Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

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Crystalline Silicotitanate Ion Exchange Media Long-Term Storage Evaluation

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November 2018
SRNL-STI-2018-00567, Revision 0

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Prepared for
U.S. Department of Energy

SRNL-STI-2018-00567
Revision 0

Keywords: *cesium, salt processing, ion exchange*

Retention: *Permanent*

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EXECUTIVE SUMMARY

Crystalline Silicotitanate[a] (CST) ion exchange media is produced in an engineered form, known as IONSIV™ IE-911. This material has been tested extensively for use in removing ^{137}Cs from Savannah River Site (SRS) and Hanford site tank waste. This inorganic material is highly selective for removing cesium ions, even in the presence of high concentrations of sodium and potassium ions and is tolerant of the harsh conditions of the varying tank chemistries. A batch of caustic washed IE-911 that had been produced by the supplier and received at SRS in 2001 was tested to verify that it was still in good condition after the extended storage. This testing involved standard batch contacts to measure the removal of Cs from simulated tank waste. This report describes the results of testing performed to verify that the IE-911 matches the performance of previous batches of this media.

To confirm that the performance of IE-911 is similar to previous batches and that no degradation had occurred during storage, batch contact testing was performed using SRNL's standard methodology using a non-radioactive SRS Average Waste Simulant composition utilized in previous studies. Batch contact kinetics testing was also conducted to determine cesium loading on this batch versus time. The cesium equilibrium loading isotherm in SRS simulant at 23°C was compared to ZAM isotherm model predictions and previous test results with IE-911 media. The measured and predicted distribution coefficients and cesium loading ("Q") are shown in Table ES-1. The physical properties of the material were also determined, including density, moisture content, and particle size.

All batch contact testing was successfully completed, and the results were generally consistent with ZAM model predictions. The ZAM prediction was performed by inputting the same initial cesium concentration and solid:liquid phase ratio as in the testing, and the model calculated the final cesium concentration which was then used to compute the K_d and Q. Results indicated that this IE-911 batch is similar to previously tested batches and that the 17 years of storage did not impact its performance. The particle size of the material is consistent with the original specification of 30x60 mesh and is roughly 408 µm average diameter with no fines observed. Other parameters, such as kinetics of Cs absorption, were also measured and are reported.

Table ES-1. Distribution Coefficient Results

SRS Average Simulant Sample	Initial Cs^+ (M)	Measured K_d mL/g	ZAM Predicted K_d mL/g	Measured Q mmol/g	ZAM Predicted Q mmol/g
A/B	1.667E-05	2423	2478	1.75E-03	1.76E-03
A/B replicate	1.667E-05	2253	2477	1.83E-03	1.84E-03
B	1.437E-04	2247	2415	1.61E-02	1.62E-02
B replicate	1.437E-04	2264	2417	1.57E-02	1.57E-02
C	1.045E-03	2626	1998	1.15E-01	1.13E-01
C replicate	1.045E-03	2712	1983	1.18E-01	1.17E-01

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[a] Crystalline Silicotitanate (CST) was developed by researchers at Texas A&M University along with Sandia National Laboratory; and is currently produced as an engineered inorganic bead by Honeywell UOP, LLC, Des Plaines, IL, USA. This batch of engineered material is identified as "IONSIV™ IE-911" and that designation is used throughout this report, shortened to "IE-911" herein, but newer versions of the caustic-washed material are referred to as IONSIV™ 9140-B.

