

Modified Isotherm Modeling to Predict Cs Exchange with Crystalline Silicotitanate in Tank Waste Simulants

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Prepared for
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Summary

The U.S. Department of Energy is working to expedite processing of Hanford tank waste supernate at the Hanford Waste Treatment and Immobilization Plant. To support this goal, Washington River Protection Solutions is designing a Tank Side Cesium Removal (TSCR) system for suspended solids and cesium ($Cs/^{137}Cs$) removal from Hanford tank waste supernate. The ion exchange media selected for Cs removal at TSCR 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).

The Zheng Anthony Miller (ZAM) isotherm model (Zheng et al. 1997) is a multicomponent ion exchange model used to predict the exchange of Group I metals onto CST. The ZAM isotherm has historically been used to predict Cs distribution values from Hanford and Savannah River Site (SRS) tank waste simulants. Figure S.1 summarizes model predictions from the ZAM isotherm that indicate poor prediction of Cs distribution values for simple and complex simulants with the engineered form of CST, IONSIV[®] R9140-B, and IONSIV[®] R9120-B where the solid line indicates a perfect fit by the model. The dotted lines indicate $\pm 20\%$ error.

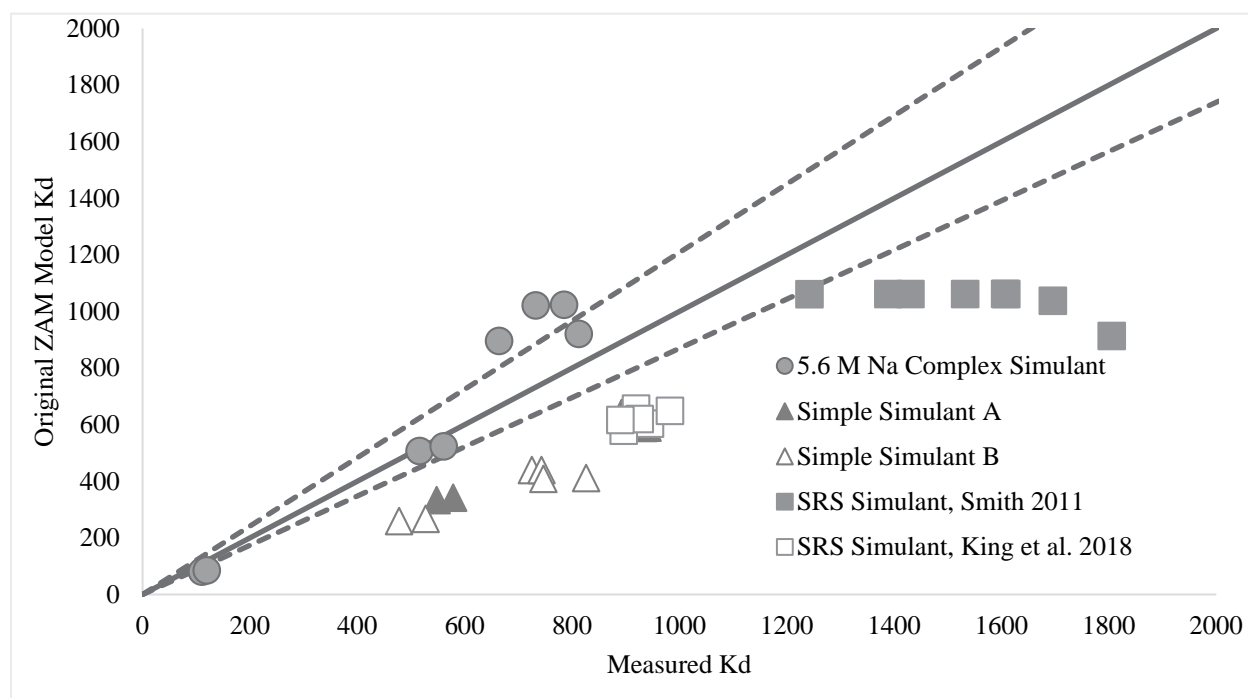


Figure S.1. Comparison of Measured Cs Distribution Coefficients (K_d) with Cs Distribution Coefficients Calculated Using the Original ZAM model

Batch contact testing with Hanford tank waste complex and simple simulants was used in conjunction with SRS simulants to experimentally determine Cs distribution values using a modification to the original isotherm model. The experimentally determined maximum Cs capacity for IONSIV[®] R9140-B CST in both the simple and complex matrices was found to be 0.53 ± 0.3 mmoles Cs/g of CST. This value is not drastically different from the maximum Cs capacity of 0.58 mmoles Cs/g TAM-5 reported by

Zheng et al. (1997).¹ However, it is important to note that TAM-5 (commercially IONSIV® IE-910) is a powder. Hamm et al. (2002)² determined that a dilution factor was needed to account for the Zr(OH)₂ binder in the engineered form of CST. Hamm et al. determined that a dilution factor of 0.68 was appropriate to account for binder contribution and correct overprediction of Cs exchange on the engineered form of CST in ZAM calculations. This reduced the total capacity from 0.58 mmol/g with TAM-5 to 0.39 mmol/g for the engineered form of CST (Hamm et al. 2002).

Despite substituting the experimentally determined maximum Cs capacity of 0.55 mmoles Cs/g for the literature-reported capacity of 0.39 mmoles Cs/g, it was determined that additional modifications to the model's equilibrium rate constants were necessary in refining the isotherm model. The modified model overpredicted K⁺ uptake by the CST when compared to digested CST results described by Campbell et al. (2019).³ The modified model was further revised to omit three of the five K⁺ exchange equilibrium reactions described by ZAM to reduce the additional K⁺ loading seen by the model. Figure S.2 summarizes the revised model isotherm predictions plotted against measured K_d values.

