Pacific Northwest
NATIONAL LABORATORY

PNNL-30185, Rev. 0
RPT-DFTP-022, Rev. 0

Crystalline Silicotitanate Batch Contact Testing with Ba, Ca, Pb, and Sr

September 2020

SK Fiskum
EL Campbell
TT Trang-Le

U.S. DEPARTMENT OF ENERGY

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

DISCLAIMER

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;
ph: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis.osti.gov

Available to the public from the National Technical Information Service
5301 Shawnee Rd., Alexandria, VA 22312
ph: (800) 553-NTIS (6847)
email: orders@ntis.gov <https://www.ntis.gov/about>
Online ordering: http://www.ntis.gov

PNNL-30185, Rev. 0
RPT-DFTP-022, Rev. 0

Crystalline Silicotitanate Batch Contact Testing with Ba, Ca, Pb, and Sr

September 2020

SK Fiskum
EL Campbell
TT Trang-Le

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

Pacific Northwest National Laboratory
Richland, Washington 99354

Summary

Washington River Protection Solutions is working to support initial production of immobilized low-activity waste (LAW) by feeding Hanford tank supernate from tank farms to the Hanford Waste Treatment and Immobilization Plant (WTP) LAW Facility. This goal incorporates the design of a Tank Side Cesium Removal system, which filters tank waste supernate to remove suspended solids and then removes Cs by processing it through crystalline silicotitanate (CST) ion exchange media manufactured by Honeywell UOP, LLC. The ^{137}Cs-depleted product is intended to be sent to the WTP for vitrification. Processing of actual tank waste supernate showed effectively complete uptake of Sr and Ba by CST and significant uptake of Ca (Walker et al. 1998[1]; Rovira et al. 2018[2]; Fiskum et al. 2019[3]). Further, Campbell et al. (2019)[4] analyzed CST post-column testing and found significant (>1E-2 mmoles/g) uptake of Ca and Pb along with some Ba, Cd, Fe, Sr, and U. This led to concern that selected metals, particularly the +2 cations, Ca, Sr, Ba, and Pb may be consuming Cs exchange sites and possibly reducing CST capacity for Cs. Exchange of +2 cations was assumed to be associated with the $M(OH)^+$ species for the metal (M) ion in the caustic solution.

A series of batch contact testing was conducted to evaluate the exchange behavior of Ba, Ca, Pb, and Sr onto CST and their effects on Cs exchange. The CST was provided in the sodium form by Honeywell UOP, as IONSIV^{TM} R9140-B, Lot 2002009604, 18 x 50 mesh. A <30-mesh aliquot was collected to match the sieve fraction expected for use in upcoming small column test configurations. Kinetic exchange rate and isotherms were measured at metal concentrations benchmarked from the AP-107 tank waste feed composition and as limited by the metal solubility in the alkaline solution. Two simplified matrices were tested: 1) 1.0 M NaOH/4.6 M $NaNO_3$ and 2) 0.1 M NaOH/5.5 M $NaNO_3$; these matrices represented the expected 5.6 M Na concentration of process feed and served to address the hydroxide concentration effect on exchange behavior.

Figure S.1 summarizes the kinetic exchange rates for the various analytes in the 1.0 M NaOH/4.6 M $NaNO_3$ matrix. The equilibrium K_d values were found to be established within about 50 h contact time for Cs and Pb. Ca, Ba, and Sr K_d values continued to slowly increase after 50 h contact time through 144 h.

[1] Walker Jr, JF, PA Taylor, and RL Cummins. 1998. *Cesium Removal Demonstration Utilizing Crystalline Silicotitanate Sorbent for Processing Melton Valley Storage Tank Supernate: Final report*. ORNL/TM-13503, Oak Ridge National Laboratory. Oak Ridge, Tennessee.

[2] Rovira AM, SK Fiskum, HA Colburn, JR Allred, MR Smoot, and RA Peterson. 2018. *Cesium Ion Exchange Testing Using Crystalline Silicotitanate with Hanford Tank Waste 241-AP-107*. PNNL-27706, Pacific Northwest National Laboratory, Richland, Washington.

[3] 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, Pacific Northwest National Laboratory. Richland, Washington.

[4] Campbell EL, AM Rovira, F Colon-Cintron, D Boglaienko, TG Levitskaia, and RA Peterson. 2019. *Characterization of Cs-Loaded CST Used for Treatment of Hanford Tank Waste in Support of Tank-Side Cesium Removal*. PNNL-28945, Rev. 0, Pacific Northwest National Laboratory. Richland, Washington.

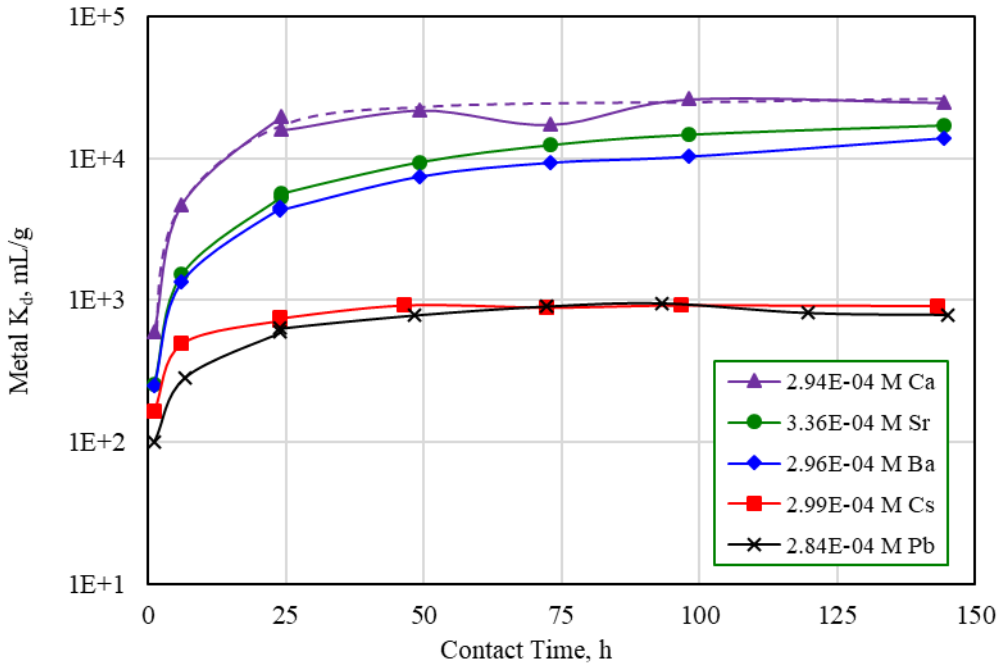


Figure Note: The dotted line accompanying Ca results is expected to more accurately represent the kinetic load profile.

Figure S.1. Kinetic Exchange Summary, Matrix: 1.0 M NaOH/4.6 M $NaNO_3$

Figure S.2 summarizes the isotherms (Q values vs. equilibrium metal concentrations) for the tested elements in each matrix. The nominal metal feed concentrations, exemplified by Hanford tank AP-107 non-complexant supernate, are shown for reference (dotted vertical lines). The isotherm testing showed the following.

- Selectivities for Ca, Ba, and Sr were similar and significantly greater than that of Pb and Cs in the 1.0 M NaOH/4.6 M $NaNO_3$ matrix.
- Decreasing the hydroxide concentration to 0.1 M had no measurable effect on Cs, Ca, Ba, or Sr exchange, but it had a profound effect on Pb exchange, with increased selectivity matching those of the Group II metals.
- Total Ba, Ca, and Sr capacities, estimated from fitting the data to the Freundlich/Langmuir hybrid equation, were 1.22, 0.616, and 1.33 mmoles/g, respectively.
- The Pb isotherm was difficult to fit to the Freundlich/Langmuir hybrid equation. The jump in Pb capacity at the higher concentration may indicate a second active exchange site on CST available for Pb exchange or may be due to continual shift in Pb equilibrium speciation.
- For Ba, Sr, and Pb, the feed composition represented by AP-107 tank waste will not be high enough to challenge Cs uptake. Ca was measured in the spent CST at ~0.13 mmoles /g (Campbell et al. 2019) and was significantly less than the measured capacity at~0.6 mmoles/g. Ca was present in the AP-107 feed at higher concentration than could be achieved during isotherm testing; the higher solubility was likely related to Ca complexation and stabilization in solution.
- The exchange affinities for complexed Ba, Ca, Pb, and Sr onto CST was not evaluated.

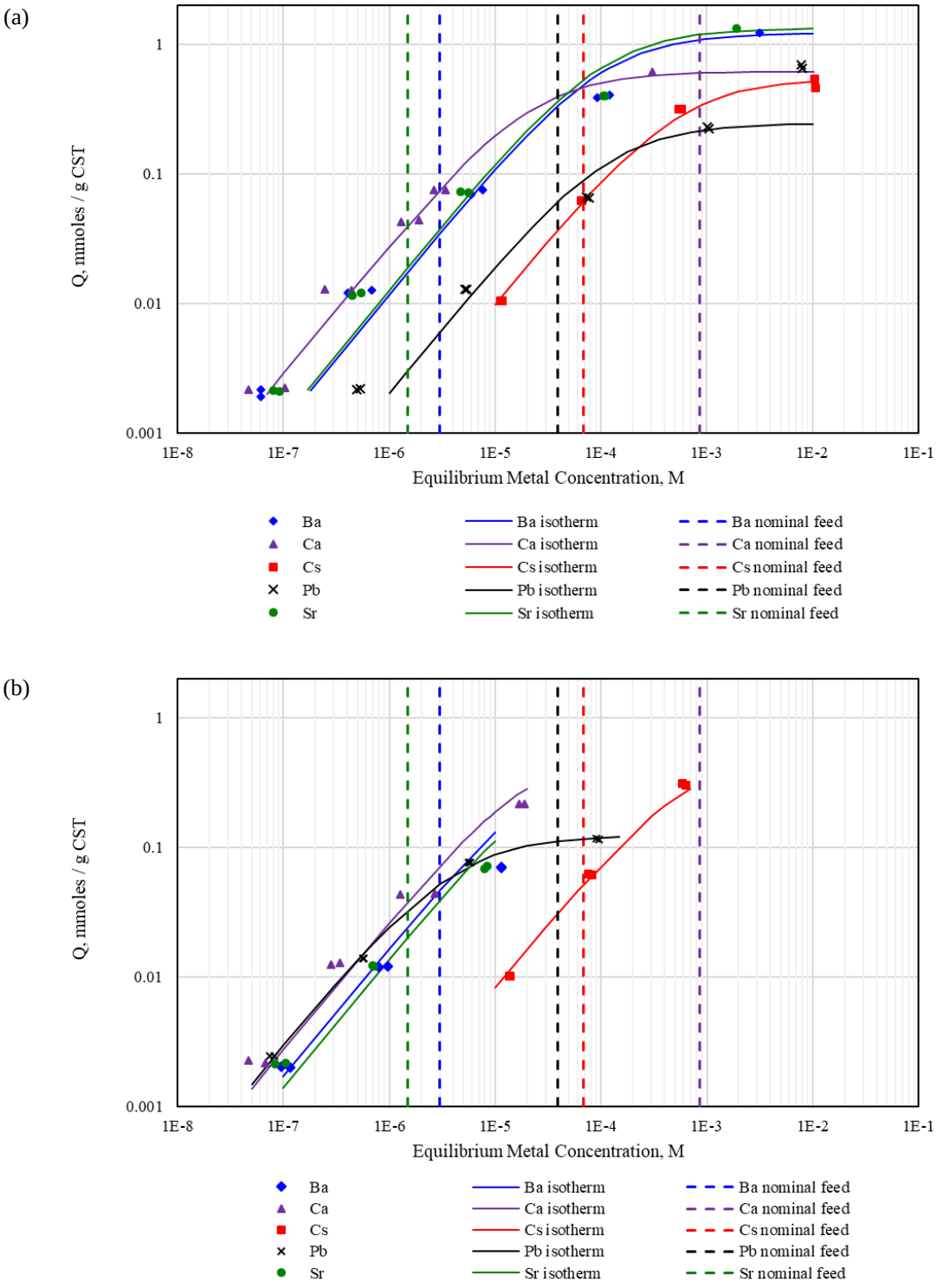


Figure S.2. Isotherm Summary: (a) 1.0 M NaOH/4.6 M $NaNO_3$, (b) 0.1 M NaOH/5.5 M $NaNO_3$

Acknowledgements

The authors thank the Analytical Support Operations and Environmental Science Laboratory Service Center for analysis. Specifically, we thank Dr. Samuel Morrison, Jenn Carter, and Denis Cherkasov for analysis by inductively coupled plasma mass spectrometry and inductively coupled plasma optical emission spectroscopy and subsequent data review. The authors thank Steven Baum and Ian Leavy for inductively coupled plasma optical emission spectroscopy analysis and Keith Geiszler and Michelle Valenta Snyder for technical review of the data. The authors thank Amy Westesen for assistance in selecting and purchasing chemicals. We thank Heather Colburn 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

BV	bed volume
CST	crystalline silicotitanate
LAW	low-activity waste
LSC	liquid scintillation counting
PNNL	Pacific Northwest National Laboratory
TSCR	Tank Side Cesium Removal
WTP	Hanford Waste Treatment and Immobilization Plant

Contents

Figures

Tables

1.0 Introduction

The U.S. Department of Energy is working to expedite processing of Hanford tank waste supernate at the Hanford Waste Treatment and Immobilization Plant (WTP). To support this goal, Washington River Protection Solutions is designing a Tank Side Cesium Removal (TSCR) system for suspended solids and cesium ($Cs/^{135}/Cs/^{137}Cs$) removal from Hanford tank waste supernate. The effluent will then be sent to the WTP Low-Activity Waste (LAW) facility for vitrification. The Cs removal is critical for eliminating the high dose rate associated with ^{137}Cs and facilitating a contact maintenance philosophy for the LAW Facility. The ion exchange media selected for Cs removal at the TSCR system is crystalline silicotitanate (CST) that is manufactured in a nearly spherical form by Honeywell UOP LLC (UOP; Des Plaines, IL) as product IONSIV™ R9140-B (Na form). 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 III et al. 2019).

A significant testing effort has been conducted with CST on simulants and actual tank wastes to prove its efficacy for removing Cs from non-complexant Hanford tank waste supernate. CST has demonstrated high Cs load capacity and chemical tolerance in highly alkaline salt solutions associated with Hanford tank waste supernates. Variable feed testing with CST focused primarily on the effect of Group I metals, where increased Na and K showed decreased Cs exchange capacity (Braun et al. 1996; Brown et al. 1996; Zheng et al. 1996; King et al. 2018a). Testing with actual tank wastes and groundwater also showed propensity for CST to exchange Ca, Sr, Ba, Pb, and Fe (Bostick and DePaoli 2000; Brown et al. 1996; Fiskum et al. 2019a; Rovira et al. 2018, 2019; Walker Jr et al. 1998; Wilmarth et al. 2004). Of these analytes, Sr exchange testing was more extensively evaluated.

Batch contact testing showed high Sr distribution coefficients (>3000 mL/g) in non-complexant basic solution (Marsh et al. 1994; Brown et al. 1996; Miller and Brown 1997). Very high Sr distribution coefficients (>10,000 mL/g) were observed with CST contacted with Fukushima process water (low salt solution) (Abe et al. 2016). The high distribution coefficients translated to high loading in the CST column. A 10% Sr breakthrough was noted after processing ~18,000 bed volumes (BVs) in the SARRY™ system used at Fukushima Daiichi Nuclear Power Plant (Abe et al. 2016). Brown et al. (1996) found that the Sr distribution coefficient in actual AW-101 tank waste was orders of magnitude lower than that of simulant. The authors speculated that Sr may be bound by organic complexants and not available for exchange.

Uptakes of other +2 cations, Ca, Ba, and Pb, were also found in earlier testing (Brown et al. 1996; Fiskum et al. 2019a; Rovira et al. 2018, 2019; Walker Jr et al. 1998, Wilmarth et al. 2004). In the actual waste column tests with low complexant wastes (AP-107 and AW-102), Sr, Ba, and Pb removal was essentially complete, as evidenced by undetected analyte in the column effluent. Evaluation of the Ca breakthrough profile during AP-107 processing showed a persistent 40% Ca retention (Fiskum et al. 2019a). This indicated that ~40% of the Ca was exchanging onto CST and ~60% of the Ca was likely complexed in a manner not amenable to ion exchange. Table 1.1 provides the *estimated* CST uptakes for selected analytes (Wilmarth et al. 2004; Campbell et al. 2019) after processing simulant and tank waste supernate through CST column beds. These uptake values do not necessarily represent CST capacity for the analytes; however, they provide a sense of the uptake propensity.