Some of the distribution coefficient (K_d) values in Table ES-1 indicate that the measured value exceeds the calculated value. This difference in measured versus predicted is attributed to error in the measurements and reference state of the material. Because of the way that the distribution coefficient is calculated, small variance in measurements of mass and analytical instrument results can cause large changes in the observed value. The predicted distribution coefficients were calculated using the ZAM computer model, which is based on the powdered form of CST, and there is typically an adjustment of the output to account for the dilution factor due to the binder present in IE-911. The absence of the need for a dilution factor adjustment for this batch of material is attributed to different initial conditions for the material such as preconditioning steps and drying. The loading measurements (Q) match the predicted values very well. This Q parameter is less sensitive than the distribution coefficient parameter to slight variance in measurements performed during testing.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Avg	average
CDF	Cumulative Density (Distribution) Function
CST	Crystalline Silicotitanate
DOE	Department of Energy
hr	hour
ICP-ES	Inductively Coupled Plasma - Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma - Mass Spectroscopy
K_d	Distribution Coefficient
PVDF	Polyvinyldifluoride
RPM	Revolutions per Minute
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TGA	Thermal Gravimetric Analysis
TIC	Total Inorganic Carbon
TTQAP	Task Technical and Quality Assurance Plan
MS	Mass Spectroscopy
ZAM	ZAM Isotherm Model

1.0 Introduction

Several years ago, SRNL collaborated with UOP, the producer of the engineered form of CST (IONSIV™ IE-911, recently renamed IONSIV™ R9120-B), to develop a preconditioning protocol to remove excess chemical phases from the ion exchange media [Wilmarth, et al., 2000]. That protocol involved extensively washing the media with sodium hydroxide solution, followed by water rinsing. Pre-production IE-911 samples were produced and tested at the time and found to be in good condition [Wilmarth, et al., 2001]. Following that, UOP produced an engineered batch (~450 kg) of the caustic-washed IE-911, which was received at SRS in 2001. This batch of material was stored at SRS as received in plastic-lined steel drums in a shed without temperature control until October of 2012. It is assumed that the drums would have occasionally been exposed to overnight temperatures below 0°C during the winter. After 2012, it was transferred to a climate-controlled building (4-60°C) where it has since been stored. The material remained dry during storage.

SRNL is evaluating the condition of this material after the ~17 years of storage to determine if it is still effective in removing cesium and to verify that it has acceptable physical properties. Two types of batch contact testing were conducted to support evaluation of the media:

1. The ion exchange media was evaluated for comparison to previous studies and model predictions by conducting IE-911 batch contact cesium loading equilibrium tests with SRS average simulant at 23°C.
2. Measurement of the rate of cesium loading at 23°C (i.e., batch contact kinetics studies).

In addition to cesium absorption, the bulk density, moisture content (by Thermal Gravimetric Analysis), and particle size of the media were measured. The IE-911 batch contact filtrate samples were also analyzed for strontium (Sr). Although Sr was not added to the simulant, it is a common impurity in laboratory chemicals and very strongly competes with Cs for ion exchange sites on IE-911.

2.0 Experimental Methods and Modeling Approach

2.1 IE-911 Sample Collection

One of the drums of IE-911 media was recently shipped to SRNL from its storage location onsite. The drum was labeled as IE-911, Lot #2081000056, Mat. #80562-556p, and drum #36232-1-5. The drum contained approximately 30 gallons of IE-911. A sample of ~100 mL of the IE-911 beads was retrieved from the drum by choosing the method of drum sampling based on ASTM D6063-11, and an adaptation of ASTM standard method D5680-14 was followed for retrieving the sample. Visually, the IE-911 beads were relatively homogeneous, unconsolidated material, and appeared to be in good condition. Three subsamples were collected by scooping ~35 mL of media from three random locations in the drum, several inches beneath the surface.

2.2 Batch Contact Test Equipment

Batch contact testing was performed by mixing the aqueous simulant with a small amount of the IE-911 in plastic bottles and agitating it for a period of time. Batch contact testing was performed using an Innova incubator shaker oven (Model 4230). Samples were agitated by orbital rotation at 150 Revolutions Per Minute (RPM) and continuously maintained at a temperature of 23°C.

2.3 IE-911 CST Property Measurements

Duplicate IE-911 subsamples were characterized under nitrogen purge gas by Thermal Gravimetric Analysis using a Model TA2050 analyzer from Thermal Analysis (TA) Instruments. During analysis, the temperature was increased at a rate of 5°C/minute up to a temperature of 400°C, at which point the temperature was held for 120 minutes. The subsamples were then heated to 1000°C at a heating rate of 5°C/minute. A water mass correction factor (F-factor) was calculated based on cumulative mass losses observed for the samples up to 400°C.