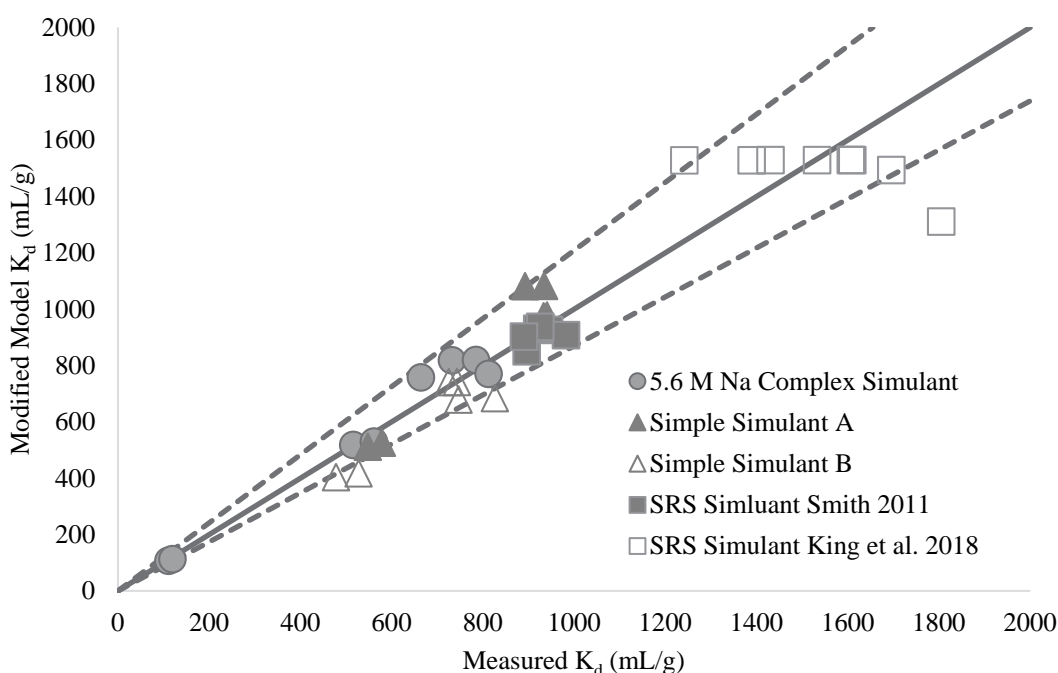


Figure S.2. Comparison of Measured Cs Distribution Coefficients (K_d) with Cs Distribution Coefficients Calculated Using the Modified Model

¹ Zheng Z, RG Anthony, and JE Miller. 1997. "Modeling Multicomponent Ion Exchange Equilibrium Utilizing Hydrrous Crystalline Silicotitanates by a Multiple Interactive Ion Exchange Site Model." *Industrial & Engineering Chemistry Research* 36(6):2427-2434. doi:10.1021/ie960546n

² Hamm LL, T Hang, DJ McCabe, and WD King. 2002. *Preliminary Ion Exchange Modeling for Removal of Cesium from Hanford Waste Using Hydrrous Crystalline Silicotitanate Material*. WSRC-TR-2001-00400; SRT-RPP-2001-00134, Westinghouse Savannah River Company, Aiken, South Carolina.

³ Campbell EL, AM Rovira, F Colon-Cintron, D Boglajenko, 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.

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Acronyms and Abbreviations

CST	crystalline silicotitanate
CWP	Campbell Westesen Peterson
DOE	U.S. Department of Energy
F/L	Freundlich/Langmuir
GEA	gamma energy analysis
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
R&D	research and development
SRS	Savannah River Site
TCCR	Tank Closure Cesium Removal
TSCR	Tank Side Cesium Removal
UOP	Honeywell UOP LLC
WRPS	Washington River Protection Solutions
WWFTP	WRPS Waste Form Testing Program
ZAM	Zheng Anthony Miller

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1.0 Introduction

The U.S. Department of Energy (DOE) has been tasked with remediating millions of gallons of aqueous radioactive waste. Much of this waste was produced during the Cold War and is currently contained in underground storage tanks at DOE facilities at Hanford, Savannah River, Oak Ridge, and other sites. Crystalline silicotitanate (CST) can selectively remove cesium (Cs), one of the key high-dose, radioactive components in tank waste, and application has been successfully demonstrated on numerous tank waste supernates and tank waste supernate simulants. Ion exchange using CST has been recently proposed for Tank Side Cesium Removal (TSCR) for Hanford and is already implemented at the Savannah River Site (SRS) for Tank Closure Cesium Removal (TCCR). In both cases, the goal is to alleviate the radiological dose hazard associated with ^{137}Cs , allowing for disposition of the treated waste as low-activity waste.

1.1 Ion Exchange Equilibrium

Ion exchange is a stoichiometric process in which an ion in one phase is replaced by an equivalent amount of ions from the other phase. Zheng et al. (1996) proposed that the cesium ion exchange for CST can be described by the following equation:



where the ratio of the activities of the products to reactants can be used to determine the thermodynamic equilibrium constant (K_{eq}), as follows:

$$K_{eq} = \frac{\overline{a_{\text{CsNa}_2\text{X}}} a_{\text{Na}^+}}{a_{\text{Na}_3\text{X}} a_{\text{Cs}^+}} \quad (1.2)$$

where the overbar represents the solid phase, a_{Na^+} , and a_{Cs^+} are the activities in the liquid phase. Activities of each phase can be calculated by the product of concentration and an activity coefficient. Thus, Eq. (1.2) can be represented as

$$K_{eq} = K_C K_\gamma \quad (1.3)$$

where

$$K_C = \frac{Q_{\text{CsNa}_2\text{X}} C_{\text{Na}^+}}{Q_{\text{Na}_3\text{X}} C_{\text{Cs}^+}} \quad (1.4)$$

$$K_\gamma = \frac{\overline{\gamma_{\text{CsNa}_2\text{X}}} \gamma_{\text{Na}^+}}{\overline{\gamma_{\text{Na}_3\text{X}}} \gamma_{\text{Cs}^+}} \quad (1.5)$$

$Q_{\text{CsNa}_2\text{X}}$ and $Q_{\text{Na}_3\text{X}}$ are the concentrations of Cs and Na in the solid phase (mmole/g), C_{Cs^+} and C_{Na^+} are the concentrations in the liquid phase, γ_{Cs^+} and γ_{Na^+} are the activity coefficients in the liquid phase, and the overbar represents the solid phase.

If the solid phase is ideal, which is commonly assumed for some zeolites (Barrer and Sammon 1955; Barrer and Falconer 1956), the solid phase activity coefficients can be dropped and K_C becomes the thermodynamic equilibrium constant. Thus, the thermodynamic equilibrium constant becomes

$$K_{eq} = \frac{Q_{Na_2CsX} a_{Na^+}}{Q_{Na_3X} a_{Cs^+}} \quad (1.6)$$

The widely used distribution coefficient (K_d), which represents the performance of an ion exchanger, is defined as the ratio of the equilibrium concentration in the solid phase to that in the liquid phase:

$$K_d = \frac{Q_{CsX}}{C_{Cs^+}} \quad (1.7)$$

K_{eq} is dependent on temperature and, for experimental conditions, can be adjusted using the Van 't Hoff equation (Holland and Anthony 1989) as follows:

$$\ln K_{eq} = \ln K_{ref} - \frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \quad (1.8)$$

where T is temperature (in Kelvin); ΔH is the enthalpy change, or heat of reaction for the ion exchange mechanism, which can be considered constant if the temperature range is not wide (Zheng et al. 1997); and R is the molar gas constant, 8.314 J/mol K.