Table 1.1. Selected Analyte Uptakes by CST (mmoles analyte/g CST)

Analyte	Simulant, ~2000 BVs[(a)]	AW-102, ~451 BVs[(b)]	AP-107, ~425 BVs[(b)]
Ba	4.4E-3	1.4E-3	2.2E-3
Ca	NA	1.5E-1	1.2E-1
Pb	2.9E-2	1.4E-2	2.6E-2
Sr	NA	5.2E-4	7.9E-4

(a) Wilmarth et al. 2004
(b) Campbell et al. 2019 recovered analyte mass divided by the nominal 10 g CST in the column
BV = bed volume

Hamm et al. (2002) postulated the +2 cations exchange onto CST as the hydroxide complex, e.g., $SrOH^+$. The existence of a single hydroxide and other hydroxide complexes has been reported in highly alkaline solutions. Kutus et al. (2016) describe the changes in aqueous Ca formations from Ca^{2+} to $CaOH^+$ and then to $Ca(OH)_{2(aq)}$ as hydroxide molarity increases from 0.01 to 4 M. Grivé et al. (2010) describe Pb formation shifting from $Pb^{+2} \rightarrow Pb(OH)^+ \rightarrow Pb(OH)_{2(aq)} \rightarrow Pb(OH)_3^- \rightarrow Pb(OH)_4^{2-}$ as pH increases from 6 to 13. Hamm et al. (2002) further postulated that the $SrOH^+$ complex competes equally with Cs^+ for CST exchange sites.

Further investigations of Ba, Ca, Pb, and Sr were conducted to elucidate their exchange behaviors onto CST and their effects on Cs exchange. The exchange behavior of Ba was of particular concern because Cs breakthrough during TSCR processing will be determined from on-line monitoring of the ^{137m}Ba (^{137}Cs daughter product with a 2.55 min half-life) gamma signal. Secular equilibrium of $^{137}Cs/^{137m}Ba$ is required for accurate Cs breakthrough assessment. Should Ba retention on CST be negligible or partial, the secular equilibrium will need to be reestablished to accurately measure Cs breakthrough. Understanding the effectiveness of ^{90}Sr removal by CST will allow for further evaluation of post-ion-exchange effluent transportation and treatment options. Understanding of Ca and Pb exchange will help model CST capacity challenges for wastes high in these components.

To this end, a series of batch contact tests was conducted to measure distribution coefficients for Cs, Ca, Ba, Pb, and Sr. Two simple simulants were used as a matrix, each at 5.6 M Na. One simulant incorporated 1.0 M OH and the other matrix incorporated 0.1 M OH; the nitrate concentration was varied between the two simulants to maintain the overall 5.6 M Na concentration. The 5.6 M Na concentration was targeted because it matched the tank waste feed condition projected for the TSCR system. The 0.1 M OH concentration did not reflect the condition of most tank wastes; it was selected to help elucidate the ion exchange mechanism for the +2 cations *vis à vis* the degree of $M(OH)_x^+$ complexation. An initial kinetics test was performed to best determine the contact/mixing time required to reach equilibrium conditions. This was followed by an array of isotherm testing as summarized in Table 1.2. The effect of the metal content on the Cs isotherm was established at three different concentrations. Additional high-metal concentration contacts were conducted after reviewing initial results.

Table 1.2. Generic Test Array

	Isotherms[a]		Effect of Metal on Cs uptake[a]		
	High [OH]	Low [OH]	Constant [Metal] on Cs Isotherm	2× [Metal] on Cs Uptake	0.25× [Metal] on Cs Uptake
Matrix	1.0 M NaOH/ 4.6 M $NaNO_3$	0.1 M NaOH/ 5.5 M $NaNO_3$	1.0 M NaOH/ 4.6 M $NaNO_3$/ 6.4E-5 M metal	1.0 M NaOH/ 4.6 M $NaNO_3$/ 4.0E-5 M Cs	1.0 M NaOH/ 4.6 M $NaNO_3$/ 4.0E-5 M Cs
Variable	1.1E-5 M	1.1E-5 M	--	--	--
	6.4E-5 M	6.4E-5 M	6.5E-5 M Cs	1.3E-4 M	1.6E-5 M
	3.8E-4 M	3.8E-4 M	3.9E-4 M Cs	--	--
	2.1E-3 M[b]	--	2.2E-3 M Cs	--	--
	1.0E-2 M[c]	--	1.3E-2 M Cs	--	--

(a) All concentrations are listed for Ba, Ca, Sr, and Pb unless otherwise stated.
(b) This value exceeded the Ca solubility threshold. An intermediate Ca concentration was tested instead.
(c) This value exceeded the Ca solubility threshold. A lower Ca concentration with higher contact volume was used instead.

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 Washington River Protection Solutions (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 Experimental

This section describes the CST and its pretreatment, reagent selection, simulant preparation, metal/radiotracer spiking, batch contact testing, and measurement methods.

3.1 CST

The CST was purchased from Honeywell LLC, as IONSIV™ R9140-B, Product 8056202-999, Lot Number 2002009604, as an 18 × 50 mesh sieve cut. Fiskum et al. (2019b) provided additional detail associated with receipt and storage of this CST sample. A 168.6-g CST aliquot was collected and transferred onto a 30-mesh sieve (ASTM E11 specification). The <30-mesh sieve fraction (47.2 g) was collected and represented 28% by weight of the starting CST sample mass. This sieve cut was selected to be comparable to that to be used in small-scale column tests conducted in fiscal year 2020 at Pacific Northwest National Laboratory (PNNL). This sieve cut best scales from the full-height column to the small 10-mL column geometry. The batch contact data obtained from this sieve cut may be used to compare to fiscal year 2020 column testing at PNNL.

The 47.2-g <30-mesh CST fraction was pretreated by contacting with 100 mL of 0.1 M NaOH six successive times. The 0.1 M NaOH rinse solution and colloidal fines from the CST were decanted. The final rinse was removed in total and the CST was allowed to air dry at room temperature until it was free-flowing.

The gross water content of the CST was determined before collecting aliquots for batch contact testing. The water content was determined as the ratio of CST mass heated to constant mass at 100 °C divided by the initial mass. It was understood that additional mass loss (10% to 12%) occurs when CST is further heated from 100 °C to 425 °C (Fiskum et al. 2019a; King et al. 2018a).

3.2 Simulant Preparation

Reagent salts were selected with the lowest metal impurities as reasonably achievable. Table 3.1 provides the reagent materials selected with vendors, purity, lot number, and given Group II metal content, K content, and Pb content (as available from the vendor-provided certificate of analysis). Sodium nitrate required very low trace metal content because large masses were used to create the simulants. Trace metal content can become significant when using large masses. At the maximum “less-than certificate” values for Ca and heavy metal impurities, no more than 3E-5 M impurity was expected in each preparation. The other metals were added at low concentrations and impurity was less of a concern.

Table 3.1. Simulant Reagents

Reagent	Vendor	Purity	Lot	Group II Metal Content
$NaNO_3$	Alfa Aesar (dist. by ThermoFisher)	99.6%	Q16F033	< 0.00005% Ca <5 ppm heavy metals K not reported
NaOH solution, 1.524 g/mL	Sigma-Aldrich	50.0%	BCBZ4353	<10 ppm Ca <10 ppm Pb <100 ppm K
$Ba(NO_3)_2$	Alfa Aesar	99.999%	N11F012	2 ppm Ca <1 ppm Pb and Sr
$Ca(NO_3)_2{\cdot}4(H_2O)$	Alfa Aesar	99.98%	61600281	<0.02% trace metals
$Pb(NO_3)_2$	Acros Organics	99.999%	A0386019	<0.001% trace metals
$Sr(NO_3)_2$	Sigma-Aldrich	99.995%	MKCG4972	2.5 ppm trace metals

Two matrix solutions were prepared as shown in Table 3.2. The sodium nitrate was weighed directly into a volumetric flask. Deionized water with a resistivity of 18 MΩ-cm was used to dissolve the salt. Once the salt dissolved, the target volume of 50% NaOH solution was added. The solution was equilibrated to room temperature (sodium nitrate dissolution is an endothermic process), then the solution was brought to volume with deionized water. The density was determined from the net solution mass and volume. The solution was filtered through a 0.2-micron pore size nylon filter and stored in the polycarbonate receipt vessel.

Table 3.2. Simulant Matrices

	Reagent, g reagent/L solution		
Matrix	$NaNO_3$	50% NaOH	Density, g/mL
1.0 M NaOH/ 4.6 M $NaNO_3$	391.2	80.0	1.272
0.1 M NaOH/ 5.5 M $NaNO_3$	467.4	7.9	1.281

Individual metal salt stock solutions were prepared from the metal nitrate salts. An aliquot of metal nitrate was weighed directly into a volumetric flask. Deionized water was added until the salt dissolved and then concentrated nitric acid was added to attain a nominal 0.03 M acid solution to help maintain solubility during the storage period. Aliquots of metal salt solutions were diluted nominally 25×. These two metal concentrations allowed for spiking to meet the requisite broad concentration range in the test matrices. The masses of all metal salt solution and matrix solution transfers were recorded and density-corrected to calculate exact volumes and concentrations.

Solubilities of the metals in 1.0 M NaOH/4.6 M $NaNO_3$ were evaluated before the test matrices were finalized. Cesium was highly soluble in the hydroxide solution and was not of concern. Solubilities of Ba, Sr, and Pb were not constrained up to 2E-3 M. Calcium solubility was limited to ~4.0E-4 M (16 µg/mL) in 1.0 M NaOH/4.6 M $NaNO_3$ and ~1.4E-3 M (~56 µg/mL) in 0.1 M NaOH/5.5 M $NaNO_3$.

Radiotracers were used where possible. Aliquots of the stock matrix were spiked with ^{85}Sr, ^{133}Ba, ^{45}Ca, or ^{137}Cs, as appropriate. No radiotracers for Pb were available. The radiotracers allowed for rapid analysis by gamma energy analysis or liquid scintillation counting (LSC); each analysis was conducted in an effort to reach a total count error of 1%. The Pb required analysis by inductively coupled plasma optical emission spectrometry or inductively coupled plasma mass spectrometry, depending on the Pb concentration. The tracer and non-radioactive metal spikes were added in close time proximity such that they could mix well before any potential in situ precipitation could occur. The tracers contained a small amount of stable

element (carrier); the carrier concentration was incorporated into the total solution analyte concentration calculations.

3.3 Kinetic Testing

The metal exchange rate was confirmed before isotherm testing was initiated. The goal was to assess the contact time duration required to reach equilibrium conditions in the 1.0 M NaOH/4.6 M $NaNO_3$ matrix. Equilibrium conditions in the 0.1 M NaOH/5.5 M $NaNO_3$ matrix were assumed to be equivalent to that of the higher hydroxide solution. A nominal 272-mL simulant was spiked with the metal nitrate and tracer solution to reach ~3E-4 M metal. A 45-mL aliquot was collected and used as a batch contact comparator containing no CST with the intent to verify precipitation had not occurred during the batch contact duration. Solution aliquots were also collected for analysis and used as the initial element concentration. A 220-mL solution aliquot was contacted with 1.1 g CST (dry mass basis) representing a liquid volume to solids mass phase ratio of 200. All solution volumes were determined based on aliquoted solution mass and density. The batch contact solutions with CST were placed in 250-mL polyethylene bottles. The headspace in this configuration allowed for significant fluid motion, assuring good mixing.

A Cole-Parmer orbital shaker with a 16-mm amplitude was used for traced solutions. It was set to 260 revolutions per minute, which was sufficient to lift the CST off the vessel floor but did not disperse the CST throughout the fluid volume. An IKA KS125 orbital shaker table with 4-mm amplitude, set to ~500 rpm, was used for the Pb solutions. Temperature during contact remained relatively constant at 21 ± 2 °C.

Two-milliliter sample aliquots were collected at various times during mixing and passed through a 0.45-micron pore size nylon syringe filter before analysis. The volume change was monitored from the measured net solution mass and accounted for in the distribution coefficient (K_d, mL/g) and metal loading onto CST (Q, mmoles metal per g CST) calculations. A 2-mL reduction during kinetic testing sampling represented 1% of the total solution volume. After seven samplings, the contact solution volume reduction was 7%. Sampling occurred after nominally 1, 6, 24, 49, 73, 98, and 144 h contact times. The 24-h sample was collected in duplicate. Each 45-mL comparator was only sampled twice, once after ~49 h and again after ~98 h. Exact contact times were recorded.

3.4 Isotherm Testing

Test solution concentrations were prepared such that the post-contacted equilibrium metal concentrations would bracket the feed metal concentrations found in tank wastes AP-105, AW-102, and AP-107 (Fiskum et al. 2018; Rovira et al. 2019; Fiskum et al. 2019a, respectively). The 1.0 M NaOH/4.6 M $NaNO_3$ matrix was tested at four metal concentrations (five concentrations for Pb) and the 0.1 M NaOH/5.5 M $NaNO_3$ matrix was tested at three metal concentrations (four concentrations for Ca and Pb). Table 3.3 provides the compositions of the individual batch contact samples tested juxtaposed with the measured metal concentrations in the three tank wastes.

Table 3.3. Isotherm Test Solutions

Matrix	Metal Concentrations, M				
	Ba	Ca	Pb	Sr	Cs
AP-105[(a)]	[3.0E-6]	[1.0E-3]	<1.2E-4	<2E-6	5.91E-5
AP-107[(b)]	[3.0E-6]	[8.6E-4]	[3.9E-5]	[1.5E-6]	6.84E-5
AW-102[(c)]	[3.7E-6]	[6.0E-4]	ND	ND	4.64E-5
1.0 M NaOH/ 4.6 M $NaNO_3$	1.12E-5	1.20E-5	1.21E-5	1.14E-5	6.72E-5
	6.59E-5	6.60E-5	6.35E-5	6.47E-5	3.97E-4
	3.91E-4	2.33E-4	3.77E-4	3.90E-4	2.24E-3
	2.19E-3	4.00E-4	2.11E-3	2.19E-3	1.32E-2
	--	--	1.18E-2	--	--
0.1 M NaOH/ 5.5 M $NaNO_3$	1.12E-5	1.17E-5	1.08E-5	1.13E-5	6.84E-5
	6.58E-5	6.61E-5	6.21E-5	6.49E-5	3.97E-4
	3.85E-4	2.35E-4	3.91E-4	3.89E-4	2.25E-3
	--	1.17E-3	2.12E-3	--	--

(a) Fiskum et al. 2018.
(b) Fiskum et al. 2019a.
(c) Rovira at al. 2019.
ND = not detected
Bracketed values indicate reported values had >15% uncertainty.

The effect of each metal on the cesium isotherm was tested in two manners. First, the competitor concentration was kept constant at ~6.4E-5 M and the Cs was varied as shown in Table 3.4. Then, the Cs was kept constant at ~4.0E-4 M and the metal competitor was doubled to ~1.3E-4 M and quartered to ~1.7E-5 M as shown in Table 3.5. In both cases, only one matrix was tested, 1.0 M NaOH/4.6 M $NaNO_3$. An additional test was conducted with Pb at 33× higher concentration (2.12E-3 M) to explore an upper boundary for impact on Cs exchange.

Table 3.4. Constant Metal on Cs Isotherm (1.0 M NaOH/4.6 M $NaNO_3$)

Metal Conc.>>	6.42E-5 M Ba	6.64E-5 M Ca	6.42E-5 M Pb	6.44E-5 M Sr	Cs only
Cs Conc., M	6.76E-5	6.63E-5	6.31E-5	6.77E-5	6.72E-5
	3.96E-4	3.98E-4	3.89E-4	3.94E-4	3.97E-4
	2.26E-3	2.18E-3	2.16E-3	2.24E-3	2.24E-3
	1.31E-2	1.28E-2	1.27E-2	1.32E-2	1.32E-2

Table 3.5. Variable Metal on Cs Isotherm (1.0 M NaOH/4.6 M $NaNO_3$)

	Ba	Ca	Pb	Sr
Metal Conc, M	1.28E-4	1.28E-4	1.22E-4	1.27E-4
	1.66E-5	1.68E-5	1.62E-5	1.64E-5
Cs Conc., M	3.82-4	3.87E-4	4.22E-4	3.82E-4

The phase ratio of 200 was maintained for these batch contact samples (15 mL liquid and 0.075 g dry CST). All contacts were conducted in 20-mL plastic scintillation vials. The samples were shaken on the same shaker used for isotherms, 260 revolutions per minute and 16 mm amplitude. Temperature remained constant at ~21 ± 2 °C for the ~140 h contact time. After processing, a nominal 2-mL sample aliquot was filtered through a 0.45-micron pore size nylon syringe filter and the filtrate was collected for ^{137}Cs analysis.