The particle size of the IE-911 was measured using a Microtrac S3500 Laser Diffraction Analyzer. Samples were suspended in water for the analysis.

Bulk density was measured by pouring a 49.538 g sample of the as-received material into a graduated cylinder (~1-inch internal diameter) and tapping the side of the cylinder until a constant level was achieved. This formed a column of CST that was approximately 3.1 inches tall. The weight of the material and volume were used to determine the bulk density of the as-received material. The exact volume of the bed was determined by weighing an equivalent volume of water and calculating the volume using the density of water.

2.4 IE-911 Pretreatment

The IE-911 media had been provided by UOP in the caustic washed form and was not further preconditioned or treated by SRNL prior to testing. Although IE-911 media is often preconditioned in the laboratory, this batch had already been preconditioned by the vendor so this as-received condition (but after ~17 years storage) is defined as the *reference state* for this media batch. Material was weighed and used in property measurements and ion exchange testing without modifications or washing.

2.5 Simulant Preparation

A sample of tank waste simulant with the composition provided in Table 2-1 was prepared following the standard recipe [Walker, 1999]. This aqueous simulant was developed to represent an average SRS waste supernate liquid and this solution has been used in the past for ion exchange media performance evaluations. The simulant contains 5.6 M Na^+ ions, with anions dominated by nitrate, free hydroxide, and nitrite. Cesium salts were excluded from the initial simulant preparation so that various cesium spike levels could be added for Cs^+ loading isotherm testing. After preparation, the simulant was filtered through a 0.45 µm polymer filter unit. Non-radioactive cesium was added to each of three separate portions of the simulant to give different total cesium concentrations within the compositional range of interest for cesium absorption onto IE-911 media. The total cesium concentration in the simulant solutions ranged from 1.7E-5 M to 1.0E-3 M. The measured simulant density was 1.2508 g/mL at ambient temperature (19°C). Its density at 23°C was estimated using OLI[a] software to be about 1.23 g/ml.

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[a] OLI refers to a computer model, OLI Studio: Stream Analyzer by OLI Systems, Inc., of Cedar Knolls, N.J., U.S.A.

Table 2.1. SRS Average Simulant Composition Developed by Walker [1999] and Total Cesium Spike Levels Utilized for Testing.

Component	**Molarity**
Na^+	5.60
K^+	0.015
OH^-	1.91
NO_3^-	2.14
NO_2^-	0.52
AlO_2^-	0.31
CO_3^{2-}	0.16
SO_4^{2-}	0.15
Cl^-	0.025
F^-	0.032
PO_4^{3-}	0.01
$C_2O_4^{2-}$	0.008
SiO_3^{2-}	0.004
MoO_4^{2-}	0.0002
Sub-Sample Cs concentration	
Simulant	**Total Cs^+ (M)**
A/B[a]	1.67 E-5
B	1.44 E-4
C	1.05 E-3

Although no strontium was added to the simulant, it is a known contaminant in laboratory chemicals and is a strong competitor for ion exchange sites in CST. Analysis of the simulant included measuring the strontium concentration so that it could be accounted for if it was present.

2.6 IE-911 Batch Contact Testing with SRS Average Simulant

Duplicate 10 mL subsamples of each of the simulant solutions (A/B, B, and C in Table 2-1) were used for batch contact equilibrium testing by mixing with separate ~0.1 g samples (as-received reference state mass basis) of IE-911 media. The simulant and IE-911 test samples were placed in 60 mL polyethylene bottles, transferred to the shaker oven, and continuously agitated. The oven temperature was set to 23ºC and the temperature was recorded daily (excluding weekends). Batch contact testing was continued for a total of 4 days, with one sample collected from each bottle at the end of the 4-day period, which was immediately filtered and submitted for Cs and Sr analysis by Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS).

An additional set of 10 mL samples with duplicates were prepared for cesium loading kinetics evaluations using Simulant B using the same liquid to solid (IE-911) ratio, but samples were collected at shorter times. Samples were collected and filtered after 1.5, 5.5, and 24 hours of agitation under identical conditions as above to determine the cesium loading kinetics versus time.