1.2 ZAM Original Isotherm Model

Zheng, Anthony, and Miller (ZAM) developed a model to predict the ion exchange of H^+ , Na^+ , K^+ , Rb^+ , and Cs^+ with CST, formally TAM-5 (Zheng et al. 1997). To predict the activity coefficients of the liquid phase, Bromley's model was used. The equilibrium compositions and distribution coefficients of the counterions were calculated by solving equilibrium equations, whose equilibrium constants were estimated from experiments with simple ion exchange and material balance equations.

The ZAM computational model identifies the ion exchange site as Na_3X and combines a series of linearly independent equilibrium reactions to predict Cs^+ loading. Modeling of Hanford or Savannah River tank waste in caustic, high Na^+ solutions used Eqs. (1.9) through (1.13). Zheng et al. (1996) indicated only one of the three sodium cations can be exchanged by Cs^+ [Eq. (1.9)] with a maximum capacity of 0.58 mmol/g. In solutions with sufficient concentrations of K^+ present, the K^+ can exchange with Na^+ to form both the singly- and doubly-substituted exchange site, Na_2KX and NaK_2X [Eqs. (1.10) and (1.11)], which can then load one Cs cation [Eqs. (1.12)].



The model was developed for the IONSIV[®] IE-910 powder, which is the commercially prepared powder form of TAM-5 by UOP (Des Plaines, IL). IONSIV[®] R9140-B CST is a generally spherical engineered form of CST prepared by combining the CST powder with a binding material. Thus, a correction factor or an experimentally determined maximum capacity needs to be applied to the original isotherm model to account for the presence of the binder.

The equilibrium behavior of the CST in both Hanford and SRS simulants and actual waste samples was estimated using the previously developed ZAM equilibrium parameters. In both cases, the isotherm model underpredicted Cs solid loading compared to what was observed experimentally. These results suggest that the model could be using an incorrect CST capacity. Using the ZAM equilibrium parameters also led to an underprediction of the impact of potassium on ion exchange capacity.

1.3 Modified Isotherm Objective

Collation of Cs exchange results from simple simulants, complex tank waste supernate simulant, and SRS simulants showed poor predictions using the original ZAM computational isotherm model, necessitating a re-evaluation of the model. The main objective of this research is to investigate the effect of various tank waste simulants on the cesium loading of CST and develop a modified isotherm model to better represent ion exchange performance of IONSIV[®] R9140-B and R9120-B, engineered forms of CST in the sodium and hydrogen form, respectively. To accomplish this goal, the previous equilibrium model developed by Zheng et al. (1997) will be modified to reflect experimental observations with the crystalline form IONSIV[®] R9140-B and R9120-B to predict the performance of commercialized CST in the radioactive solutions.

2.0 Quality Assurance

All research and development (R&D) work at 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 Experimental

This section describes the 5.6 M Na simulated tank waste, CST, and batch contact conditions.

3.1 5.6 M Na Simulant Compositions

Both Hanford and SRS simulant compositions were used for model development. It is important to note that the SRS data used in model development is published by Smith (2011) and King et al. (2018) and the experimental data was not recreated herein.

PNNL contracted the production of a 5.6 M Na simulant to Noah Technologies, Inc. (San Antonio, TX). The complex simulant preparation was conducted as defined by Russell et al. (2017), with the exception that the Cs concentration was set to 8 $\mu\text{g/mL}$ (instead of 13.8 $\mu\text{g/mL}$). This Cs concentration approximated the Cs concentration in AP-107 Hanford tank waste (Rovira et al. 2018). The sodium oxalate component was omitted to mitigate solids precipitation. The reagents used to make the simulant were assayed at 99.2% or better.

In addition to the complex simulant, two simplified tank waste supernate solutions were prepared as a fundamental basis for batch contacts: simple simulant A (1 M NaOH/4.6 M NaNO₃) and simple simulant B (0.1 M NaOH/5.5 M NaNO₃). The sodium nitrate was weighed directly into a volumetric flask. Deionized water was used to dissolve the salt. Once the salt dissolved, a 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 0.45-micron pore size nylon filter and stored in the polycarbonate receipt vessel.

The analytical compositions of the simulants used in model development are shown in Table 3.1. The SRS simulant composition, along with Cs distribution values, were transcribed from previously published work by Smith (2011) and King et al. (2018).

Table 3.1. Simulant Composition, Molar Scale

	Complex Simulant ^(a)	Simple Simulant A ^(b)	Simple Simulant B ^(b)	SRS Simulant ^(c)		SRS Simulant ^(d)					
				SRS Average Simulant	SRS Simulant Batch 1	SRS Simulant Batch 2	SRS Simulant Batch 3	SRS Simulant Batch 4	SRS Simulant Batch 1x	SRS Simulant Batch 2x	
Na ⁺	4.81	5.6	5.6	5.60	6.83	6.71	6.20	6.24	6.40	6.29	
K ⁺	0.102	--	--	0.02	0.01	0.02	0.03	0.03	0.01	0.02	
CS ⁺	6E-5	1E-4	1E-4	--	0.00	0.00	0.00	0.00	0.00	0.00	
NO ₃ ⁻	1.55	4.6	5.5	2.22	1.90	1.82	2.47	1.84	1.96	1.88	
OH ⁻	1.68	1.0	0.1	1.91	3.35	3.60	2.67	3.20	2.80	3.08	
NO ₂ ⁻	0.92	--	--	0.52	0.77	0.72	0.55	0.75	0.80	0.74	
AlO ₂ ⁻	0.15	--	--	0.31	0.28	0.14	0.15	0.21	0.29	0.14	
CO ₃ ²⁻	0.39	--	--	0.16	0.23	0.19	0.13	0.08	0.24	0.20	
SO ₄ ²⁻	0.058	--	--	0.14	0.02	0.01	0.04	0.03	0.02	0.01	
Cl ⁻	0.10	--	--	0.03	0.01	0.01	0.01	0.01	0.01	0.01	
PO ₄ ³⁻	0.043	--	--	0.01	0.01	0.01	0.01	0.01	0.01	0.01	

(a) Fiskum et al. 2018

(b) Campbell et al. 2020

(c) King et al. 2018

(d) Smith 2011

3.2 Ion Exchange Media

Two lots (2002009604 and 2081000057) of CST ion exchange material were received from Honeywell UOP LLC (Des Plaines, IL) as IONSIV[®] R9140-B. As the engineered form of CST, this product is manufactured in a spherical form screened to a 18x50 mesh size.