3.5 Maximum Analyte Loading

Tests were conducted to determine the maximum analyte load capacity in CST and the effect of analyte-loaded CST on subsequent Cs exchange. CST was first contacted with ~1E-2 M Ba, Pb, and Sr in the 1.0 M NaOH/4.6 M $NaNO_3$ matrix solution at a phase ratio of 200, matching previous test phase ratios. Because of Ca solubility limitations, the 0.1 M NaOH/5.5 M $NaNO_3$ matrix was used (higher Ca solubility than found in 1.0 M NaOH/4.6 M $NaNO_3$), spiked at 1E-3 M Ca, and employed a higher phase ratio of ~670, allowing availability of adequate Ca mass to saturate the CST. Specific as-measured metal concentrations are provided in Table 3.6; they agreed with the make-up values within 15% (analytical uncertainty). Before CST contact, the Ca-spiked simulant underwent a 24-h equilibration period and then was filtered. No radiotracers were used in this test. The dry CST mass was ~0.3 g. The CST/simulant was contacted in the IKA orbital shaker as previously described for 49 h at ~23 °C.

After contact with the specific metal, the CST was separated from the aqueous phase. The aqueous phase was sent for analysis. The CST was rinsed three times with 10 mL 0.1 M NaOH and dried at room temperature to a free-flowing condition. The dried CST was subdivided for F-factor measurement and duplicate batch contacts with 2.12E-3 M Cs solution traced with ^{137}Cs. The contact phase ratio of 326 was higher than the targeted 200 because the measured F-factor was much lower than anticipated.

Table 3.6. Metal Loading Concentrations (Molarity, as measured)

Matrix	Ba	Ca	Pb	Sr
1.0 M NaOH/ 4.6 M $NaNO_3$	9.17E-03	--	1.27E-02	8.53E-03
0.1 M NaOH/ 5.5 M $NaNO_3$	--	1.23E-03	--	--

3.6 Analysis

The samples traced with ^{85}Sr, ^{133}Ba, and ^{137}Cs were analyzed using a suite of high-purity lithium drifted germanium gamma detectors. The samples traced with ^{45}Ca were prepared for LSC by aliquoting 200 microliters of filtered sample into 20 mL of Ultima Gold™ scintillation cocktail; background subtraction samples were similarly prepared with 200 microliters of the un-spiked matrix solution. The ^{45}Ca beta activity was measured with a PerkinElmer Tri-Carb 3100 LSC equipped with QuantaSmart™ software by PerkinElmer Inc. The untraced Pb sample analyses were conducted by inductively coupled plasma optical emission spectrometry or inductively coupled plasma mass spectrometry. Comparator samples were prepared from aliquots collected from the starting feed matrix and measured identically to the samples.

The batch distribution coefficients were calculated according to Eq. (3.1).

$$\frac{(C_0 - C_1)}{C_1} \times \frac{V}{M \times F} = K_d \qquad (3.1)$$

where C_0 = initial analyte concentration (µCi/mL, dpm/mL, or µg/mL)
C_1 = final (equilibrium) analyte concentration (µCi/mL, dpm/mL, or µg/mL)
V = volume of the batch contact liquid (mL)
M = measured mass CST (g)
F = F-factor, mass of the dried CST divided by the mass of the undried CST
K_d = batch-distribution coefficient (mL/g)

Final (equilibrium) metal concentrations (C_{MEq}) were calculated relative to the tracer recovered in the contacted samples (C_1) and the initial metal concentration (C_{M0}) according to Eq. (3.2).

$$C_{M0} \times \left(\frac{C_1}{C_0}\right) = C_{MEq} \tag{3.2}$$

where C_{M0} = initial metal concentration in solution (µg/mL or M)
C_1 = equilibrium tracer concentration in solution (µCi/mL, dpm/mL or µg/mL)
C_0 = initial tracer concentration in solution (µCi/mL, dpm/mL or µg/mL)
C_{MEq} = equilibrium metal concentration in solution (µg/mL or M)

The equilibrium metal concentrations loaded onto the CST (Q in units of mmoles metal per gram of dry CST mass) were calculated according to Eq. (3.3).

$$\frac{C_{M0} \times V \times \left(1 - \frac{C_1}{C_0}\right)}{M \times F \times 1000 \times FW} = Q \tag{3.3}$$

where Q = equilibrium metal concentration in the CST (mmole/g CST)
C_{M0} = initial metal concentration in solution (µg/mL)
V = volume of the batch contact liquid (mL)
C_1 = final tracer or metal concentration in solution (µCi/mL, dpm/mL or µg/mL)
C_0 = initial tracer or metal concentration in solution (µCi/mL, dpm/mL or µg/mL)
M = mass of CST (g)
F = F-factor, mass of the dried CST divided by the mass of the undried CST
1000 = conversion factor to convert µg to mg
FW = formula weight of the metal

4.0 Results

This section summarizes Ba, Ca, Pb, and Sr kinetic testing and isotherm testing results. Cs was similarly tested to provide benchmark results in the test matrix solutions.

4.1 Kinetic Testing

Table 4.1, Table 4.2, and Table 4.3 provide results from the kinetic testing. These tables show the contact duration and corresponding equilibrium analyte molarity (C_1), distribution coefficient (K_d, mL per g CST), and analyte loading onto CST (Q, mmoles per g CST). Also shown are the calculated starting concentrations (C_0) for each analyte. The comparator sample concentrations and recoveries at ~49-h and ~98-h contact times for Ba, Ca, Pb, and Sr are also provided. Comparators for Cs were not measured because Cs solubility is high in the simulant solution. The comparator samples were not contacted with CST and were used to verify that precipitation had not occurred as the sample processing was conducted; ideally, the comparator sample concentrations will match the initial sample concentration. Only Pb comparators, at 2.07E-04 M, deviated from the starting Pb concentration, 2.84E-4 M Pb, representing a 27% reduced concentration. This variance could be an artifact of the analysis technique where an accuracy of ±15% was reported or a result of partial Pb precipitation. All other comparator metals recovered at ~100%, indicating they maintained solubility during the contact period.

Table 4.1. Ba and Ca Kinetic Testing Results

Barium, C_0 2.96E-4 M				Calcium, C_0 2.94E-4 M			
Time, h	C_1, M	K_d, mL/g	Q, mmoles/g	Time, h	C_1, M	K_d, mL/g	Q, mmoles/g
1.0	1.32E-4	249	3.26E-2	1.0	7.35E-05	593	4.36E-02
6.0	3.83E-5	1,341	5.12E-2	6.0	1.19E-05	4,685	5.58E-02
24.0	1.25E-5	4,496	5.64E-2	24.0	2.92E-06	19,512	5.75E-02
24.0	1.28E-5	4,342	5.63E-2	24.0	3.59E-06	15,874	5.74E-02
49.1	7.50E-6	7,455	5.74E-2	49.2	2.59E-06	21,812	5.76E-02
73.0	5.95E-6	9,357	5.77E-2	73.0	3.25E-06	17,260	5.75E-02
98.0	5.35E-6	10,330	5.78E-2	98.1	2.15E-06	26,084	5.77E-02
144.4	3.95E-6	13,927	5.81E-2	144.3	2.26E-06	24,683	5.77E-02
Comparators		Recovery		Comparators		Recovery	
49.1	3.00E-4	101%		49.2	3.00E-04	102%	
98.0	3.15E-4	106%		98.1	3.00E-04	102%	

Table 4.2. Pb and Sr Kinetic Testing Results

Lead, C_0 2.84E-4 M				Strontium, C_0 3.36E-4 M			
Time, h	C_1, M	K_d, mL/g	Q, mmoles/g	Time, h	C_1, M	K_d, mL/g	Q, mmoles/g
1.0	1.71E-04	101	1.74E-02	1.0	1.47E-4	257	3.80E-2
6.6	1.06E-04	286	3.06E-02	6.0	3.88E-5	1,520	5.98E-2
24.0	6.42E-05	594	3.90E-02	24.0	1.19E-5	5,354	6.52E-2
24.0	6.13E-05	631	3.96E-02	24.0	1.12E-5	5,642	6.53E-2
48.2	5.12E-05	780	4.16E-02	49.2	6.77E-6	9,392	6.62E-2
72.3	4.51E-05	902	4.29E-02	73.0	5.09E-6	12,418	6.66E-2
93.3	4.30E-05	948	4.33E-02	98.0	4.28E-6	14,670	6.67E-2
119.8	5.77E-05	812	4.73E-02	144.3	3.65E-6	17,064	6.68E-2
145.1	5.91E-05	788	4.72E-02				
Comparators		Recovery		Comparators		Recovery	
48.2	2.06E-04	73%[a]		49.2	3.28E-4	98%	
93.3	2.08E-04	73%[a]		98.0	3.32E-4	99%	

(a) Repeated analysis associated with the Pb comparator samples indicated recovery was 107%.

Table 4.3. Cs Kinetic Testing Results

Cesium, C_0 2.99E-4 M			
Time, h	C_1, M	K_d, mL/g	Q, mmoles/g
1.0	1.64E-04	165	2.71E-02
6.0	8.59E-05	494	4.27E-02
24.0	6.42E-05	722	4.71E-02
24.0	6.25E-05	746	4.74E-02
46.5	5.19E-05	921	4.95E-02
72.4	5.31E-05	888	4.93E-02
96.7	5.12E-05	920	4.97E-02
143.1	5.12E-05	912	4.97E-02

Figure 4.1 shows the distribution coefficients from Table 4.1, Table 4.2, and Table 4.3 as a function of time. Both Cs and Pb show constant K_d values after about 50- to 75-h contact time. However additional small quantities of Ba, Sr, and Ca continued to be removed beyond the 75-h contact time through 144 h. The K_d values for Ba, Sr, and Ca are clearly at least an order of magnitude higher than those of Pb and Cs. The higher variability of the Ca results (lack of smoothness of fit) was likely associated with the analysis of very low count rate samples by LSC due to nearly quantitative uptake of Ca; the smoothed fit is shown in a dashed line.

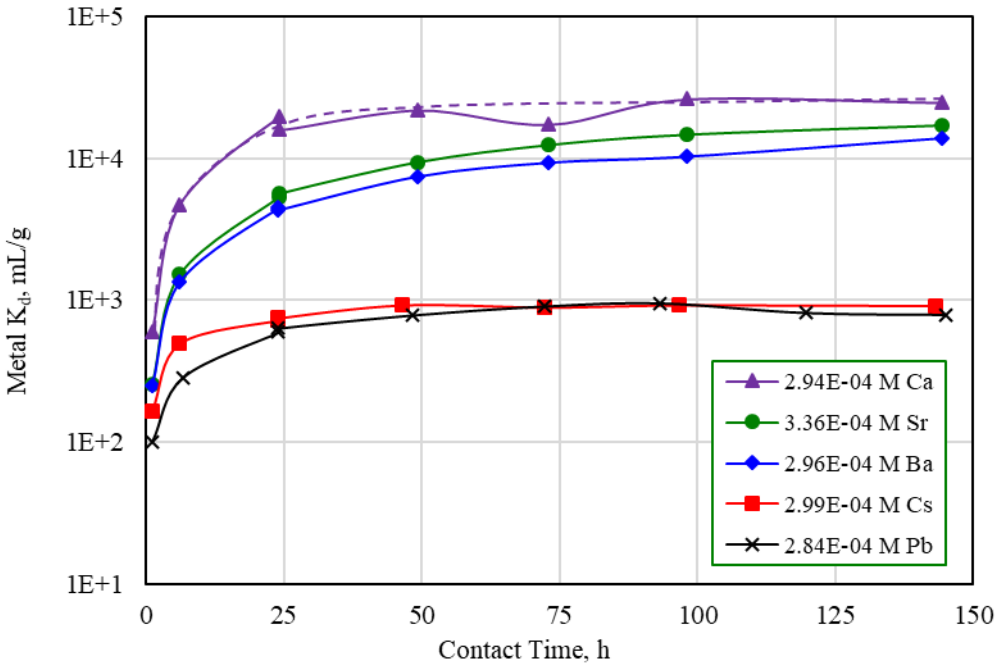


Figure 4.1. Analyte Distribution Coefficient onto CST as a Function of Time in 1.0 M NaOH/4.6 M $NaNO_3$

Figure 4.2 graphs the Q values from Table 4.1, Table 4.2, and Table 4.3 as a function of time. The Ba, Ca, Cs, and Sr loading of CST occurred quickly (within 24 h) as observed by Q reaching nearly the maximum value within 24 h. The starting analyte concentrations were similar at ~3E-4 M with one exception: The initial Sr concentration was 12% higher and this resulted in the corresponding 15% higher Sr loading. Had the concentrations more closely aligned, the Sr curve would likely overlay the Ca and Ba curves. The Cs loading was ~14% lower than that of Ba and Ca at the starting 3E-4 M metal concentration. The Pb loading was lower than Ba, Ca, Sr, and Cs. Note that the increased values for the final two Pb data points were artifacts of different analysis runs and was not considered a real step function.

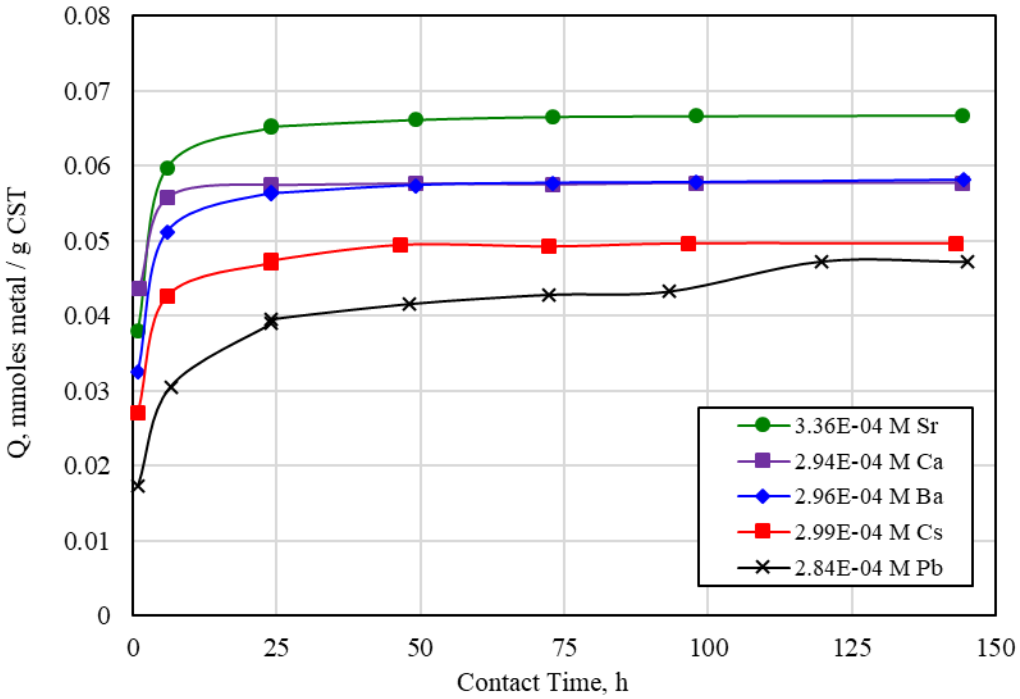


Figure 4.2. Analyte Distribution Coefficient onto CST as a Function of Time in 1.0 M NaOH/4.6 M $NaNO_3$

These data show that Ba, Ca, and Sr exchanges are more favorable than that of Cs and Pb in this matrix condition. Similarly, the exchange rates for Ba, Ca, and Sr are more rapid and complete in about 24 h relative to Cs and Pb, which took about 50 h to reach equilibrium. It is noted that K_d values for Ba, Ca, and Sr continued to rise during the extended contact period. This was consistent with previous observations where most of the analyte mass was essentially loaded in short order (measured by Q), but trace masses, more accurately measured by K_d, continued to load (King et al. 2018b). Based on these results, the 144-h contact time was selected for all subsequent isotherm measurements.

4.2 Isotherms

This section compares Cs exchange in the test matrix with other recent tests, discusses binary isotherms, and examines the effect of the potential competitors on Cs exchange. Appendix A provides the raw data, including the contact solution volumes, CST masses, and analytical results (initial and equilibrium analyte concentrations in solution), as well as the K_d values and concentrations on the CST (Q values) from the extensive isotherm testing.

