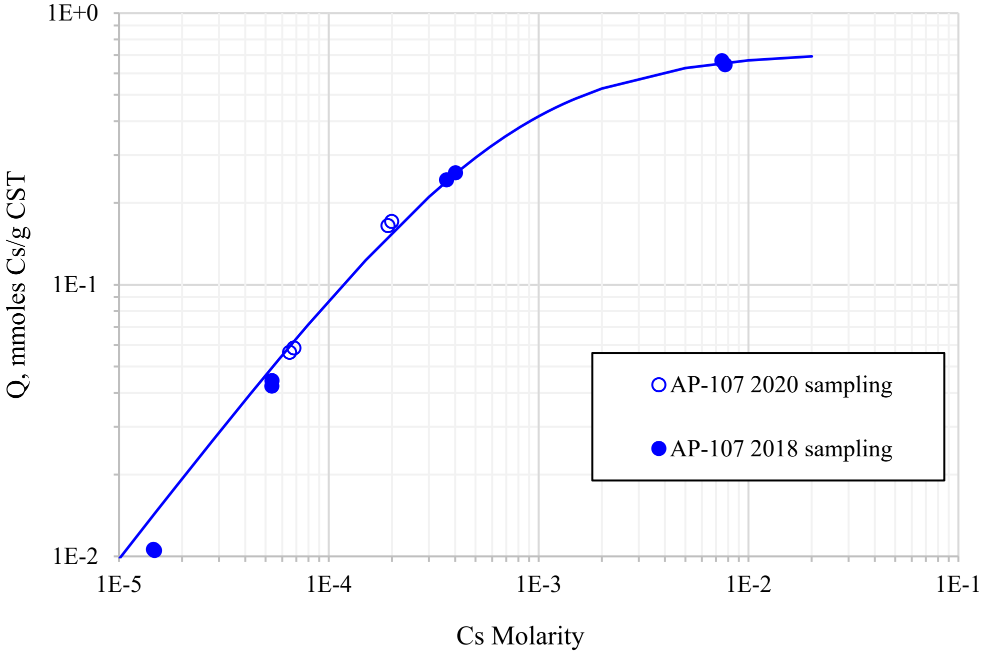

Figure 5.11. Q vs. Equilibrium Cs Concentration, Comparing Isotherms Generated with AP-107 Tank Waste Collected at Different Depths

6.0 Conclusions

Cesium isotherms were developed for two tank wastes, AP-107 and AP-105, at 12.7, 15.9, 21.0, and 34.5 °C, and two simulants, Baseline (Russell et al. 2017) and Simple (4.6 M $NaNO_3$ and 1.0 M NaOH) at 12.7, 21.0, and 34.5 °C. The two tank wastes had been processed to remove Cs/^{137}Cs such that testing could be conducted with contact handling. Batch contact testing was conducted with CST lot 2002009604 in nominal contact phase ratios of 200 (0.075 g dry CST per 15 mL of solution). Contact times lasted nominally 238 h at temperature. The equilibrium Cs concentration of 6.91×10^{-5} M (AP-107 feed condition, reference date March 2019) was applied to the AP-107 tank waste and simulants; equilibrium Cs concentration of 5.65×10^{-5} M (AP-105 feed condition, reference date February 2021) was applied to the AP-105 tank waste. The isotherm data were fit to the Freundlich/Langmuir hybrid equilibrium model (Hamm et al. 2002) and K_d and Q values were determined at the feed conditions. Results were compared to the TSCR DSA (Q = 0.10 mmoles Cs/g CST and K_d = 1400 mL/g), which corresponds to a maximum TSCR column loading of 141,600 Ci (^{137}Cs). The following conclusions were made from this testing:

1. AP-107 tank waste contacted at 12.7 °C slightly exceeded the DSA limit where K_d = 1500 mL/g and Q = 0.104 mmoles Cs/g CST.
2. The Baseline simulant contacted at 12.7 °C reached the DSA limit where K_d = 1434 mL/g and Q = 0.099 mmoles Cs/g CST.
3. Results for tank wastes and simulants at all other process temperatures were below the TSCR DSA limits.
4. A linear relationship for Q versus temperature was established in all matrices, where Q decreased as temperature increased.
5. A generally common maximum Cs capacity (within ~20%) was reached for a given test matrix regardless of the process temperature. One exception to this was the AP-105 in-cell test, where the matrix had not undergone initial ion exchange processing for Cs removal. In this case, the maximum Cs capacity was ~2× higher than the average of the companion tests. This anomaly did not affect the feed condition portion of the isotherm.
6. The Cs activation energy for exchange onto CST in the Simple simulant matrix was determined from application of the Arrhenius equation to be -3.07×10^4 J/mole; this value is 41% lower than the Zheng et al. (1997) value of -2.18×10^4 J/mole.

It is recommended that tank wastes (and blends) be tested using batch contacts to develop isotherms and assess the ^{137}Cs loading relative to the DSA limit. A complex set of matrix parameters affect Cs uptake. Therefore, generating simulants that properly reflect the tank waste compositions and their concomitant interactions for Cs uptake onto CST is difficult.

7.0 References

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Appendix A – Batch Contact Results

Table A.1 provides the experimental results used to produce the AP-107 Cs distribution coefficient (K_d) curves and isotherms at four contact temperatures (Figure 5.1 and Figure 5.5 in the body of this report). The dry crystalline silicotitanate (CST) masses were based on the 105 °C drying temperature. Using the higher 427 °C drying temperature decreased the F-factor ~9%. Thus, applying the 427 °C F-factor would increase K_d and Q values by ~9%.

Table A.1. AP-107 Tank Waste Isotherm Data

Sample ID	Dry CST Mass (g)	AP-107 Vol. (mL)	Initial Cs Conc. (M)	Equil. Cs Conc. (M)	K_d (mL/g)	Q (mmoles Cs/g)
12.7 °C(a)						
TI109-S1-13	0.0728	14.447	1.24E-04	1.39E-05	1570	2.19E-02
TI109-S2-13	0.0737	14.563	3.33E-04	3.70E-05	1566	5.85E-02
TI109-S3-13	0.0743	14.486	8.83E-04	9.92E-05	1538	1.53E-01
TI109-S4-13	0.0749	14.538	1.53E-02	1.20E-02	52	6.32E-01
TI109-S1-13-d	0.0742	14.562	1.24E-04	1.41E-05	1526	2.16E-02
TI109-S2-13-d	0.0749	14.566	3.33E-04	3.33E-05	1763	5.83E-02
TI109-S3-13-d	0.0744	14.498	8.83E-04	9.37E-05	1637	1.54E-01
TI109-S4-13-d	0.0745	14.516	1.53E-02	1.16E-02	61	7.15E-01
15.9 °C(b)						
TI109-S1-16	0.0737	14.430	1.24E-04	1.68E-05	1259	2.10E-02
TI109-S2-16	0.0802	14.528	3.33E-04	3.69E-05	1457	5.36E-02
TI109-S3-16	0.0745	14.422	8.83E-04	1.16E-04	1274	1.49E-01
TI109-S4-16	0.0771	14.535	1.53E-02	1.18E-02	56	6.60E-01
TI109-S1-16-d	0.0785	14.472	1.24E-04	1.61E-05	1239	1.99E-02
TI109-S2-16-d	0.0742	14.586	3.33E-04	4.32E-05	1326	5.70E-02
TI109-S3-16-d	0.0733	14.533	8.83E-04	1.17E-04	1311	1.52E-01
TI109-S4-16-d	0.0749	14.489	1.53E-02	1.08E-02	80	8.64E-01
21.0 °C(a)						
TI109-S1-21	0.0742	14.586	1.24E-04	1.89E-05	1096	2.07E-02
TI109-S2-21	0.0744	14.550	3.33E-04	4.60E-05	1216	5.61E-02
TI109-S3-21	0.0749	14.524	8.83E-04	1.29E-04	1129	1.46E-01
TI109-S4-21	0.0756	14.576	1.53E-02	1.13E-02	68	7.69E-01
TI109-S1-21-d	0.0738	14.555	1.24E-04	1.80E-05	1164	2.09E-02
TI109-S2-21-d	0.0727	14.602	3.33E-04	4.58E-05	1253	5.77E-02
TI109-S3-21-d	0.0760	14.521	8.83E-04	1.27E-04	1139	1.45E-01
TI109-S4-21-d	0.0759	14.503	1.53E-02	1.13E-02	67	7.58E-01
34.5 °C(b)						
TI109-S1-35	0.0775	15.043	1.24E-04	2.99E-05	614	1.83E-02
TI109-S2-35	0.0732	15.068	3.33E-04	7.45E-05	716	5.32E-02
TI109-S3-35	0.0726	15.076	8.83E-04	1.96E-04	731	1.43E-01
TI109-S4-35	0.0761	15.574	1.53E-02	1.09E-02	82	8.91E-01
TI109-S1-35-d	0.0749	14.501	1.24E-04	2.95E-05	625	1.83E-02
TI109-S2-35-d	0.0737	14.429	3.33E-04	7.15E-05	719	5.12E-02
TI109-S3-35-d	0.0774	14.603	8.83E-04	1.85E-04	722	1.32E-01
TI109-S4-35-d	0.0752	15.648	1.53E-02	1.08E-02	87	9.35E-01