Experiments with 5.6 M Na complex simulant were conducted with CST lot 2081000057, sieved to <25-mesh using an ASTM E11 specification stainless-steel sieve. The sieved media was rinsed with deionized water at a solution-to-mass ratio of 2 for a total of seven contacts. The deionized water was decanted and the CST was air-dried to free flowing.

For simple simulant experiments, lot 2002009604 was used. As received material was sieved using a 30-mesh ASTM E11 specification stainless-steel sieve to remove larger diameter particles. The CST sieve fractions were washed with dilute sodium hydroxide to remove colloidal fines. Aliquots of CST were washed with 0.1 M NaOH in a phase proportion of nominally 1 volume CST to 1.5 volumes 0.1 M NaOH. The aqueous portion was decanted and an additional amount of 0.1 M NaOH was added. This process was repeated nominally five times until the vast majority of CST fines were removed.

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 to 425 °C (Fiskum et al. 2019; King et al. 2018a).

The CST reported in the literature for batch contacts with SRS simulant used IONSIV[®] R9120-B procured from Honeywell UOP LLC (Des Plaines, IL) as the hydrogen form of the ion exchanger with a dry mass basis corrected to 425 °C. Details on procurement, conversion to the Na-form, and thermogravimetric analysis of this material are reported by Smith (2011) and King et al. (2018).

3.3 Isotherm Testing

Batch-distribution contact testing is a rapid method for determining relative equilibrium performance of ion exchange materials in a given matrix. Batch contact solutions consist of the target test matrix plus various amounts of added ^{133}Cs . The equilibrium Cs concentrations are determined after batch contacts to assess Cs loading capacity on the CST and the Cs distribution coefficient (K_d) under nominal process conditions.

Test solution Cs concentrations were prepared such that the post-contacted equilibrium Cs concentrations would bracket the feed Cs concentrations found in tank wastes. Table 3.2 provides the compositions of the individual batch contact samples tested juxtaposed with the as-prepared Cs concentrations. Batch contact testing was not conducted for SRS simulant data reported by Smith (2011).

Table 3.2. Isotherm Test Solutions

Matrix	Cs Concentrations (M)
5.6 M Na Complex Simulant	6.02E-5
	2.94E-4
	1.49E-3
	7.00E-3
	4.63E-2
Simple Simulant A (1 M NaOH/ 4.6 M NaNO ₃)	6.72E-5
	3.97E-4
	2.24E-3
Simple Simulant B (0.1 M NaOH/ 5.5 M NaNO ₃)	1.32E-2
	6.84E-5
	3.97E-4
SRS Average Simulant	2.25E-3
	3.09E-6
	1.35E-4
	9.91E-4
	5.13E-6

A targeted phase ratio of 200 was maintained for batch contacts in the 5.6 M Na complex simulant as well as simple simulants A and B. Batch contacts with 5.6 M Na complex simulant combined nominally 0.1 g dry CST with 20 mL of each Cs stock solution (in duplicate). Samples were contacted at 700 rpm on an IKA KS125 orbital shaker for 24 h and the duplicates were contacted for 45 h (Fiskum et al. 2018). After contact, the CST was gravity settled and the aqueous fractions were filtered through 0.45- μm pore size nylon-membrane syringe filters for analysis.

For simple simulants A and B, nominally 0.075 g dry CST was contacted with 15 mL of each Cs concentration in the corresponding simulant. These samples were agitated at 260 rpm on a Cole-Palmer orbital shaker table for ~140 h at ambient temperature (21 ± 2 °C) (Fiskum et al. 2020; Campbell et al. 2020). After equilibrium was achieved, samples were filtered through a 0.45-micron pore size nylon syringe filter and 2 mL was subject to gamma energy analysis (GEA).

SRS average simulant contacts are described in detail by King et al. (2018) and the data were used for model development in this manuscript. Briefly, a phase ratio of 100 was selected for batch contacts, duplicate samples were contacted for 16 days with temperature maintained at 23 °C using a water bath (King et al. 2018). Post-contacted samples were filtered using a 0.45-micron filter and analyzed by GEA.

Cs concentrations in the samples were measured by GEA and used to calculate the distribution coefficient K_d (mL/g). The Cs batch K_d values were determined according to the standard formula shown in Eq. (3.1):

$$K_d = \frac{(C_0 - C_{1t})}{C_1} \times \frac{V}{M \times F} \quad (3.1)$$

where:

- C_0 = initial ^{137}Cs concentration ($\mu\text{Ci/mL}$)
- C_{1t} = ^{137}Cs concentration ($\mu\text{Ci/mL}$) at time, t
- C_1 = ^{137}Cs concentration ($\mu\text{Ci/mL}$)
- V = volume of the batch contact liquid (mL) at the sampling time
- M = measured mass of CST (g)
- F = F-factor, mass of the dried CST divided by the mass of sampled CST (100 °C dry mass basis)
- K_d = batch-distribution coefficient (mL/g)

Final Cs concentrations (C_{SF}) were calculated relative to the ^{137}Cs recovered in the batch contacted samples according to Eq. (3.2):

$$C_{S_0} \times \left(\frac{C_{1t}}{C_0}\right) = C_{SF} \quad (3.2)$$

where:

- C_{S_0} = initial Cs concentration in solution (mM)
- C_{SF} = final Cs concentration in solution (mM)

The equilibrium Cs concentrations loaded onto the CST ($C_{S_{IX}}$ in units of mmoles Cs per g of dry CST mass) were calculated according to Eq. (3.3):

$$\frac{C_{S_0} \times V \times \left(1 - \frac{C_1}{C_0}\right)}{M \times F} = C_{S_{IX}} \quad (3.3)$$

where:

- $C_{S_{IX}}$ = equilibrium Cs concentration in the CST (mmole Cs/g CST)

3.4 Calculation of Activity Coefficients

The activity coefficient describes the deviation of a real solution from an ideal mixture. The activity coefficient γ is defined as the ratio between activity a and mole fraction x of the species in the mixture shown in Eq. (3.4):

$$\gamma = \frac{a}{x} \quad (3.4)$$

Activity coefficients for the various components in the Hanford tank waste simulant solutions were calculated using the Aqua Module in HSC Chemistry version 7.193 (Roine 2002). The Harvie formalism was applied in the calculation of the activity coefficients. Charge balance between anions and cations in the projected feed solutions was adjusted by changing the sodium nitrate concentration as needed to result in complete electrical neutrality. Calculations were typically done for temperature of 25 °C. For variable

temperature calculation, the Equilibrium Compositions Module in HCS Chemistry was used. In these cases, the temperature was varied from 15 to 50 °C in 0.7 °C increments.