4.2.1 Comparison of Matrix Conditions on Cs Exchange

The Cs isotherm in the 1.0 M NaOH/4.6 M $NaNO_3$ simulant was compared to previous test results with the same CST lot to establish the efficacy of using the simple simulant in lieu of a more complex simulant to study exchange behaviors. The previous tests used a slightly larger particle sieve cut (<25 mesh vs. <30 mesh); however, at equilibrium contact times of ~140 h, performance differences between the two mesh sizes with respect to Cs loading were not expected. Figure 4.3 plots the Cs isotherm generated in the 1.0 M NaOH/4.6 M $NaNO_3$ matrix overlaid with isotherms generated from samples of two Hanford tank waste matrices (AP-107 and AW-102, Fiskum et al. 2019a and Rovira et al. 2019, respectively) and one

data point for the more complex 5.6 M Na simulant (Fiskum et al. 2019b). The Cs selectivities and capacities for the various matrices were reasonably similar to the isotherm defined for the 1.0 M NaOH/4.6 M $NaNO_3$ simulant, indicating that this simplified simulant provided a relevant test basis to evaluate the effects Ca, Ba, Sr, and Pb on Cs exchange. It is assumed that other anion/cation interferences can also be tested in this simplified simulant to reasonably predict effects of other tank waste constituents on Cs exchange behavior.

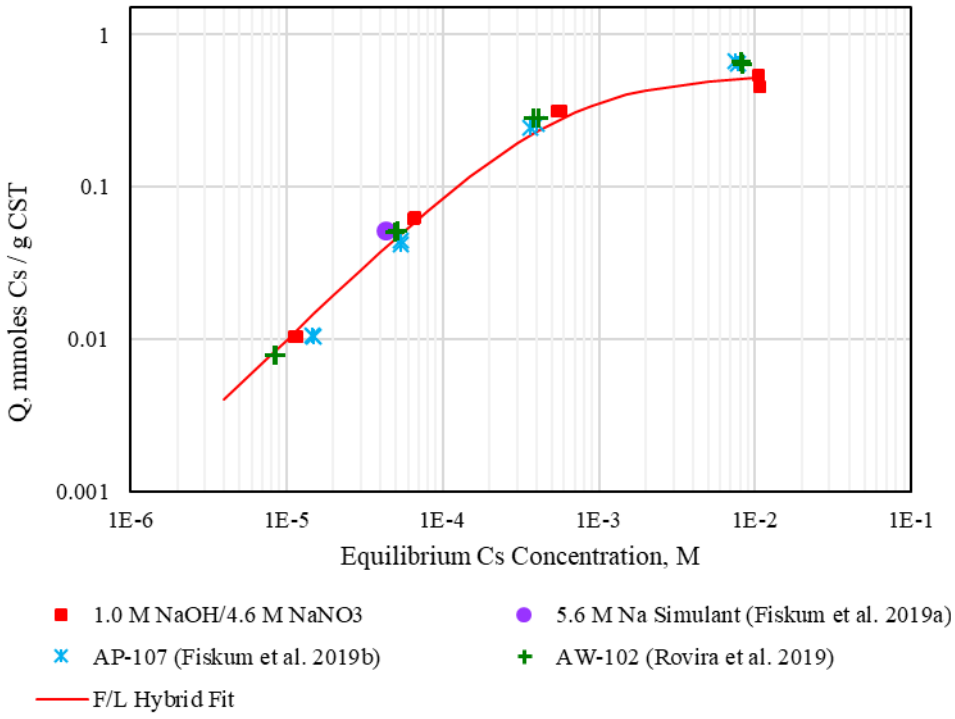


Figure 4.3. Comparison of Cs Isotherms in 1.0 M NaOH/4.6 M $NaNO_3$ Relative to Other Matrices

4.2.2 Single Element Exchange

The binary isotherm data in the 1.0 M NaOH/4.6 M $NaNO_3$ matrix are plotted in Figure 4.4. For reference, the nominal analyte feed concentrations found in AP-107 tank waste supernate (Fiskum et al. 2019a) are also shown (vertical dashed lines). The CST resulted in higher selectivity for the alkaline earth metals Ca, Sr, and Ba than for Cs and Pb, as shown by their left offsets from the Cs and Pb isotherms. The experimental capacities for the alkaline earths and Pb were assessed from separate maximum analyte loading tests (displayed as the right/highest data points, see Section 4.2.3). Ca solubility in 1.0 M NaOH/4.6 M $NaNO_3$ was limited to 4E-4 M; therefore, the maximum Ca capacity was determined using the 0.1 M NaOH/5.5 M $NaNO_3$ matrix to exploit the higher solubility limit in conjunction with an increase in the phase ratio ~3.3× higher than the other element contact solutions.

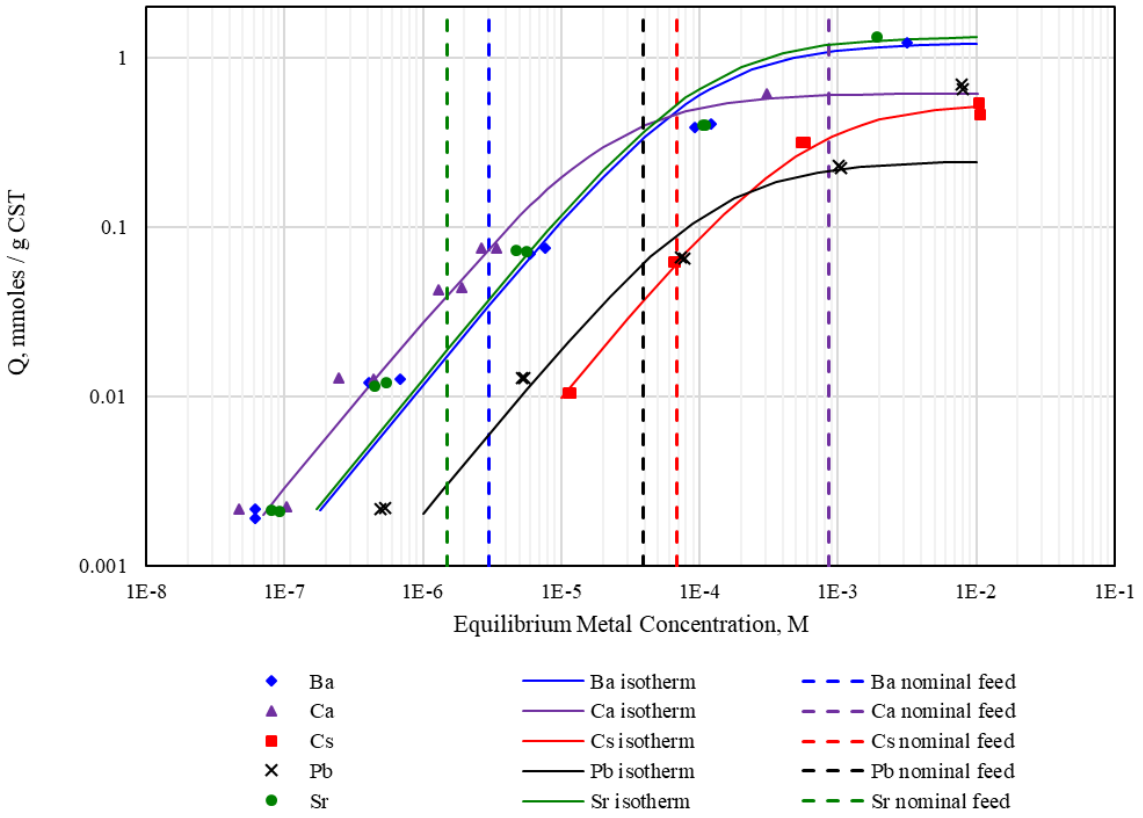


Figure 4.4. Cs, Ba, Sr, Ca, and Pb Isotherm Comparison, 1.0 M NaOH/4.6 M $NaNO_3$

The Freundlich/Langmuir (F/L) hybrid isotherm model (Hamm et al. 2002) was difficult to fit to the Pb results (Figure 4.4). The total CST capacity for Pb at ~0.65 mmoles per gram CST was similar to that of Cs at ~0.55 mmoles per gram CST at an equilibrium feed composition of ~9E-3 M. Yet the best fit Pb isotherm indicated a nominal capacity of 0.25 mmoles per g CST. The observed variation may be related to availability of a second exchange site for $Pb(OH)^+$ with Pb concentrations >1E-4 M similar to K and Rb exchange proposed by Zheng et al. (1997):

$$Pb(OH)^+ + Na_3X \leftrightarrows [Pb(OH)]Na_2X + Na^+ \quad (4.1)$$

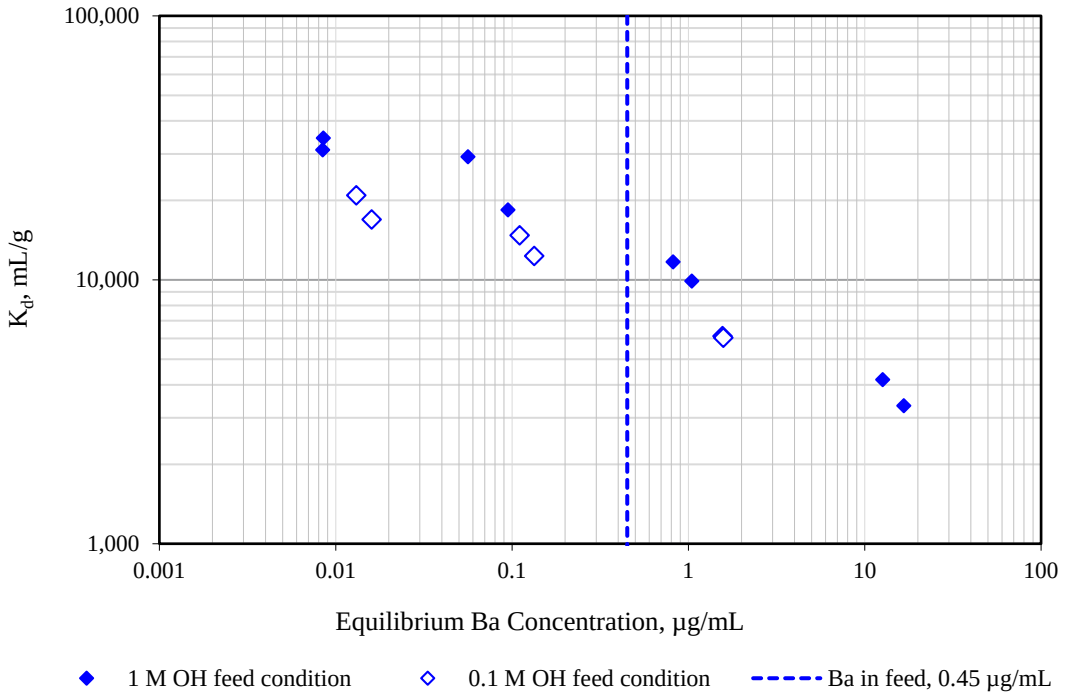
$$Pb(OH)^+ + (PbOH)Na_2X \leftrightarrows [(Pb(OH)]_2NaX + Na^+ \quad (4.2)$$

Also, Pb exists in a multiplicity of cationic and anionic forms in hydroxide solution; depletion of one ionic form may shift the equilibrium, confounding the isotherm evaluation. Additional testing at various Pb concentrations would be needed to ascertain this assumption.

The typical feed Ba, Sr, and Pb concentrations in tank waste supernate are generally low, limited by the total hydroxide and sulfate concentrations in tank waste. These analytes have primarily been found in the sludge phase. Their supernate concentrations are exemplified by AP-107 and are shown in Figure 4.4 as vertical dashed lines. Because Sr and Ba equilibrium feed concentrations are far to the left of the Cs equilibrium concentration, they will not adversely impact CST Cs selectivity or capacity. The Pb equilibrium concentration is closer to that of Cs and its effect on Cs exchange is of more concern (see Section 4.2.3). Within the bounds tested and based on these isotherms, the presence of Ba, Sr, and Pb in the contact solution is expected to have negligible demonstrable effect on the Cs exchange capacity.

Clearly, the Ca equilibrium concentration in tank waste at 1E-3 M in AP-107 was much higher than that established by the isotherm in 1.0 M NaOH/4.6 M $NaNO_3$. Testing at higher Ca concentration was not possible because of the Ca solubility-limitation to ~4E-4 M. It is likely that Ca is complexed in tank waste with oxalate or another complexant to enhance its solubility.

The effect of analyte exchange from a 0.1 M hydroxide concentration relative to 1.0 M hydroxide concentration was evaluated (Figure 4.5 through Figure 4.9). A slight lowering of K_d values can be discerned for Ba with decreased hydroxide concentration; however, the slight shift may simply be an artifact of the variability at high K_d values. Sr, Ca, and Cs showed no discernable effects from varying hydroxide concentrations. In contrast, Pb exchange demonstrated significantly higher selectivity and capacity at 0.1 M hydroxide relative to 1.0 M hydroxide (Figure 4.8). Grivé et al. (2010) showed that Pb can exist in a variety of hydroxide complexes depending on pH (from predominantly Pb^{2+} at pH 6 to predominantly $Pb(OH)_4^{2-}$ at pH 13). It is hypothesized that the $Pb(OH)^+$ is the exchangeable cation onto CST and will be present at increasing concentration with decreasing hydroxide concentration. In contrast, Kutus et al. (2016) showed that Ca exists predominantly as Ca^{2+} at 0.1 M OH to predominantly $Ca(OH)_{2(aq)}$ at 2 M OH. The fraction of $Ca(OH)^+$, the form thought to exchange onto CST, at 0.1 M hydroxide is about 20% and is essentially the same fraction at 1 M hydroxide, albeit the total Ca solubility substantially decreases with increasing hydroxide concentration. Testing Ca at an intermediate hydroxide concentration where the fraction of $Ca(OH)^+$ is highest may demonstrate a shift in K_d values. Hydroxide concentration reduction to 0.1 M resulted in Pb selectivity similar to those for Ba, Sr, and Ca (see Figure 4.10).



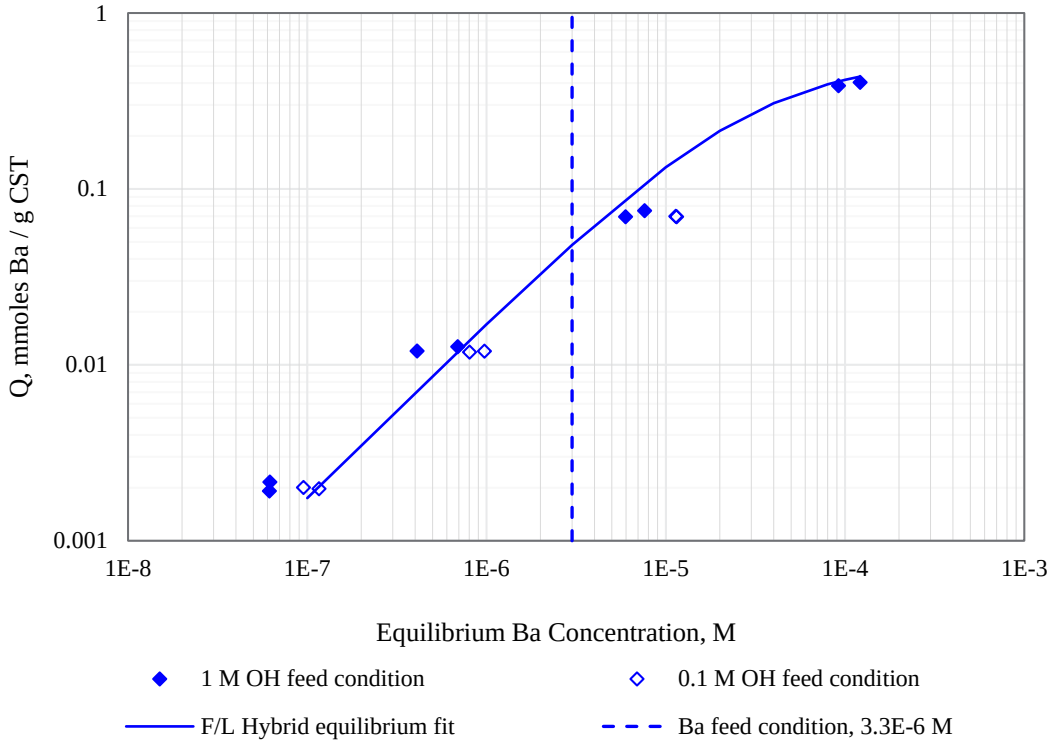


Figure 4.5. Ba K_d and Isotherm as Functions of Equilibrium Ba Concentrations 1.0 M NaOH/4.6 M $NaNO_3$ and 0.1 M NaOH/5.5 M $NaNO_3$