(a) Based on 105 °C F-factor = 0.9208 (427 °C F-factor = 0.8444).
(b) Based on 105 °C F-factor = 0.9162 (427 °C F-factor = 0.8408).

Table A.2, Table A.3, and Table A.4 provide the experimental results to produce the K_d curves and isotherms for the following:

- AP-105 at four contact temperatures (Figure 5.2 and Figure 5.6). Note that Figure 5.6 also includes data for a fifth temperature that was used in previous testing (Fiskum et al. 2021a).
- Baseline simulant at three temperatures (Figure 5.3 and Figure 5.7)
- Simple simulant at three temperatures (Figure 5.4 and Figure 5.8)

The dry CST masses were based on the 105 °C drying temperature. The F-factor samples supporting the 12.7 °C and 21.0 °C tests were left in the oven for ~70 h—far longer than normal operations—and the plastic vial lid likely was placed on the vial glass threads before they cooled appropriately (Section 4.2 describes the process for F-factor determination). Their associated F-factor was closer to that of material heated to 427 °C (differing by only 3.3%). The second set of samples processed at 15.9 °C and 34.5 °C was associated with a 105 °C F-factor of 0.9191, which was determined after 23 and 47 h heating time. This latter value was 9.4% higher than the F-factor determined at 427 °C drying temperature.