A summary of activity coefficients for each feed; complex simulant, simple simulant A (4.6 M NaNO₃/1 M NaOH), and simple simulant B (0.1 M NaOH/ 5.5 M NaNO₃), are shown in molar scale below in Table 3.3. These activity coefficients feed into Eq. (1.5) which is then used to determine the thermodynamic equilibrium constant (K_{eq}).

Table 3.3. HSC Activity Coefficient Measurements (molar scale)

Species	Temp (°C)	Complex Simulant	Simple Simulant A	Simple Simulant B
H ₂ O	25	0.98	1.00	1.03
Na ⁺	25	0.69	0.51	0.40
K ⁺	25	0.49	--	--
Cs ⁺	25	0.32	0.10	0.05
NO ₃ ⁻	25	0.41	0.39	0.39
OH ⁻	25	1.06	1.41	1.44
NO ₂ ⁻	25	0.61	--	--
Al(OH ₄) ⁻	25	0.29	--	--
CO ₃ ²⁻	25	0.09	--	--
SO ₄ ²⁻	25	0.03	--	--
Cl ⁻	25	0.62	--	--

4.0 Results

4.1 CST Cs Capacity

The maximum Cs capacity with UOP IONSIV® R9140-B CST was determined using the Freundlich/Langmuir (F/L) hybrid isotherm model described by the following equation:

$$Q = \frac{\alpha_1 [Cs]}{(\beta + [Cs])} \quad (4.1)$$

where Q (mmol/g) is the equilibrium solid phase concentration, [Cs] is the equilibrium Cs concentration (mmol/mL), and α_1 and β represent the ion exchange capacity and selectivity factor, respectively (Hamm et al. 2002). The maximum capacities calculated from three simulant matrices are provided in Table 4.1. The average maximum Cs capacity was found to be 0.53 ± 0.3 mmoles Cs/g of CST between the two different lots of IONSIV® R9140-B CST tested. While this value is not drastically different from the maximum Cs capacity of 0.58 mmoles Cs/g CST reported by Zheng et al. (1997), using the dilution factor of 0.68 determined by Hamm et al. (2002) to account for the binder of the CST reduces the Cs capacity to 0.39 mmoles Cs/g CST. Solely changing the maximum Cs capacity from 0.39 mmoles Cs/g to the experimentally derived maximum Cs capacity from these three experiments is a significant improvement to the ZAM isotherm model.

Table 4.1. Freundlich/Langmuir (F/L) Hybrid Isotherm Parameters

	Complex Simulant	1 M NaOH/ 4.6 M NaNO ₃	0.1 M NaOH/ 5.5 M NaNO ₃
CST lot	2081000057	2002009604	2002009604
Maximum capacity (α_1), mmoles Cs/g CST	0.50	0.55	0.55
Selectivity parameter (β), mmole Cs/mL	6.2E-4	5.4E-4	6.6E-4

4.2 Isotherm Modeling

Figure 4.1 and Figure 4.2 show ZAM-predicted K_d vs. measured K_d for the three tank waste simulants tested inclusive of previously reported SRS tank waste simulants (Smith 2011; King et al. 2018). The first iteration of the isotherm model, Model I (shown in Figure 4.1), uses original ZAM model parameters (K_{eq} and ΔH) for Eqs. (1.9) through (1.13) with the following exceptions: 1) capacity of 0.39 mmoles Cs/g was used to account for the binder dilution factor deemed necessary for the engineered form of CST and 2) Pitzer parameters calculated using HSC software were used in place of Bromley's parameters.

Model I significantly underpredicted Cs uptake from simple simulants A and B, as well as the SRS average simulant; all of which have low (or no) K^+ present in the simulant. The second iteration, Model II (shown in Figure 4.2) used the same parameters as Model I, but replaced the literature-reported capacity of 0.39 mmoles Cs/g CST with 0.55 mmoles Cs/g CST, the capacity experimentally determined from batch contacts with the current lot of IONSIV® R9140-B based on the observed higher capacity for these materials. Note that the production of CST has changed since the original isotherm data was developed, and it appears that this resulted in higher overall capacity for the CST. Significant agreement between measured and predicted Cs K_d values is observed for Model II with the simple simulants; however, the Cs distribution in 5.6 M Na complex simulant with 0.1 M K^+ is significantly overpredicted. A perfect representation from the model would land on the solid black line. The dashed lines represent $\pm 20\%$ error from the solid line.