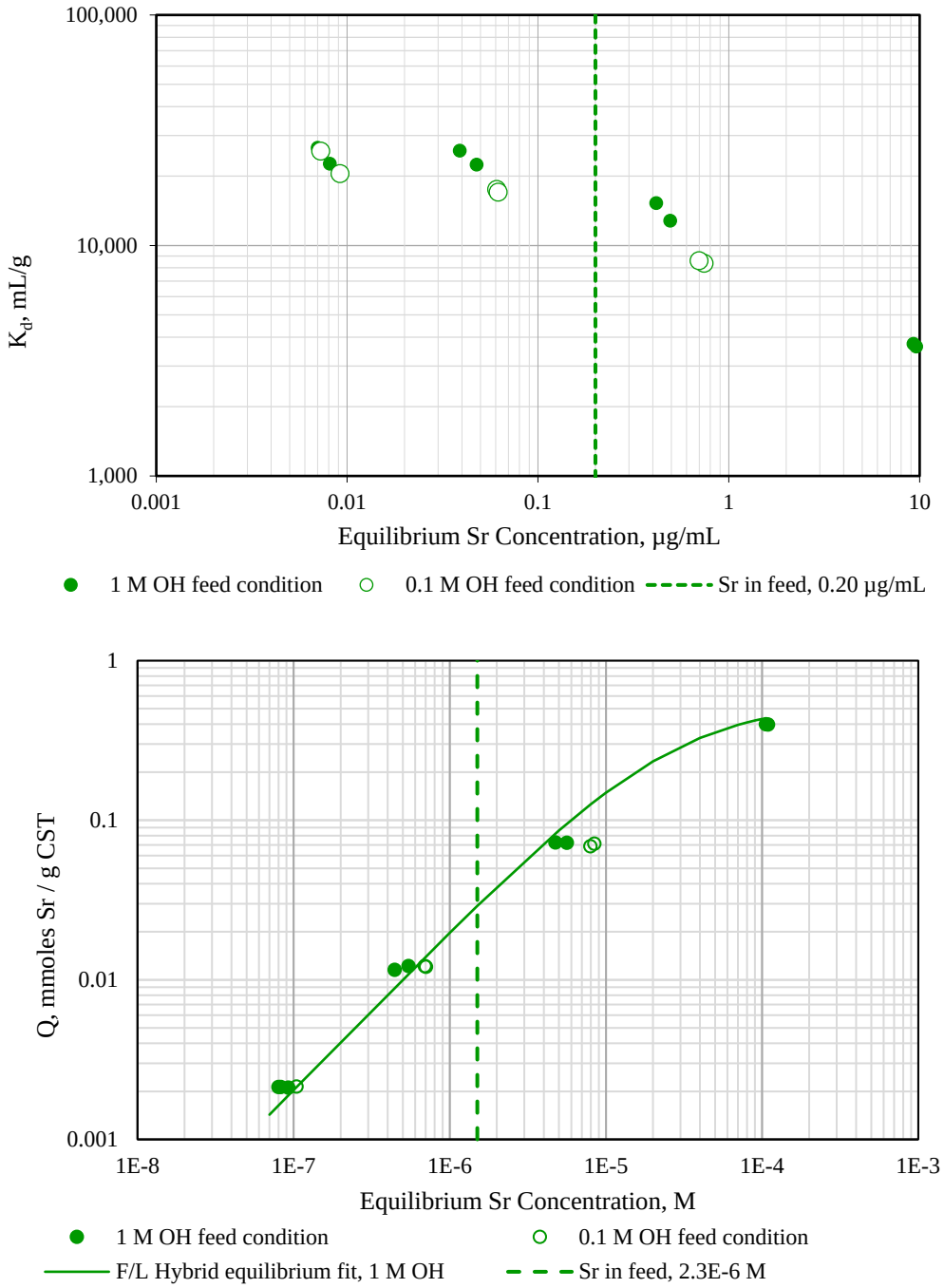
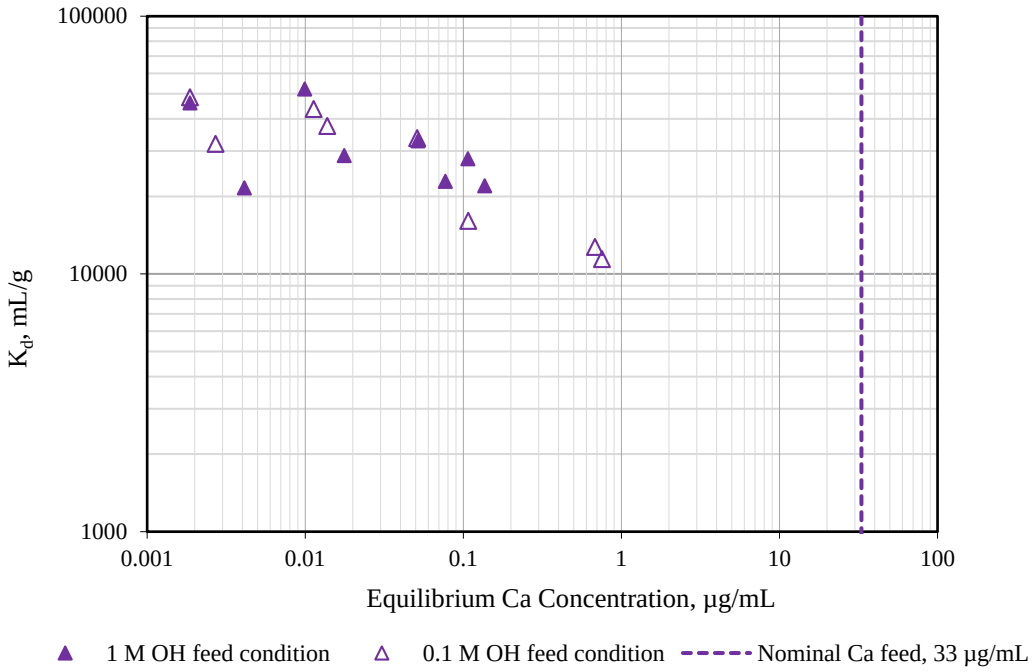


Figure 4.6. Sr K_d and Isotherm as Functions of Equilibrium Sr Concentrations 1.0 M NaOH/4.6 M $NaNO_3$ and 0.1 M NaOH/5.5 M $NaNO_3$



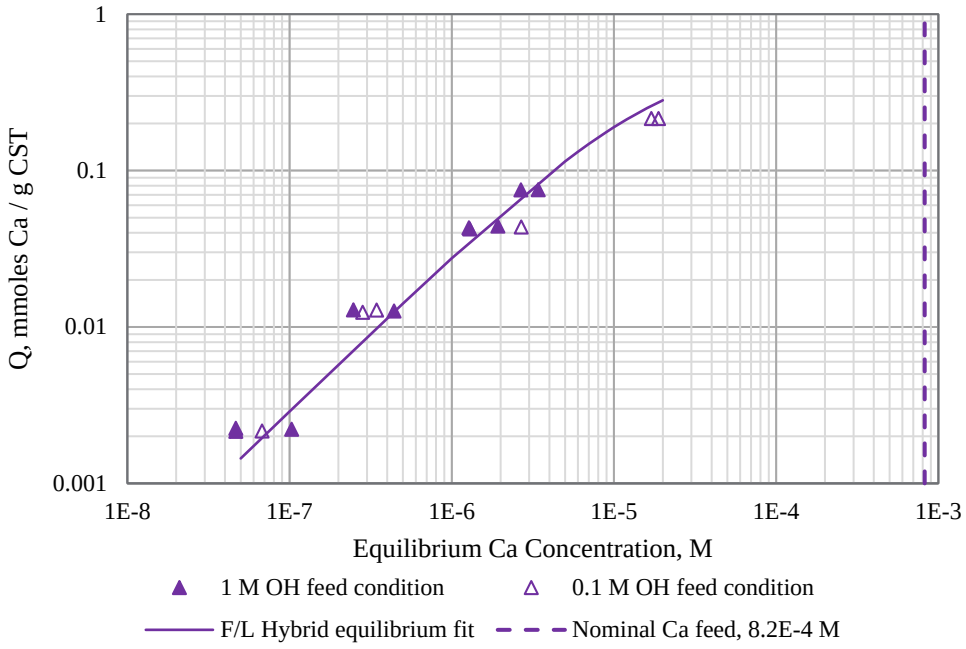
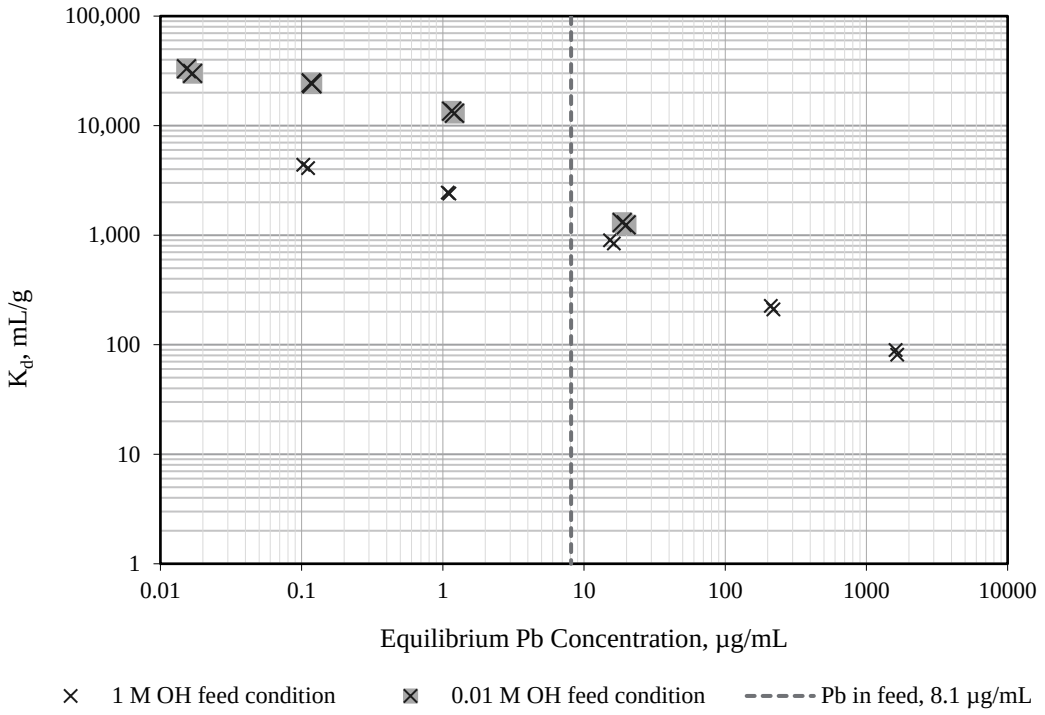


Figure 4.7. Ca K_d and Isotherm as Functions of Equilibrium Ca Concentrations 1.0 M NaOH/4.6 M $NaNO_3$ and 0.1 M NaOH/5.5 M $NaNO_3$



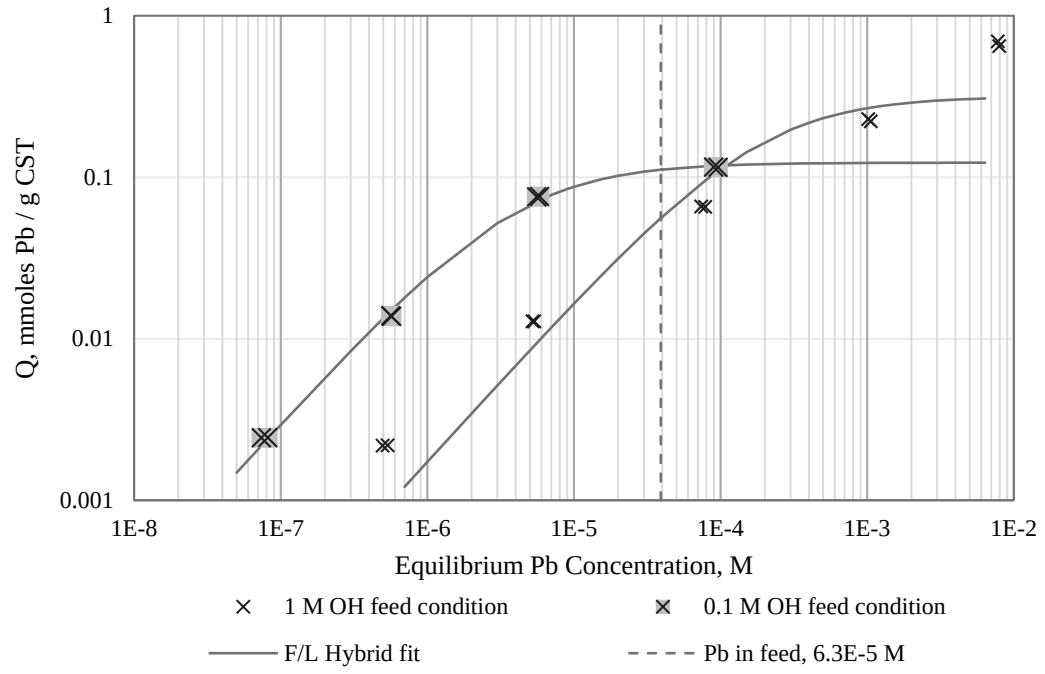
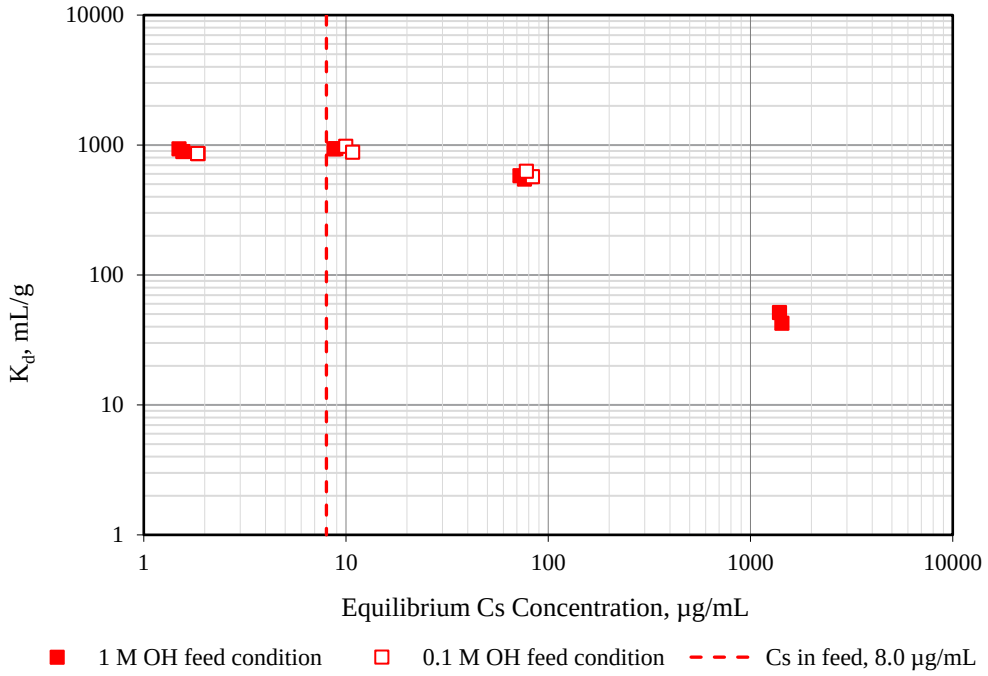


Figure 4.8. Pb K_d and Isotherm as Functions of Equilibrium Pb Concentrations 1.0 M NaOH/4.6 M $NaNO_3$ and 0.1 M NaOH/5.5 M $NaNO_3$



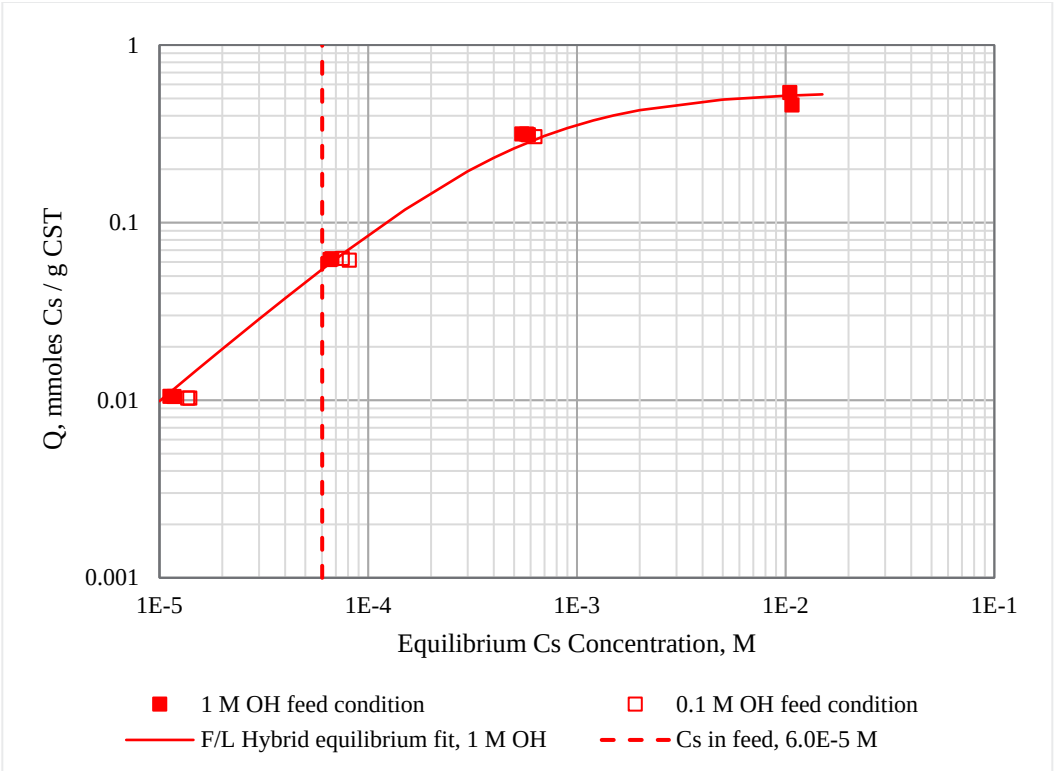


Figure 4.9. Cs K_d and Isotherm as Functions of Equilibrium Cs Concentrations 1.0 M NaOH/4.6 M $NaNO_3$ and 0.1 M NaOH/5.5 M $NaNO_3$