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[a] “A/B” refers to a mixture of simulants A and B from prior testing (King, 2018b) that were mixed for this test to target an intermediate Cs concentration

During testing, the average temperature based on the recorded data was 23.0°C and the temperature ranged from 22.9 to 23.1°C, except when the oven door was opened briefly during sample loading/unloading. During each sampling event, individual samples were removed from the shaker, filtered through 0.45 µm syringe filters, and submitted for analysis.

OLI calculations were also performed based on the simulant composition listed in Table 2-1 at 23ºC. The key OLI estimated parameters that were employed in the following ZAM and VERSE analyses are:

- Liquid density = 1.2278 g/ml
- Absolute viscosity = 2.547 cP
- Cs^+ liquid diffusivity = 5.604×10^{-4} cm^2/min

The liquid density value is required as input to the ZAM code, while all three of the above parameters are required as input into the VERSE code.

2.7 ZAM Isotherm Model Calculations

The ZAM Isotherm Model code was developed at Texas A&M University by Rayford G. Anthony and Zhixin Zheng and designed to simulate ion-exchange equilibria of electrolytic solutions and CST solids. The ZAM code is a product of several years of development and research in Professor R. G. Anthony's Kinetics, Catalysis and Reaction Engineering Laboratory in the Department of Chemical Engineering Texas A&M University. A description of the current ZAM model is available [Zheng et al., 1997].

Two types of ZAM Isotherm Model analyses were employed during this effort:

- Specific numerical batch contact calculations were performed to make direct comparisons between measured loadings (and K_d values) and ZAM predicted values; and
- Series of runs were conducted by varying the CsCl concentration (while maintaining charge balance) to map out a specific isotherm at 23°C.

IE-911 is a form of ion exchange media that is composed of the submicron-sized CST "powder" bound into an engineered bead with a binding agent. ZAM only calculates the CST media performance in its powdered form; therefore, in order to adjust for the engineered IE-911 media, a fixed amount of engineered-form media must be mathematically converted into its powdered form (i.e., to maintain the actual amount of exchange sites present in each batch contact sample). Once the media is put into its equivalent powdered-form dry mass basis, ZAM calculation runs are performed. Upon completion of the ZAM batch contact runs, the resulting ZAM loadings and K_d values are then converted back to an engineered-form basis. Also, all ZAM runs were made using version-4. Although version-5 was developed to improve the calculated competition between $SrOH^+$ and Cs^+. The outcome is identical to version-4 in SRS tank waste compositions and version-4 converges more easily than the later version-5. The ZAM model was developed based on batch contact data in the 25-44 °C range [Hamm et al., 2002]. ZAM input and output files for a subset of the batch contact cases are provided in Appendix B.

2.8 Quality Assurance

The performance of this work was consistent with controls identified in the Technical Task and Quality Assurance Plan for testing CST [King, 2018a]. Results of testing are recorded in an Electronic Laboratory Notebook A2341-00117-11. The ZAM Model is classified as a Quality Assurance Level D software package.

3.0 Results and Discussion

3.1 Property Measurements

The IE-911 vendor supplied the following information on the sieve size analysis of this batch of IE-911 from the original manufacturing date (see Table 3-1):

Table 3.1. Vendor IE-911 Sieve Size Analysis Results

Screen cut	Weight %
(+30)	2.7
(30x40)	37.3
(40x50)	53.4
(50x60)	6.0
(-60)	0.5
Average Diameter (mm)	0.44

SRNL computed the CST size characteristics from the vendor's sieve data. Below (Figure 3-1) shows a log-normal distribution fit:

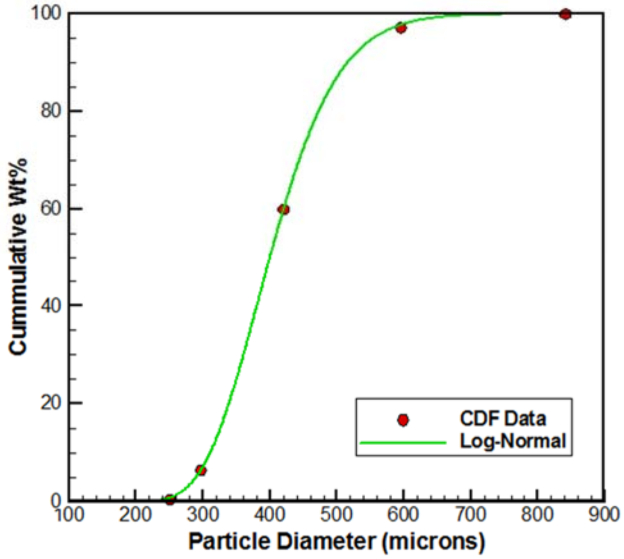

Figure 3-1 Cumulative Distribution Function of Vendor Sieve Data

From the log-normal distribution fit of vendor sieve analysis, one can calculate a variety of different mean particle diameter sizes. The mean volume diameter is 408 microns. Below (Table 3-2) is the output from a calculation tool developed by SRNL, providing a variety of ways to express the particle size distribution:

Table 3.2. Computed Log-Normal Distribution of Particle Size Based on Vendor Sieve Analysis

Particle Size	Cumulative Distribution	Residual
(µm)	(weight % passing)	(observed-computed)
250	0.50	-0.3787
297	6.50	-0.1296
420	59.90	0.1439
595	97.20	-0.5628
841	99.90	-0.0914
Log-Normal median size (xg) = 400 µm		
Log-Normal standard deviation (sg) = 1.22		
Minimum particle size for integration = 210 µm		
Maximum particle size for integration = 1000 µm		
Number mean diameter = 363 µm		
Volume mean diameter = 408 µm		

The Sauter mean diameter (SMD, d_{32}), identified as Volume mean diameter above, was chosen as the best estimator for addressing mass transport aspects. It is defined as the diameter of an "effective" sphere that has the same volume/surface area ratio as the particles of interest. Specifically, SMD is the ratio of the volume average to surface area average values based on a given probability density function (i.e., here we have chosen the log-normal distribution). We have been using this SMD for all our VERSE simulations.

The particle size of the current sample of IE-911 (after extended storage) was also measured using a laser diffraction analyzer (Microtrac S3500). Samples were suspended in water for the analysis. Five subsamples were removed from the bottle that had been sampled from the drum, being careful to obtain representative subsamples. The average mean area (MA) diameter of the five samples was 433 µm with a range of 413 – 480 µm. The results from the sample nearest the average of the five (subsample #1) are shown in Figure 3-2 and Table 3-3, and the data from all five analyses are shown in Appendix A.

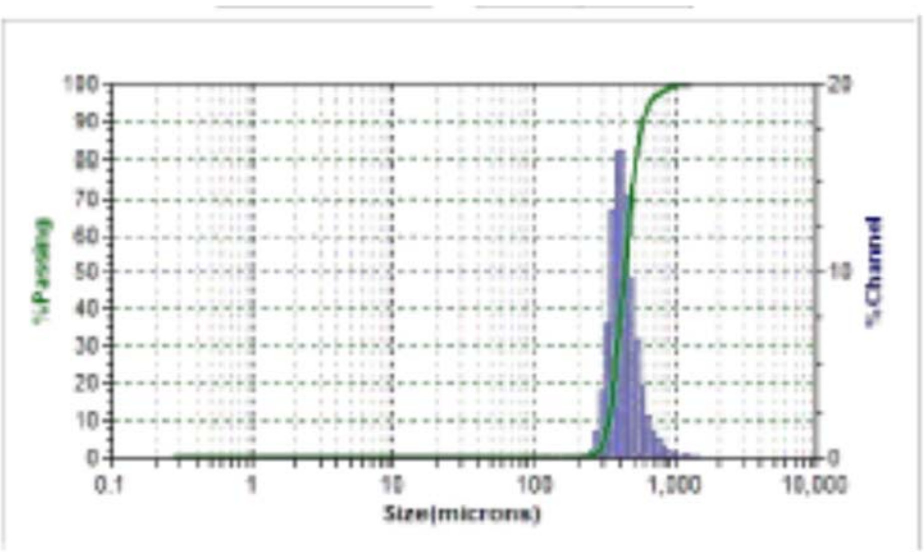

Figure 3-2. Microtrac Particle Size Analysis Results Plot for IE-911 CST Media

Table 3.3. Microtrac Particle Size Analysis Data for IE-911 CST Media.