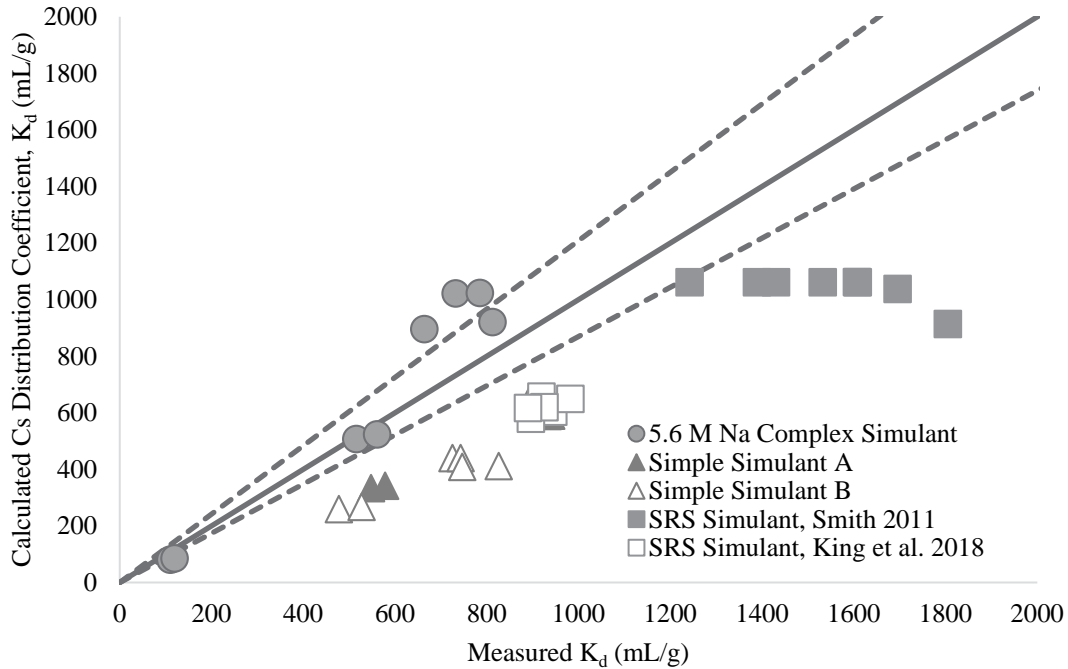


Figure 4.1. Measured Cs Distribution Coefficient, K_d (mL/g) for Model I

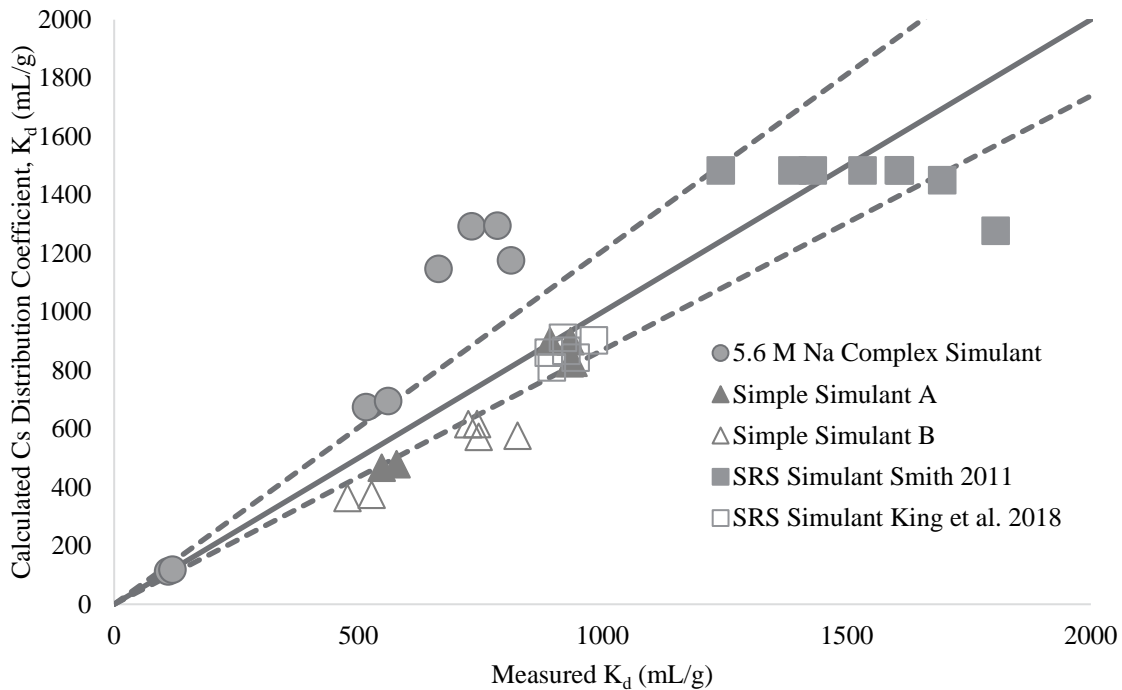


Figure 4.2. Measured Cs Distribution Coefficient, K_d (mL/g) for Model II

The next iteration, Model III, used Excel solver to refine K_{eq} for all five equilibria expressions, preserving literature-reported ΔH values and a capacity of 0.55 mmol/g CST. An improvement to literature-reported equilibrium parameters is validated by the batch contacts experiments performed and the K_{eq} determined from the data in Figure 4.1. The results for Model III distribution predictions (Figure 4.3) show improvement in predicted Cs K_d values with refinement of equilibrium parameters. The K_{eq} for

Eq. (1.9) with Cs⁺/Na⁺ exchange was increased from 4.4E-4 to 4.7E-4, and K_{eq} for Eq. (1.13) with K⁺/Na⁺ exchange was decreased by nearly half as reported in Table 4.2. Although simulants with low (or no) K⁺ fit reasonably well using Model III parameters, the modeled Cs K_d values in 5.6 M Na complex simulant remain much higher than the Cs K_d values measured experimentally.

Table 4.2. Equilibrium Constants for Original and Modified Isotherm Models

Test	K _{eq} Cs	K _{eq} K	K _{eq} K-K	K _{eq} K-Cs	K _{eq} K-K-Cs
Model I and II	4.4E4	9.7E1	1.8E1	1.9E4	1.5E4
Model III	4.7E4	4.5E1	5.5E1	5.0E2	5.0E2