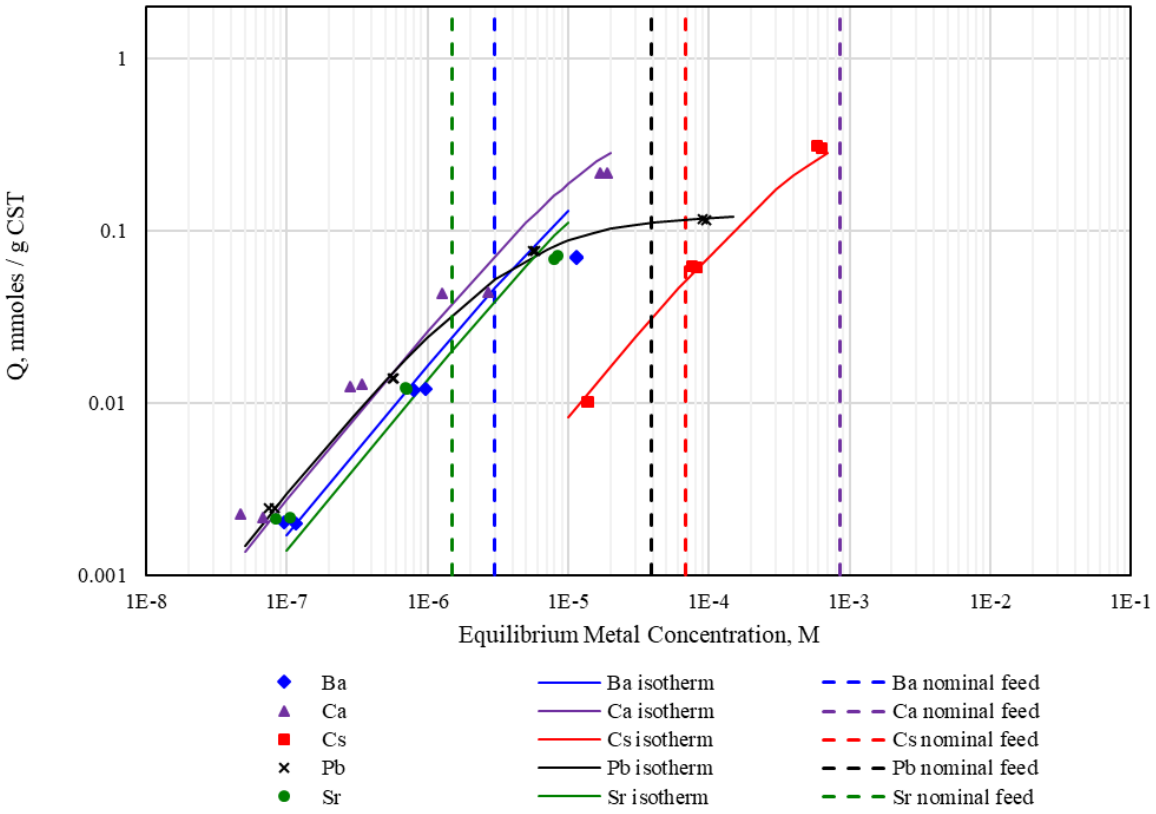


Figure 4.10. Cs, Ba, Sr, Ca, and Pb Isotherm Comparison, 0.1 M NaOH/5.5 M $NaNO_3$

4.2.3 Impacts of Ba, Ca, Pb, and Sr on Cs Exchange

Ba, Ca, Sr, and Pb were added to Cs solutions to assess whether their presence would adversely affect Cs exchange by consuming Cs ion exchange sites. The metal additions were added to reach ~6.4E-5 M, mimicking the concentrations found in non-complexant tank waste (except in the case of Ca, where higher concentrations were measured in tank waste). The Cs concentrations were varied per the established isotherm while each competing element concentration was held constant. Figure 4.11 shows the Cs isotherms in the presence of each element. The Cs isotherms remained constant below the equilibrium Cs concentration of 1E-4 M. However, at higher Cs equilibrium concentrations, a slight enhancement of the Cs capacity is discerned. At the equilibrium ~1E-2 M Cs, the total Cs capacity increased from 14% in the presence of Ca to 54% in the presence of Pb.[1] Figure 4.12 shows the effect of increasing the Pb concentration 33× to 2.1E-3 M on the Cs isotherm. No loss in Cs capacity or selectivity was discerned and, similar to the previous study depicted in Figure 4.11, a 37% enhancement in total Cs capacity was measured. These results indicated that Ba, Ca, Pb, and Sr likely exchange onto different sites than the Cs CST exchange sites.

Because high (2.1E-3M) Pb levels did not affect the Cs exchange capacity, additional interference testing with Ca was not pursued. It is likely that Ca is stabilized in tank waste with complexants such as oxalate,

[1] The value of 1.20 mmoles Cs/g CST in the presence of 6.5E-4 M Sr was excluded from this assessment as an anomalous high-flier; the duplicate sample was half this value.

giving it a higher achievable concentration than obtained in the simple simulant. The affinity for complexed Ca (or other complexed species) to exchange onto CST was not investigated.

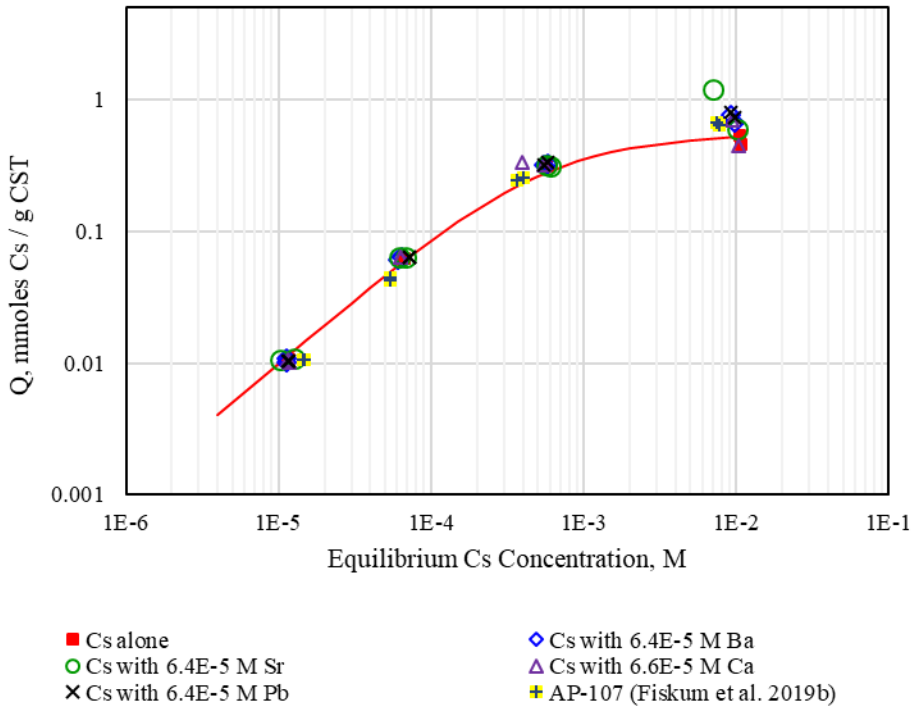


Figure 4.11. Effect of Ba, Ca, Sr, and Pb on Cs Isotherm, 1.0 M NaOH/4.6 M $NaNO_3$

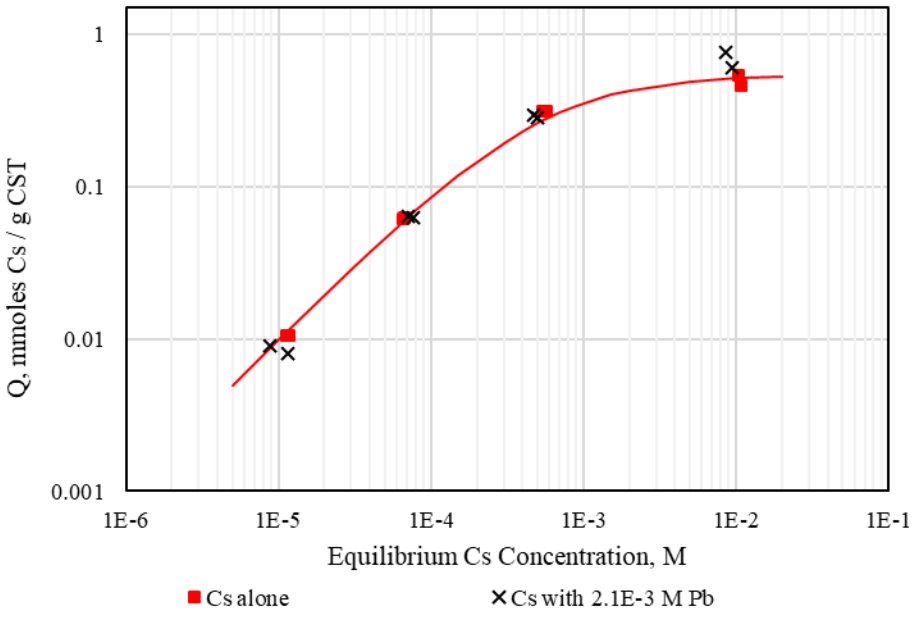


Figure 4.12. Effect of High Pb on Cs Isotherm, 1.0 M NaOH/4.6 M $NaNO_3$

The Ba, Ca, Pb, and Sr concentrations were adjusted around the nominal feed concentrations of 6.4E-5 M to assess their influences on Cs exchange at one Cs feed point: targeted equilibrium Cs concentration of 6.7 E-5 M. Specifically, the metal feed concentrations were adjusted to ~1.27E-4 M (2×) and ~1.64E-5 M (0.25×) while holding the feed Cs concentration constant at 3.8E-4 M. Figure 4.13 shows the effect of the high and low metal concentration on Q. The highest variations were for Pb (+7% to 9%) and Ca (+5% to -12%); all other results were within 3% of the Q value established by Cs alone. The observed variances were generally within the expected overall experimental uncertainty. Therefore, no effect on Cs selectivity or capacity was measured with added metals at high and low concentrations relative to Cs alone at the nominal *equilibrium* Cs condition of ~6.7E-5 M (3.8 E-4 M feed Cs concentration).

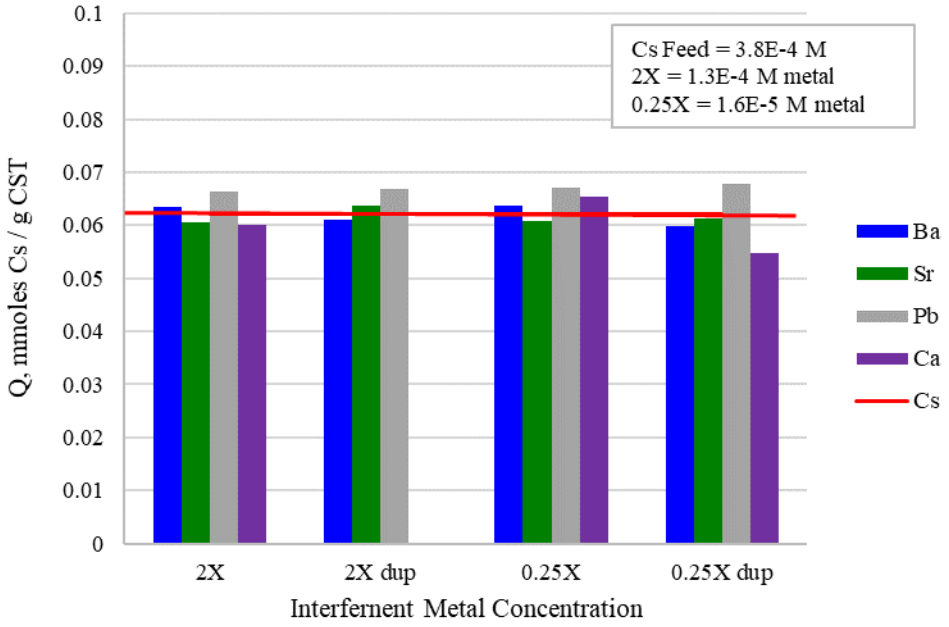


Figure 4.13. Effect of High/Low Ba, Ca, Pb, and Sr on Cs Exchange, 1.0 M NaOH/4.6 M $NaNO_3$ at Nominal Equilibrium of 7E-5 M Cs (3.8E-4 M Feed Cs)

The CST capacities for Ba, Ca, Pb, and Sr were determined from batch contact testing with high metal concentrations (Ba, Pb, and Sr) or high phase ratio (Ca). Figure 4.14 shows the results. Ba and Sr responded similarly with overall capacity; likewise, Ca and Pb responded similarly. These results were incorporated into the isotherms depicted in Figure 4.4.

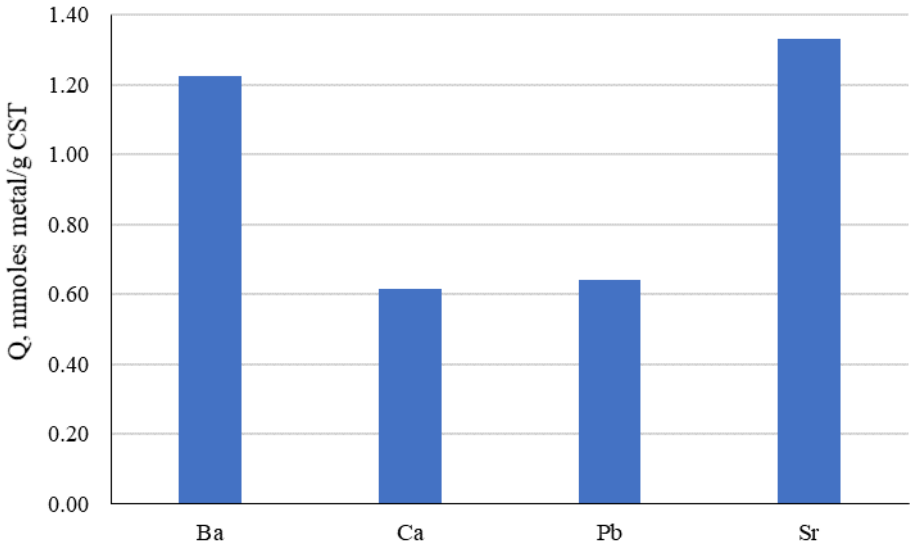


Figure 4.14. Maximum Metal Loading onto CST

Figure 4.15 shows the effect of CST individually pre-loaded with Ba, Ca, Pb, and Sr on Cs exchange. Data are shown relative to the established isotherm for Cs with no metal pre-loaded on the CST. A Cs control (CST without pre-loaded metals) was also run with this sample set. Except for Ba, the new data set is clustered above the established isotherm. The position above the isotherm may be related to a biased F-factor. The measured F-factors for this set averaged 0.56, well below other air-dried, free-flowing CST sample of ~0.75 to 0.85. Credibility for a bias is based on the Cs control result that aligns with the high cluster. Only the Ba result dropped below the established Cs isotherm and 40% below the control Cs sample/duplicate pair, indicating it uniquely had a possible negative effect on Cs exchange onto CST. Neither the presence of Ca, Pb, nor Sr preloaded onto CST had any negative or positive effect on Cs exchange when compared to the control sample/duplicate pair.