Table A.2. AP-105 Tank Waste Isotherm Data

Sample ID	Dry CST Mass (g)	AP-105 Vol. (mL)	Initial Cs Conc. (M)	Equil. Cs Conc. (M)	K_d (mL/g)	Q (mmoles Cs/g)
12.7 °C(a)						
TI111AP-1-13	0.0714	13.923	1.28E-04	1.76E-05	1210	2.15E-02
TI111AP-2-13	0.0718	14.840	3.36E-04	4.37E-05	1377	6.03E-02
TI111AP-3-13	0.0711	14.349	8.84E-04	1.23E-04	1247	1.54E-01
TI111AP-4-13	0.0708	14.120	1.61E-02	1.39E-02	32	4.48E-01
TI111AP-1-13-d	0.0721	13.943	1.28E-04	1.68E-05	1265	2.14E-02
TI111AP-2-13-d	0.0720	14.311	3.36E-04	4.55E-05	1263	5.76E-02
TI111AP-3-13-d	0.0710	14.534	8.84E-04	1.31E-04	1173	1.54E-01
TI111AP-4-13-d	0.0713	14.173	1.61E-02	1.38E-02	33	4.56E-01
15.9 °C(b)						
TI111AP-1-16	0.0778	15.024	1.28E-04	1.94E-05	1080	2.09E-02
TI111AP-2-16	0.0745	15.017	3.36E-04	5.38E-05	1062	5.68E-02
TI111AP-3-16	0.0742	15.035	8.84E-04	1.49E-04	1000	1.49E-01
TI111AP-4-16	0.0769	15.186	1.61E-02	1.40E-02	29	4.11E-01
TI111AP-1-16-d	0.0763	15.075	1.28E-04	2.25E-05	924	2.08E-02
TI111AP-2-16-d	0.0739	15.205	3.36E-04	4.94E-05	1196	5.89E-02
TI111AP-3-16-d	0.0762	15.057	8.84E-04	1.52E-04	951	1.45E-01
TI111AP-4-16-d	0.0754	15.018	1.61E-02	1.41E-02	29	4.06E-01
21.0 °C(a)						
TI111AP-1-21	0.0713	14.571	1.28E-04	2.45E-05	853	2.11E-02
TI111AP-2-21	0.0720	15.116	3.36E-04	5.31E-05	1113	5.93E-02
TI111AP-3-21	0.0714	14.980	8.84E-04	1.59E-04	956	1.52E-01
TI111AP-4-21	0.0706	14.017	1.61E-02	1.37E-02	35	4.89E-01
TI111AP-1-21-d	0.0706	14.507	1.28E-04	2.35E-05	909	2.14E-02
TI111AP-2-21-d	0.0711	14.365	3.36E-04	5.62E-05	994	5.65E-02
TI111AP-3-21-d	0.0722	13.952	8.84E-04	1.45E-04	975	1.43E-01
TI111AP-4-21-d	0.0722	14.594	1.61E-02	1.38E-02	34	4.67E-01
34.5 °C(b)						
TI111AP-1-35	0.0765	14.104	1.28E-04	3.69E-05	456	1.68E-02
TI111AP-2-35	0.0778	14.628	3.36E-04	8.63E-05	543	4.68E-02
TI111AP-3-35	0.0740	15.151	8.84E-04	2.55E-04	506	1.29E-01
TI111AP-4-35	0.0753	15.266	1.61E-02	1.35E-02	39	5.23E-01
TI111AP-1-35-d	0.0754	14.826	1.28E-04	3.75E-05	472	1.77E-02
TI111AP-2-35-d	0.0773	14.724	3.36E-04	8.51E-05	562	4.77E-02
TI111AP-3-35-d	0.0759	14.626	8.84E-04	2.46E-04	495	1.23E-01
TI111AP-4-35-d	0.0744	14.488	1.61E-02	1.40E-02	30	4.19E-01

(a) Based on 105 °C F-factor = 0.8743 (427 °C F-factor = 0.8464).
(b) Based on 105 °C F-factor = 0.9191 (427 °C F-factor = 0.8404).

Table A.3. Baseline Simulant Isotherm Data

Sample ID	Dry CST Mass (g)	Baseline Simulant Vol. (mL)	Initial Cs Conc. (M)	Equil. Cs Conc. (M)	K_d (mL/g)	Q (mmoles Cs/g)
12.7 °C[(a)]						
TI111BS-S1-13	0.0715	14.994	1.34E-04	1.66E-05	1468	2.46E-02
TI111BS-S2-13	0.0727	15.027	3.44E-04	3.95E-05	1606	6.30E-02
TI111BS-S3-13	0.0713	14.922	8.91E-04	1.06E-04	1547	1.64E-01
TI111BS-S4-13	0.0707	14.950	1.58E-02	1.32E-02	41	5.46E-01
21.0 °C[(a)]						
TI111BS-S1-21	0.0718	14.933	1.34E-04	1.97E-05	1204	2.38E-02
TI111BS-S2-21	0.0710	14.897	3.44E-04	5.19E-05	1184	6.14E-02
TI111BS-S3-21	0.0714	15.189	8.91E-04	1.36E-04	1180	1.61E-01
TI111BS-S4-21	0.0715	14.880	1.58E-02	1.30E-02	45	5.88E-01
34.5 °C[(b)]						
TI111BS-S1-35	0.0751	15.102	1.34E-04	3.30E-05	616	2.03E-02
TI111BS-S2-35	0.0744	14.931	3.44E-04	8.12E-05	649	5.28E-02
TI111BS-S3-35	0.0732	14.906	8.91E-04	2.14E-04	643	1.38E-01
TI111BS-S4-35	0.0763	14.998	1.58E-02	1.29E-02	43	5.62E-01