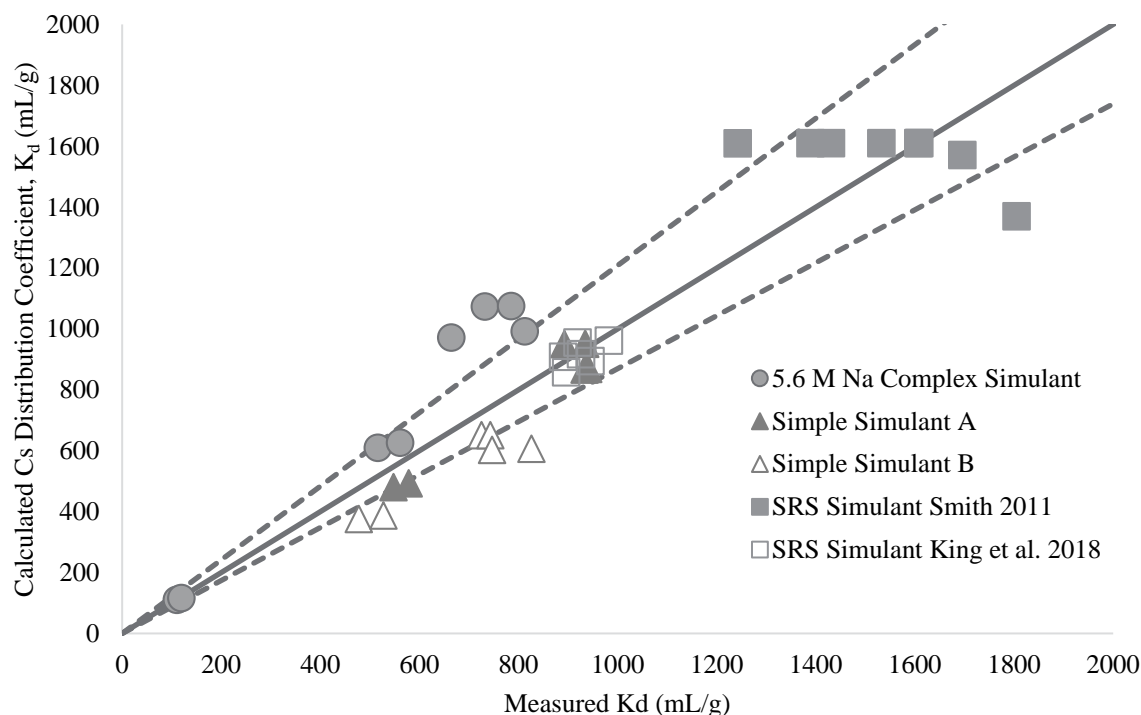


Figure 4.3. Measured Cs Distribution Coefficient, K_d (mL/g) for Model III

Modifying the rate constants helped the model significantly, but poor estimates were still observed when predicting the complex and simple Hanford and SRS simulants; both of which contained K⁺ at nominally 0.1 and 0.02 M, respectively. The original model assumes K⁺ loads on two CST sites with the ability of Cs to load onto both Na- and K-substituted sites. One hypothesis for the misprediction of Cs loading is that it is due to the sequential loading of Cs on K-substituted sites. Campbell et al. (2019) reported K⁺ loading onto CST post processing Hanford tank waste at significantly less mmole/g CST than the isotherm model predicts. Eliminating the exchange mechanism for Cs on K-substituted sites [Eqs. (1.11) and (1.12)] has been proposed to simplify the equilibrium reactions to only Eqs. (1.9) and (1.10), reiterated below. This led to the development of the Campbell Westesen Peterson (CWP) model.



This suggests that Cs can only exchange initially on a Na-substituted site. Additional adjustments to the original isotherm model's equilibrium rate constants were explored to better refine the proposed simplified model. The simple simulant A and B batch contact data were used in the isotherm model but were not used to refine the parameters due to the lack of K⁺ in the feeds. Equilibrium constants for Cs and K for the isotherm models are shown in Table 4.3.

Table 4.3. Equilibrium Constants for Modified Models

Test	Capacity (mmol/g)	K _{eq} Cs	K _{eq} K
Model I	0.39	4.4E4	9.7E1
Model II	0.55	4.4E4	9.7E1
Model III	0.55	4.7E4	3.5E1
CWP Model	0.55	5.6E4	1.8E2

The predicted distribution ratios (K_d) and Cs loading (mmole Cs/g CST) from the original and refined isotherm models are compared in Table 4.4. Modified isotherm predictions are significantly enhanced when the K-substituted exchange site is removed from the calculation, as indicated by the reduction of % difference in the measured vs. calculated Cs distribution constants. The experimental and calculated Cs distribution coefficients (K_d) from all simulants examined can be displayed graphically as shown by the parity plot in Figure 4.4.

Table 4.4. Measured and Modeled Cs Kd (mL/g) and Loading (mmole/g)

Feed	Equil.Cs Concentration, M	Measured		Modification II			Modification III			CWP Model		
		Cs ⁺ K _d	Cs ⁺ mmol/g CST	Cs ⁺ K _d	Cs ⁺ mmol/g CST	% differ- ence	Cs ⁺ K _d	Cs ⁺ mmol/g CST	% differ- ence	Cs ⁺ K _d	Cs ⁺ mmol/g CST	% differ- ence
Complex Simulant	1.2E-05	732	9.1E-03	1293	1.6E-02	55%	1074	1.3E-02	38%	886	1.10E-02	19%
	6.6E-05	664	4.4E-02	1148	7.6E-02	53%	971	6.4E-02	38%	809	5.34E-02	20%
	4.0E-04	516	2.1E-01	675	2.7E-01	27%	610	2.4E-01	17%	525	2.10E-01	2%
	4.4E-03	111	4.9E-01	113	5.0E-01	2%	111	4.9E-01	0%	100	4.45E-01	10%
	1.2E-05	785	9.1E-03	1295	1.5E-02	49%	1075	1.3E-02	31%	887	1.03E-02	12%
	5.4E-05	812	4.4E-02	1177	6.4E-02	37%	992	5.4E-02	20%	825	4.48E-02	2%
	3.8E-04	561	2.1E-01	696	2.6E-01	21%	627	2.4E-01	11%	539	2.02E-01	4%
	4.2E-03	119	5.0E-01	119	5.0E-01	1%	116	4.9E-01	3%	105	4.42E-01	13%
Simple Simulant A	1.1E-05	934	1.0E-02	900	1.0E-02	4%	951	1.1E-02	2%	1083	1.22E-02	15%
	6.7E-05	933	6.3E-02	825	5.5E-02	12%	867	5.8E-02	7%	975	6.54E-02	4%
	5.7E-04	548	3.1E-01	467	2.7E-01	16%	480	2.8E-01	13%	512	2.94E-01	7%
	1.2E-05	892	1.0E-02	900	1.1E-02	1%	950	1.1E-02	6%	1082	1.27E-02	19%
	6.6E-05	941	6.2E-02	826	5.4E-02	13%	869	5.7E-02	8%	977	6.42E-02	4%
	5.4E-04	578	3.2E-01	479	2.6E-01	19%	493	2.7E-01	16%	526	2.87E-01	9%
Simple Simulant B	1.4E-05	725	1.0E-02	616	8.6E-03	16%	651	9.1E-03	11%	742	1.04E-02	2%
	7.5E-05	826	6.2E-02	577	4.3E-02	36%	607	4.6E-02	31%	685	5.15E-02	19%
	6.3E-04	478	3.0E-01	364	2.3E-01	27%	376	2.4E-01	24%	404	2.54E-01	17%
	1.4E-05	743	1.0E-02	617	8.4E-03	19%	651	8.9E-03	13%	742	1.01E-02	0%
	8.1E-05	747	6.1E-02	573	4.7E-02	26%	603	4.9E-02	21%	679	5.52E-02	9%
	5.9E-04	527	3.1E-01	375	2.2E-01	34%	387	2.3E-01	31%	418	2.45E-01	23%
SRS Simulant, Smith 2011	2.1E-07	1607	3.3E-04	1485	3.1E-04	8%	1611	3.3E-04	0%	1611	3.32E-04	0%
	8.8E-06	1696	1.5E-02	1451	1.3E-02	16%	1571	1.4E-02	8%	1571	1.38E-02	8%
	6.0E-05	1805	1.1E-01	1278	7.7E-02	34%	1370	8.2E-02	27%	1370	8.20E-02	27%
	3.9E-07	1389	5.5E-04	1484	5.9E-04	7%	1610	6.3E-04	15%	1610	6.34E-04	15%
	3.5E-07	1609	5.7E-04	1484	5.2E-04	8%	1610	5.7E-04	0%	1610	5.65E-04	0%
	3.8E-07	1430	5.5E-04	1484	5.7E-04	4%	1610	6.1E-04	12%	1610	6.13E-04	12%
	3.7E-07	1532	5.6E-04	1484	5.4E-04	3%	1610	5.9E-04	5%	1610	5.89E-04	5%
	4.4E-07	1242	5.5E-04	1484	6.6E-04	18%	1610	7.1E-04	26%	1610	7.13E-04	26%
SRS Simulant, King et al. 2018	1.8E-04	945	1.7E-01	844	1.5E-01	11%	895	1.6E-01	5%	950	1.73E-01	1%
	2.0E-04	896	1.8E-01	811	1.6E-01	10%	858	1.7E-01	4%	878	1.77E-01	2%
	9.6E-05	982	9.4E-02	903	8.6E-02	8%	962	9.2E-02	2%	967	9.25E-02	2%
	1.7E-04	919	1.6E-01	912	1.6E-01	1%	955	1.7E-01	4%	982	1.70E-01	7%
	1.9E-04	926	1.8E-01	868	1.6E-01	6%	917	1.7E-01	1%	960	1.82E-01	4%
	2.1E-04	890	1.9E-01	861	1.8E-01	3%	909	1.9E-01	2%	937	1.96E-01	5%