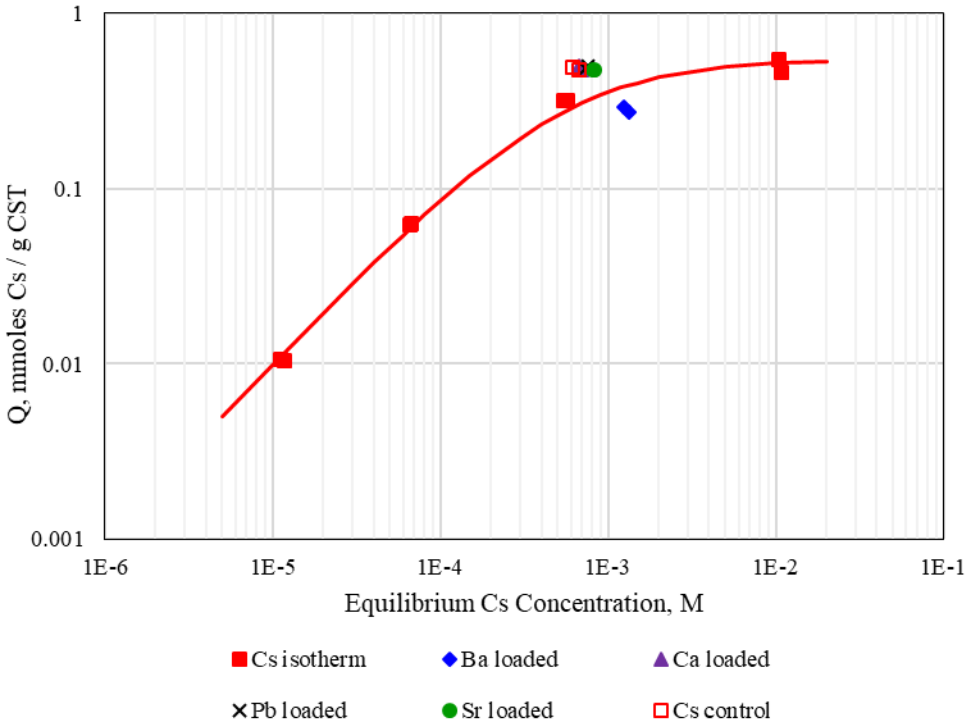


Figure 4.15. Effects of Metal-loaded CST on Cs Exchange

5.0 Conclusions

Two simple simulants consisting of 1.0 M NaOH/4.6 M $NaNO_3$ and 0.1 M NaOH/5.5 M $NaNO_3$ were used to evaluate the exchange behavior of Ba, Ca, Pb, and Sr onto CST. The total Na concentration was adjusted to match the expected feed condition in the TSCR system processing (5.6 M Na). The following were discerned from batch contact testing.

- Results of Cs exchange in 1.0 M NaOH/4.6 M $NaNO_3$ simulant matched reasonably well with AP-107 and AW-102 tank waste isotherms, indicating the matrix was a useful, simplified model to test exchange behavior. By inference, the 0.1 M NaOH/5.5 M $NaNO_3$ simulant was also a useful model because the Cs isotherm was constant between the two matrices.
- CST selectivity for Ba, Ca, Sr, and Pb are higher than for Cs.
- The Ba, Ca, Sr, and Cs exchange behaviors are not measurably affected by the difference in hydroxide concentration (0.1 to 1.0 M).
- The selectivity exchange behavior for Pb is improved by nearly one order of magnitude in 0.1 M NaOH/5.5 M $NaNO_3$ compared to 1.0 M NaOH/4.6 M $NaNO_3$, indicating hydroxide concentration will greatly affect the amount of Pb loaded onto CST.
- Increasing Ba, Ca, Pb, and Sr concentrations to 1.3E-4 M had no effect on the Cs exchange selectivity or capacity at the nominal equilibrium tank waste supernate condition of 6.7E-5 M Cs.
- Increasing Pb concentration to 2.1E-3 M had no effect on the Cs exchange selectivity or capacity from equilibrium conditions of 1E-5 to 1E-2 M Cs.
- Preloading CST with Ca, Sr, and Pb to maximum achievable content also had no effect on Cs exchange capacity at nominally 7.5 E-4 M equilibrium Cs concentration. Preloading Ba may have resulted in a 40% reduced Cs exchange capacity at 1.3 E-4 M equilibrium Cs concentration.

Based on these results, the following conclusions were inferred:

- Alkaline earths and Pb exchanged likely as a $M(OH)^+$ complex onto exchange sites not favored by Cs. Increasing the hydroxide concentration from 0.1 M to 1.0 M will shift the $M(OH)^+$ equilibrium to other $M(OH)_x^{2-x}$ species and can alter the metal uptake onto CST. This propensity was found to affect Pb significantly but not Ba, Ca, or Sr.
- Despite their higher selectivities onto CST, the presence of Sr, Ba, Ca, and Pb in tank waste and their uptake onto CST will not adversely affect Cs uptake.

The role of complexed alkaline earths was not assessed as part of this work. In addition, the nature of Pb exchange is not well understood at this point. These two uncertainties may warrant further examination if future batches to be processed through TSCR include either complexed wastes (such as present in AN-102 and AN-107) or significantly higher Pb concentrations than have been observed in AP-105 and AP-107. These tests would include the following:

- Test complexed alkaline earths and assess if exchange onto CST can be favored and eventually diminish Cs exchange.
- Study Pb exchange as a function of hydroxide concentration and Pb concentration to assess if different CST exchange sites are available to Pb.

6.0 References

Abe H, S Susa, T Sugimori, N Tajima, S Yamamoto, H Oomura, A Ikeda, M Saso and K Ishikawa. 2016. "Radioactive Waste Water Treatment for Fukushima Daiichi Nuclear Power Plant." Waste Management Symposia 2016, Phoenix, Arizona.

Bostick DT and SM DePaoli. 2000. *Evaluation of Improved Techniques for the Removal of Fission Products from Process Wastewater and Groundwater: FY 1998 and 1999 Status*. ORNL/TM-13689, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Braun R, TJ Dangieri, DJ Fennelly, N Brown, J Miller, R Anthony, C Philip, L Bray, GN Brown, D Lee, T Borek, and W Connors. 1996. "Ion Exchange Performance of Commercial Crystalline Silicotitanates for Cesium Removal." Spectrum '96, Proceedings – International Topical Meeting on Nuclear and Hazardous Waste Management. SAND-96-0656C; CONF-960212-65, Sandia National Laboratories. Albuquerque, New Mexico.

Brown GN, LA Bray, CD Carlson, K Carson, JR DesChane, RJ Elovich, FV Hoopes, DE Kurath, L Nenninger, and P Tanaka. 1996. *Comparison of Organic and Inorganic Ion Exchangers for Removal of Cesium and Strontium from Simulated and Actual Hanford 241-AW-101 DSSF Tank Waste*. PNNL-11120, Pacific Northwest National Laboratory, Richland, Washington.

Campbell EL, AM Rovira, F Colon-Cintron, D Boglaienko, TG Levitskaia, and RA Peterson. 2019. *Characterization of Cs-Loaded CST Used for Treatment of Hanford Tank Waste in Support of Tank-Side Cesium Removal*. PNNL-28945, Rev. 0, RPT-TCT-005, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

Fiskum SK, AM Rovira, HA Colburn, AM Carney, and RA Peterson. 2019a. *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, Washington.

Fiskum SK, AM Rovira, JR Allred, HA Colburn, MR Smoot, AM Carney, TT Trang-Le, MG Cantaloub, EC Buck, and RA Peterson. 2019b. *Cesium Removal from Tank Waste Simulants Using Crystalline Silicotitanate at 12% and 100% TSCR Bed Heights*. PNNL-28527, Rev. 0, RPT-TCT-001, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

Fiskum SK, JR Allred, HA Colburn, AM Rovira, MR Smoot, and RA Peterson. 2018. *Multi-Cycle Cesium Ion Exchange Testing Using Spherical Resorcinol-Formaldehyde Resin with Diluted Hanford Tank Waste 241-AP-105*. PNNL-27432, RPT-DFTP-006, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

Grivé M, C Domènech, V Montoya, D García, and L Duro. 2010. *Determination and assessment of the concentration limits to be used in SR-Can.* Svensk Kärnbränslehantering AB Swedish Nuclear Fuel and Waste Management Co., Stockholm, Sweden.

Hamm L, T Hang, DJ McCabe, and WD King. 2002. *Preliminary Ion Exchange Modeling for Removal of Cesium from Hanford Waste Using Hydrous Crystalline Silicotitanate Material*. WSRC-TR-2001-00400, Westinghouse Savannah River Company, Aiken, South Carolina.

King WD, LL Hamm, CJ Coleman, FF Fondeur, and SH Reboul. 2018a. *Crystalline Silicotitanate (CST) Ion Exchange Media Performance Evaluations in SRS Average Supernate Simulant and Tank 10H Waste Solution to Support TCCR*. SRNL-STI-2018-00277, Savannah River National Laboratory, Aiken, South Carolina.

King WD, LL Hamm, DJ McCabe, CA Nash, and FF Fondeur. 2018b. *Crystalline Silicotitanate Ion Exchange Media Long-Term Storage Evaluation*. SRNL-STI-2018-00567, Savannah River National Laboratory, Aiken, South Carolina.

Kutus B, A Gácsi, A Pallagi, I Pálinkó, G Peintler and P Sipos. 2016. "A comprehensive study on the dominant formation of the dissolved $Ca(OH)_2(aq)$ in strongly alkaline solutions saturated by Ca(II)." *RSC Advances* 6:45231-45240.

Marsh SF, ZV Svitra, and SM Bowen. 1994. *Distributions of 14 Elements on 63 Absorbers from Three Simulant Solutions (Acid-Dissolved Sludge, Acidified Supernate, and Alkaline Supernate) for Hanford HLW Tank 102-SY*. LA-12654, Los Alamos National Laboratory, Los Alamos, New Mexico.

Miller J and N Brown. 1997. *Development and Properties of Crystalline Silicotitanate (CST) Ion Exchangeres for Radioactive Waste Applications.* SAND97-0771, Sandia National Laboratories, Albuquerque, New Mexico.

Pease III LF, SK Fiskum, HA Colburn, and PP Schonewill. 2019. *Cesium Ion Exchange with Crystalline Silicotitanate Literature Review*. PNNL-28343, Pacific Northwest National Laboratory, Richland, Washington.

Rovira AM, SK Fiskum, HA Colburn, JR Allred, MR Smoot, and RA Peterson. 2018. *Cesium Ion Exchange Testing Using Crystalline Silicotitanate with Hanford Tank Waste 241-AP-107*. PNNL-27706, RPT-DFTP-011, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

Rovira AM, SK Fiskum, JR Allred, JGH Geeting, HA Colburn, AM Carney, TT Trang-Le, and RA Peterson. 2019. *Dead-End Filtration and Crystalline Silicotitanate Cesium Ion Exchange with Hanford Tank Waste AW-102*. PNNL-28783, Rev. 0, RPT-TCT-003, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

Walker Jr, JF, PA Taylor, and RL Cummins. 1998. *Cesium Removal Demonstration Utilizing Crystalline Silicotitanate Sorbent for Processing Melton Valley Storage Tank Supernate: Final Report.* ORNL/TM-13503, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Wilmarth BR, VH Dukes, and JT Mills. 2004. *Reactivity of Crystalline Silicotitanate (CST) and Hazardous Metal/Actinide Loading during Low Curie Salt Use* WSRC-TR-2004-00588, Westinghouse Savannah River Company, Aiken, South Carolina.

Zheng Z, CV Philip, RG Anthony, JL Krumhansl, DE Trudell, and JE Miller. 1996. "Ion Exchange of Group I Metals by Hydrous Crystalline Silicotitanates." *Industrial & Engineering Chemistry Research* 35(11):4246-4256.

Appendix A – Isotherm Batch Contact Results

A.1 Single-Element Isotherms

The following tables provide the results that were used to produce the isotherm figures in Figure 4.4 through Figure 4.10.

Table A.1. Ba Isotherm Data

Sample ID	Dry CST mass, g	Simulant Vol. mL	Initial Ba Conc., M	Equil. Ba Conc., M	K_d, mL/g	Q, Equil. Ba in CST, mmoles Ba/g
1.0 M NaOH/4.6 M $NaNO_3$						
TI078-Ba1-1-CST	0.0771	15.0	1.12E-05	6.18E-08	3.44E+04	2.16E-03
TI078-Ba1-2-CST	0.0772	15.0	6.59E-05	6.90E-07	1.84E+04	1.27E-02
TI078-Ba1-3-CST	0.0768	15.1	3.91E-04	7.60E-06	9.89E+03	7.53E-02
TI078-Ba1-4-CST	0.0766	15.0	2.19E-03	1.21E-04	3.33E+03	4.04E-01
TI078-Ba1-1-CST-d	0.0826	14.2	1.12E-05	6.14E-08	3.11E+04	1.92E-03
TI078-Ba1-2-CST-d	0.0790	14.4	6.59E-05	4.09E-07	2.93E+04	1.20E-02
TI078-Ba1-3-CST-d	0.0789	14.2	3.91E-04	5.95E-06	1.17E+04	6.95E-02
TI078-Ba1-4-CST-d	0.0779	14.4	2.19E-03	9.19E-05	4.19E+03	3.86E-01
0.1 M NaOH/5.5 M $NaNO_3$						
TI078-Ba01-1-CST	0.0848	15.1	1.12E-05	1.16E-07	1.69E+04	1.98E-03
TI078-Ba01-2-CST	0.0832	15.1	6.58E-05	8.03E-07	1.47E+04	1.18E-02
TI078-Ba01-3-CST	0.0811	15.2	3.85E-04	1.14E-05	6.12E+03	6.99E-02
TI078-Ba01-1-CST-d	0.0787	14.2	1.12E-05	9.51E-08	2.09E+04	2.01E-03
TI078-Ba01-2-CST-d	0.0791	14.6	6.58E-05	9.72E-07	1.23E+04	1.20E-02
TI078-Ba01-3-CST-d	0.0772	14.4	3.85E-04	1.15E-05	6.03E+03	6.95E-02

Table A.2. Ca Isotherm Data

Sample ID	Dry CST mass, g	Simulant Vol. mL	Initial Ca Conc., M	Equil. Ca Conc., M	K_d, mL/g	Q, Equil. Ca in CST, mmoles Ca/g
1.0 M NaOH/4.6 M $NaNO_3$						
TI091-Ca1-1-CST	0.0795	14.9	1.20E-5	1.03E-07	2.16E+04	2.22E-03
TI091-Ca1-2-CST	0.0776	14.9	6.60E-5	4.40E-07	2.88E+04	1.26E-02
TI091-Ca1-3-CST	0.0788	15.0	2.33E-4	1.92E-06	2.29E+04	4.41E-02
TI091-Ca1-4-CST	0.0792	15.0	4.00E-4	2.67E-06	2.80E+04	7.51E-02
TI091-Ca1-1-CST-d	0.0806	14.5	1.20E-5	4.66E-08	4.61E+04	2.15E-03
TI091-Ca1-2-CST-d	0.0791	15.4	6.60E-5	2.47E-07	5.22E+04	1.28E-02
TI091-Ca1-3-CST-d	0.0802	14.6	2.33E-4	1.29E-06	3.28E+04	4.23E-02
TI091-Ca1-4-CST-d	0.0789	15.0	4.00E-4	3.41E-06	2.20E+04	7.53E-02
TI091-Ca01-1-CST	0.0806	15.0	1.17E-5	6.76E-08	3.20E+04	2.16E-03
TI091-Ca01-2-CST	0.0798	15.0	6.61E-5	2.82E-07	4.36E+04	1.24E-02
TI091-Ca01-3-CST	0.0806	15.1	2.35E-4	2.68E-06	1.61E+04	4.35E-02
TI091-Ca01-4-CST	0.0803	14.9	1.17E-3	1.88E-05	1.14E+04	2.15E-01
TI091-Ca01-1-CST-d	0.0786	15.2	1.17E-5	4.66E-08	4.85E+04	2.25E-03
TI091-Ca01-2-CST-d	0.0783	15.3	6.61E-5	3.44E-07	3.75E+04	1.28E-02
TI091-Ca01-3-CST-d	0.0791	14.5	2.35E-4	1.28E-06	3.36E+04	4.30E-02
TI091-Ca01-4-CST-d	0.0784	14.6	1.17E-3	1.70E-05	1.27E+04	2.15E-01