(a) Based on 105 °C F-factor = 0.8743 (427 °C F-factor = 0.8464).
(b) Based on 105 °C F-factor = 0.9191 (427 °C F-factor = 0.8404).

Table A.4. Simple Simulant Isotherm Data

Sample ID	Dry CST Mass (g)	Simple Simulant Vol (mL)	Initial Cs Conc. (M)	Equil. Cs Conc. (M)	K_d (mL/g)	Q (mmoles Cs/g)
12.7 °C[(a)]						
TI111SS-S1-13	0.0709	14.157	1.32E-04	1.76E-05	1296	2.28E-02
TI111SS-S2-13	0.0713	14.220	3.34E-04	4.74E-05	1205	5.72E-02
TI111SS-S3-13	0.0705	14.716	8.78E-04	1.26E-04	1241	1.57E-01
TI111SS-S4-13-d	0.0716	14.550	1.57E-02	1.32E-02	37	4.89E-01
21.0 °C[(a)]						
TI111SS-S1-21	0.0706	14.258	1.32E-04	2.65E-05	804	2.13E-02
TI111SS-S2-21	0.0726	14.126	3.34E-04	6.09E-05	874	5.32E-02
TI111SS-S3-21	0.0714	13.989	8.78E-04	1.45E-04	987	1.44E-01
TI111SS-S4-21	0.0711	15.764	1.57E-02	1.26E-02	55	6.85E-01
34.5 °C[(b)]						
TI111SS-S1-35	0.0797	14.613	1.32E-04	3.99E-05	422	1.69E-02
TI111SS-S2-35	0.0736	15.111	3.34E-04	9.41E-05	521	4.92E-02
TI111SS-S3-35	0.0743	14.976	8.78E-04	2.53E-04	496	1.26E-01
TI111SS-S4-35	0.0728	15.021	1.57E-02	1.26E-02	50	6.36E-01

(a) Based on 105 °C F-factor = 0.8743 (427 °C F-factor = 0.8464).
(b) Based on 105 °C F-factor = 0.9191 (427 °C F-factor = 0.8404).

Table A.5 provides the experimental results used to produce the neat AP-107 isotherm points at the hot cell contact temperature (Figure 5.1 and Figure 5.5 in the body of the report). The dry CST masses were based on the 105 °C drying temperature. Using the higher 427 °C drying temperature decreased the F-factor 10%. Thus, applying the 427 °C F-factor would increase K_d and Q values by ~10%.

Table A.5. Neat AP-107 Tank Waste Isotherm Data

Sample ID	Dry CST Mass (g)	Neat AP-107 Vol. (mL)	Initial Cs Conc. (M)	Equil. Cs Conc. (M)	K_d (mL/g)	Q (mmoles Cs/g)
28 °C[(a)]						
TI114-S1-CST	0.0747	15.075	3.58E-04	6.82E-05	855	5.85E-02
TI114-S2-CST	0.0770	14.782	1.05E-03	1.92E-04	862	1.65E-01
TI114-S1-CST-d	0.0752	14.458	3.58E-04	6.51E-05	865	5.63E-02
TI114-S2-CST-d	0.0755	15.143	1.05E-03	2.00E-04	850	1.71E-01

(a) Based on 105 °C F-factor = 0.9270 (427 °C F-factor = 0.8420).

"Neat AP-107" indicates material that had not been previously processed through ion exchange media or filtration.

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