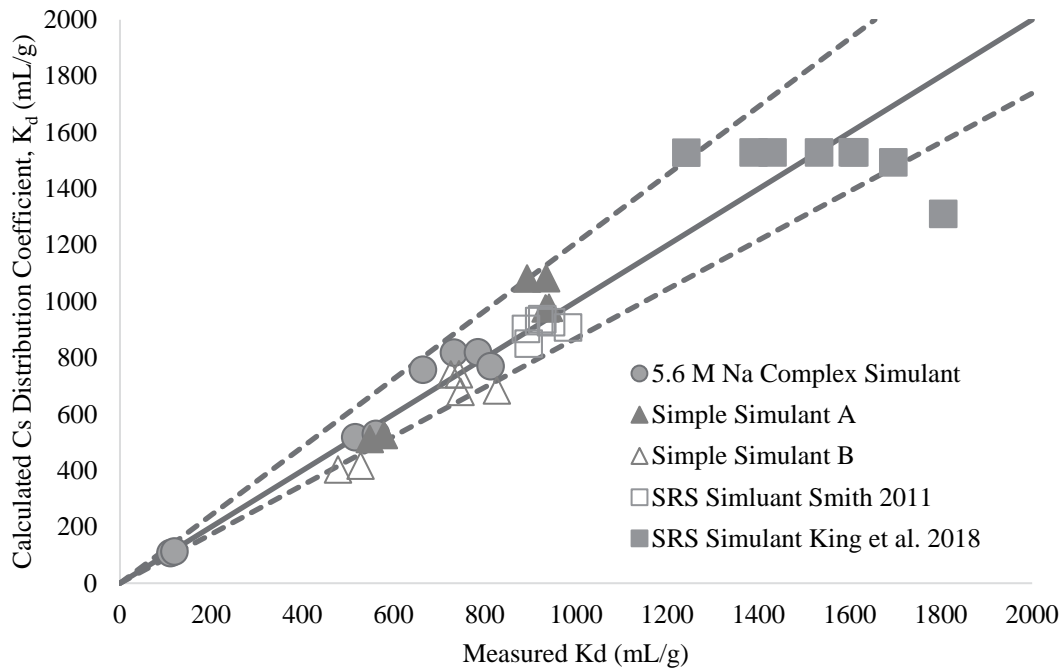


Figure 4.4. Measured Cs Distribution Coefficient, K_d (mL/g) for CWP Model

4.2.1 Least Squares F Test

Table 4.5 shows the sum of squares used to estimate the fit of the predicted vs. measured K_d values for each model fit with F-statistic (also known as the F-test). The F-test is used when comparing statistical models that have been fitted to a data set. The F-statistic is used in combination with an R-squared value to determine the overall strength of the relationship between the model and the data. The R-squared value ranges from 0-1, with 1 being a perfect fit.

The F-statistic can be calculated using the following equation:

$$F = \frac{MSR}{MSE} \quad (4.2)$$

where:

MSR = mean square due to regression

MSE = mean square due to error

The MSR is computed by dividing the sum of squared residuals by its degrees of freedom. In a similar manner, the MSE is computed by dividing the sum of squared estimate of errors by its degrees of freedom. All parameters were regressed simultaneously for the three sets of Hanford simulant data. Based on the F-factor tests, solely changing the CST capacity from 0.39 to 0.55 mmols Cs/g CST, as seen in Model I and II values, was not enough to have the model represent experimental data. By changing the ZAM equilibrium constants in Model III, the model was better fit to the data but did not accurately represent the K^+ uptake. The CWP model statistically fits the data best. This is partially due to reducing the number of parameters used to fit the data. Even without changing K_{eq} values for Cs and K, reducing the number of parameters will lead to a larger R-squared value.

Table 4.5. F-test Statistical Values for Isotherm Models

Test	F-value	R ²
Model I	5.08	0.28
Model II	5.75	0.63
Model III	6.23	0.84
CWP Model	10.89	0.90

5.0 Conclusions

Modification of the original ZAM isotherm model to adjust equilibrium coefficients determined that additional alterations were necessary to better predict Cs distribution from caustic, high-salt tank waste simulants.

The CST capacity used in the isotherm model was altered from 0.39 mmoles Cs/g to an experimentally determined maximum Cs capacity of 0.55 mmoles Cs/g based on observed Cs capacity for CST in tank waste simulants. A poor prediction by the isotherm model, even with a change to the CST capacity, resulted in refining the equilibrium constants used in the model. Although modifying the equilibrium rate constants significantly improved the model, poor estimates were observed when predicting the Hanford and SRS simulants containing K^+ . Exchange mechanisms for additional K^+ and Cs^+ loading were omitted from the isotherm model to suggest that Cs can only exchange on a Na-substituted site. Additional adjustments to the isotherm model's equilibrium rate constants were executed to better refine the simplified model.

However, simplifying the ZAM isotherm model expressions from five equations down to two equations, along with implementing the experimental Cs capacity in the calculations, has significantly improved our ability to predict Cs loading from complex matrices. By omitting the equilibria expression for Cs loading on K-substituted sites, along with inclusion of experimental capacity of UOP IONSIV[®] R9140-B CST, a new, simplified model was generated. The predicted K_d vs. measured K_d correlation factor increased to 0.9 – much higher than the baseline ZAM correlation. The revised model can be applied to Hanford and SRS tank waste Cs removal efforts involved in the developing and applying TCCR and TSCR technologies.

Additional experiments are necessary to better understand the impact of K^+ on the ZAM modeling parameters and to refine equilibrium constants necessary for accurate prediction of Cs loading. Further advancement of the model would include batch contact experiments with K^+ for independent refinement of the $K K_{eq}$, as well as verification of the activation energies reported by Zheng et al. (1997).

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