Table A.3. Cs Isotherm Data

Sample ID	Dry CST Mass, g	Simulant Vol. mL	Initial Cs Conc., M	Equil. Cs Conc., M	K_d, mL/g	Q, Equil. Cs in CST, mmoles Cs/g
1.0 M NaOH/4.6 M $NaNO_3$						
TI078-Cs1-1-CST	0.0808	15.1	6.72E-05	1.12E-05	936	1.05E-02
TI078-Cs1-2-CST	0.0794	15.0	3.97E-04	6.70E-05	937	6.25E-02
TI078-Cs1-3-CST	0.0798	15.0	2.24E-03	5.74E-04	547	3.15E-01
TI078-Cs1-4-CST	0.0804	15.0	1.32E-02	1.07E-02	43	4.59E-01
TI078-Cs1-1-CST-d	0.0782	14.8	6.72E-05	1.17E-05	892	1.05E-02
TI078-Cs1-2-CST-d	0.0822	15.3	3.97E-04	6.57E-05	935	6.18E-02
TI078-Cs1-3-CST-d	0.0808	15.0	2.24E-03	5.45E-04	581	3.15E-01
TI078-Cs1-4-CST-d	0.0775	15.3	1.32E-02	1.05E-02	51	5.39E-01
0.1 M NaOH/5.5 M $NaNO_3$						
TI078-Cs01-1-CST	0.0803	15.0	6.84E-05	1.40E-05	837	1.01E-02
TI078-Cs01-2-CST	0.0774	14.9	3.97E-04	7.52E-05	953	6.21E-02
TI078-Cs01-3-CST	0.0810	15.0	2.25E-03	6.30E-04	556	3.01E-01
TI078-Cs01-1-CST-d	0.0783	14.6	6.84E-05	1.37E-05	837	1.02E-02
TI078-Cs01-2-CST-d	0.0793	15.2	3.97E-04	8.13E-05	857	6.07E-02
TI078-Cs01-3-CST-d	0.0799	14.8	2.25E-03	5.86E-04	611	3.09E-01

Table A.4. Pb Isotherm Data

Sample ID	Dry CST mass, g	Simulant Vol. mL	Initial Pb Conc., M	Equil. Pb Conc., M	K_d, mL/g	Q, Equil. Pb in CST, mmoles Pb/g
1.0 M NaOH/4.6 M $NaNO_3$						
TI085-Pb1-1-CST	0.0722	15.0774	1.22E-05	4.96E-07	4.39E+03	2.18E-03
TI085-Pb1-2-CST	0.0713	15.0552	6.40E-05	5.22E-06	2.45E+03	1.28E-02
TI085-Pb1-3-CST	0.0711	15.0680	3.78E-04	7.38E-05	8.98E+02	6.60E-02
TI085-Pb1-4-CST	0.0709	15.0870	2.13E-03	1.06E-03	2.10E+02	2.22E-01
TI085-Pb1-5-CST	0.0744	14.8860	1.18E-02	7.77E-03	8.95E+01	6.95E-01
TI085-Pb1-1-CST-d	0.0716	15.0948	1.22E-05	5.36E-07	4.09E+03	2.19E-03
TI085-Pb1-2-CST-d	0.0711	15.0366	6.40E-05	5.36E-06	2.39E+03	1.28E-02
TI085-Pb1-3-CST-d	0.0707	15.1161	3.78E-04	7.84E-05	8.39E+02	6.55E-02
TI085-Pb1-4-CST-d	0.0712	15.0513	2.13E-03	1.02E-03	2.26E+02	2.29E-01
TI085-Pb1-5-CST-d	0.0752	14.8692	1.18E-02	7.96E-03	8.10E+01	6.49E-01
0.1 M NaOH/5.5 M $NaNO_3$						
TI085-Pb01-1-CST	0.0718	15.1524	1.09E-05	8.15E-08	3.00E+04	2.44E-03
TI085-Pb01-2-CST	0.0716	15.1420	6.25E-05	5.63E-07	2.46E+04	1.39E-02
TI085-Pb01-3-CST	0.0714	15.1250	3.92E-04	5.83E-06	1.30E+04	7.60E-02
TI085-Pb01-4-CST	0.0753	15.0953	2.12E-03	9.60E-05	1.24E+03	1.15E-01
TI085-Pb01-1-CST-d	0.0716	15.1117	1.09E-05	7.37E-08	3.30E+04	2.44E-03
TI085-Pb01-2-CST-d	0.0720	15.1087	6.25E-05	5.71E-07	2.41E+04	1.38E-02
TI085-Pb01-3-CST-d	0.0719	15.1623	3.92E-04	5.57E-06	1.35E+04	7.57E-02
TI085-Pb01-4-CST-d	0.0758	15.0966	2.12E-03	8.98E-05	1.31E+03	1.16E-01

Table A.5. Sr Isotherm Data

Sample ID	Dry CST mass, g	Simulant Vol. mL	Initial Sr Conc., M	Equil. Sr Conc., M	K_d, mL/g	Q, Equil. Sr in CST, mmoles Sr/g
1.0 M NaOH/4.6 M $NaNO_3$						
TI078-Sr1-1-CST	0.0796	15.0	1.14E-05	8.01E-08	2.65E+04	2.13E-03
TI078-Sr1-2-CST	0.0834	15.0	6.47E-05	4.44E-07	2.58E+04	1.15E-02
TI078-Sr1-3-CST	0.0793	14.9	3.90E-04	5.64E-06	1.28E+04	7.22E-02
TI078-Sr1-4-CST	0.0779	14.9	2.19E-03	1.06E-04	3.74E+03	3.98E-01
TI078-Sr1-1-CST-d	0.0779	14.6	1.14E-05	9.27E-08	2.26E+04	2.11E-03
TI078-Sr1-2-CST-d	0.0777	14.7	6.47E-05	5.45E-07	2.24E+04	1.22E-02
TI078-Sr1-3-CST-d	0.0773	14.5	3.90E-04	4.76E-06	1.53E+04	7.24E-02
TI078-Sr1-4-CST-d	0.0777	14.8	2.19E-03	1.09E-04	3.64E+03	3.97E-01
0.1 M NaOH/5.5 M $NaNO_3$						
TI078-Sr01-1-CST	0.0786	15.0	1.13E-05	1.05E-07	2.05E+04	2.14E-03
TI078-Sr01-2-CST	0.0791	15.0	6.49E-05	6.93E-07	1.75E+04	1.22E-02
TI078-Sr01-3-CST	0.0805	15.0	3.89E-04	8.45E-06	8.37E+03	7.11E-02
TI078-Sr01-1-CST-d	0.0768	14.6	1.13E-05	8.30E-08	2.57E+04	2.13E-03
TI078-Sr01-2-CST-d	0.0796	14.9	6.49E-05	7.05E-07	1.70E+04	1.20E-02
TI078-Sr01-3-CST-d	0.0820	14.7	3.89E-04	7.96E-06	8.59E+03	6.85E-02

A.2 Impurity Effect on Cesium Isotherm

The following table data were graphed in Figure 4.11 through Figure 4.13.

Table A.6. Cs Isotherm Data with Added Ba, Ca, Pb, and Sr in 1.0 M NaOH/4.6 M $NaNO_3$

Sample ID	Dry CST mass, g	Simulant Vol. mL	Initial Cs Conc., M	Equil. Cs Conc., M	K_d, mL/g	Q, Equil. Cs in CST, mmoles Cs/g
With 6.42E-5 M Ba						
TI078-CsBa1-CST	0.0814	14.6	6.76E-05	1.14E-05	887	1.01E-02
TI078-CsBa2-CST	0.0824	15.0	3.96E-04	6.11E-05	998	6.11E-02
TI078-CsBa3-CST	0.0768	15.1	2.26E-03	5.85E-04	561	3.29E-01
TI078-CsBa4-CST	0.0760	15.0	1.31E-02	9.71E-03	70	6.78E-01
TI078-CsBa1-CST-d	0.0770	14.9	6.76E-05	1.14E-05	948	1.08E-02
TI078-CsBa2-CST-d	0.0789	15.1	3.96E-04	6.45E-05	988	6.37E-02
TI078-CsBa3-CST-d	0.0771	14.3	2.26E-03	5.44E-04	586	3.19E-01
TI078-CsBa4-CST-d	0.0787	15.2	1.31E-02	9.18E-03	84	7.63E-01
With 6.64E-5 M Ca						
TI091-CsCa1-CST	0.0798	14.9	6.63E-05	1.18E-05	866	1.02E-02
TI091-CsCa2-CST	0.0788	14.9	3.98E-04	6.35E-05	994	6.33E-02
TI091-CsCa3-CST	0.0799	15.1	2.18E-03	3.92E-04	860	3.38E-01
TI091-CsCa4-CST	0.0809	15.0	1.28E-02	1.04E-02	43	4.49E-01
TI091-CsCa1-CST-d	0.0785	15.2	6.63E-05	1.16E-05	907	1.06E-02
TI091-CsCa2-CST-d	0.0813	15.3	3.98E-04	6.26E-05	1006	6.30E-02
TI091-CsCa3-CST-d	0.0792	15.6	2.18E-03	5.51E-04	587	3.21E-01
TI091-CsCa4-CST-d	0.0803	16.1	1.28E-02	9.35E-03	74	6.97E-01
With 6.42E-5 M Pb						
TI085-CsPb1-CST	0.0780	15.0749	6.48E-05	1.19E-05	864	1.02E-02
TI085-CsPb2-CST	0.0775	15.0278	3.99E-04	7.27E-05	864	6.32E-02
TI085-CsPb3-CST	0.0771	15.1099	2.28E-03	5.78E-04	574	3.34E-01
TI085-CsPb4-CST	0.0778	15.0144	1.34E-02	9.22E-03	86	8.05E-01
TI085-CsPb1-CST-d	0.0774	15.0797	6.48E-05	1.15E-05	891	1.04E-02
TI085-CsPb2-CST-d	0.0784	15.4116	3.99E-04	7.19E-05	897	6.43E-02
TI085-CsPb3-CST-d	0.0788	14.6778	2.28E-03	5.50E-04	581	3.22E-01
TI085-CsPb4-CST-d	0.0785	15.4773	1.34E-02	9.68E-03	75	7.32E-01
With 2.12E-3 M Pb						
TI085-Cs-A2-CST	0.0770	14.9878	5.31E-05	1.16E-05	717	8.07E-03
TI085-Cs-B2-CST	0.0748	14.9876	3.91E-04	7.11E-05	931	6.42E-02
TI085-Cs-C2-CST	0.0742	15.0185	1.94E-03	4.69E-04	603	2.97E-01
TI085-Cs-D2-CST	0.0737	14.7618	1.25E-02	8.67E-03	87	7.66E-01
TI085-Cs-A2-CST-d	0.0725	14.8476	5.31E-05	8.74E-06	1065	9.08E-03
TI085-Cs-B2-CST-d	0.0750	14.8560	3.91E-04	7.74E-05	814	6.22E-02
TI085-Cs-C2-CST-d	0.0755	14.9815	1.94E-03	5.02E-04	578	2.84E-01
TI085-Cs-D2-CST-d	0.0762	14.7257	1.25E-02	9.37E-03	64	6.04E-01
With 6.44E-5 M Sr						
TI078-CsSr1-CST	0.0761	15.1	6.77E-05	1.28E-05	855	1.09E-02
TI078-CsSr2-CST	0.0769	15.0	3.94E-04	6.86E-05	929	6.36E-02
TI078-CsSr3-CST	0.0774	15.0	2.24E-03	5.71E-04	566	3.24E-01
TI078-CsSr4-CST	0.0781	15.0	1.32E-02	7.00E-03	171	1.20E+00
TI078-CsSr1-CST-d	0.0774	14.2	6.77E-05	1.02E-05	1040	1.06E-02
TI078-CsSr2-CST-d	0.0810	15.3	3.94E-04	6.14E-05	1031	6.30E-02
TI078-CsSr3-CST-d	0.0774	14.9	2.24E-03	6.04E-04	520	3.13E-01
TI078-CsSr4-CST-d	0.0770	15.1	1.32E-02	1.02E-02	59	6.05E-01

Table A.7. Ba, Ca, Pb and Sr Added at High/Low Concentrations to 4E-4 M Cs in 1.0 M NaOH/4.6 M $NaNO_3$

Sample ID	Dry CST mass, g	Simulant Vol. mL	Added Metal Conc., M	Equil. Cs Conc., M[(a)]	K_d, mL/g	Q, Equil. Cs in CST, mmoles Cs/g
			Ba			
TI078CsBa-X-CST	0.0799	15.0	1.28E-04	4.36E-05	1460	6.36E-02
TI078CsBa-X-CSTd	0.0812	15.2	1.28E-04	5.48E-05	1113	6.11E-02
TI078CsBa-Y-CST	0.0749	15.1	1.66E-05	6.49E-05	984	6.36E-02
TI078CsBa-Y-CSTd	0.0808	15.2	1.66E-05	6.27E-05	965	5.99E-02
			Ca			
TI091CsCa-X-CST	0.0804	14.9	1.28E-04	6.34E-05	952	6.01E-02
TI091CsCa-X-CSTd	0.0799	16.4	1.28E-04	6.93E-05	947	6.55E-02
TI091CsCa-Z-CST-d	0.0807	13.7	1.68E-05	6.38E-05	863	5.48E-02
			Pb			
TI085-CsPb-2x-CST	0.0783	15.0510	1.25E-04	7.43E-05	900	6.68E-02
TI085-CsPb-2x-CST-d	0.0789	15.4890	1.25E-04	7.68E-05	882	6.77E-02
TI085-CsPb-025-CST	0.0774	15.1365	1.57E-05	8.27E-05	805	6.64E-02
TI085-CsPb-025-CST-d	0.0771	14.9861	1.57E-05	7.66E-05	879	6.71E-02
			Sr			
TI078CsSr-X-CST	0.0774	15.0	1.27E-04	6.92E-05	874	6.06E-02
TI078CsSr-X-CSTd	0.0768	15.5	1.27E-04	6.61E-05	965	6.38E-02
TI078CsSr-Y-CST	0.0788	15.1	1.64E-05	6.36E-05	966	6.09E-02
TI078CsSr-Y-CSTd	0.0768	15.0	1.64E-05	6.82E-05	901	6.14E-02

(a) See Table 3.5 for initial Cs concentrations.

Table A.8. CST Capacity for Metal in 1.0 M NaOH/4.6 M $NaNO_3$

Sample ID	Dry CST mass, g	Simulant Vol. mL	Added Metal Conc., M	Equil. Metal Conc., M	K_d, mL/g	Q, Equil. Metal in CST, mmoles/g
TI095-Ba-CST	0.3409	69.6	9.17E-03	3.18E-03	381	1.22E+00
TI095-Ca-CST	0.2909	193.2	1.23E-03	3.04E-04	2014	6.16E-01
TI095-Pb-CST	0.3434	70.3	1.27E-02	9.56E-03	67	6.42E-01
TI095-Sr-CST	0.3430	69.2	8.53E-03	1.93E-03	690	1.33E+00

Table A.9. Cs Exchange onto Metal-Preloaded CST in 1.0 M NaOH/4.6 M $NaNO_3$

Sample ID	Dry CST Mass, g	Simulant Vol., mL	Pre-loaded Metal Content, mmole/g	Equil. Cs Conc., M	K_d, mL/g	Q, Equil. Cs in CST, mmoles Cs/g
TI095-Ba-Cs	0.0364	12.5428	1.22E+00	1.32E-03	207	2.74E-01
TI095-Ba-Cs-d	0.0378	12.5722	1.22E+00	1.24E-03	236	2.92E-01
TI095-Ca-Cs	0.0377	12.5224	6.16E-01	6.95E-04	679	4.74E-01
TI095-Ca-Cs-d	0.0363	12.5408	6.16E-01	6.75E-04	732	4.99E-01
TI095-Pb-Cs	0.0341	12.5479	6.42E-01	7.60E-04	657	5.01E-01
TI095-Pb-Cs-d	0.0357	12.5404	6.42E-01	7.38E-04	654	4.85E-01
TI095-Sr-Cs	0.0340	12.4883	1.33E+00	8.36E-04	562	4.72E-01
TI095-Sr-Cs-d	0.0343	12.5269	1.33E+00	8.13E-04	583	4.77E-01
TI095-Blank-Cs	0.0385	12.5678	0E+00	6.20E-04	793	4.90E-01
TI095-Blank-Cs-d	0.0381	12.5722	0E+00	6.75E-04	705	4.77E-01

Distribution List

Number of Copies	
WRPS	
	Kris Colosi
	Matt Landon
	Jacob Reynolds
	Todd Wagnon
	Jason Vitali
Office of River Protection	
	Anne Mccartney
North Wind Solutions, LLC	
	Ivan Papp

Number of Copies	
Pacific Northwest National Laboratory	
	Tom Brouns
	Emily Campbell
	Sandy Fiskum
	Matthew Fountain
	David Peeler
	Reid Peterson
	Philip Schonewill
	Truc Trang-Le
	Information Release

*All copies will be distributed electronically

Pacific Northwest National Laboratory

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99354
1-888-375-PNNL (7665)

www.pnnl.gov