Data Item	**Value**
Mean Volume (diameter) (μm)	457.8
Mean Number (diameter) (μm)	395.1
Mean (diameter) Area (μm)	432.8
Calculated (exterior) Surface area (m^2/mL)	1.39E-2
Standard deviation	93.92

The particle size analysis results by laser diffraction match reasonably well with the average size computed from the sieve analysis results. The Mean Area diameter is the value most representative of the overall size, and the average for the five subsamples is 433 μm. It should be noted that a sieve will tend to indicate the smallest dimension because the particle is shaken until its orientation allows it to pass through the screen. The laser diffraction method takes the average dimension, and therefore tends to be higher than the sieve analysis with irregular particles. It was also important to just visually examine the material to see if there were any fractures, fines, or unusual particles. An optical microscope image is shown in Figure 3-3. There is no indication of significant bead fracturing or degradation.

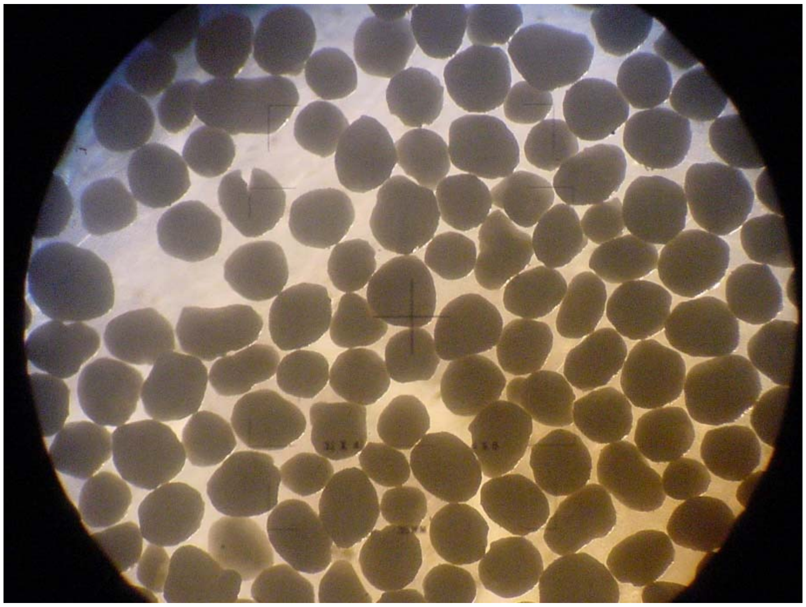

Figure 3-3. Back-lit Optical Microscope Image of IE-911 Media

Overall, the particle size measurements and physical inspection of the IE-911 do not indicate any physical degradation of the material due to the ~17 years of storage. There are no fines, and the beads do not appear cracked or more irregularly shaped than usual. Duplicate Thermal Gravimetric Analysis (Figure 3-4 and Table 3-4) of the as-received IE-911 media revealed that the cumulative percentages of both physisorbed and chemisorbed water in the samples was an average of 16.3% based on heating to 400°C in the TGA instrument. Conversion of the as-received media reference state mass to a dry mass basis can be accomplished by multiplying the reference mass by a factor of 0.8374 (F-factor). It should be noted that it is assumed that all mass losses from the media across this temperature range are associated with water loss, although the identity of the off-gas components was not confirmed by separate analysis. One of the TGA plots is shown in Figure 3-4, and the data from both measurements is provided in Table 3-4. The green line shows the weight loss as a function of temperature. The blue line is the derivative of that weight loss. These results are consistent with historical measurements, and do not indicate any change in properties or degradation due to the ~17 years of storage.

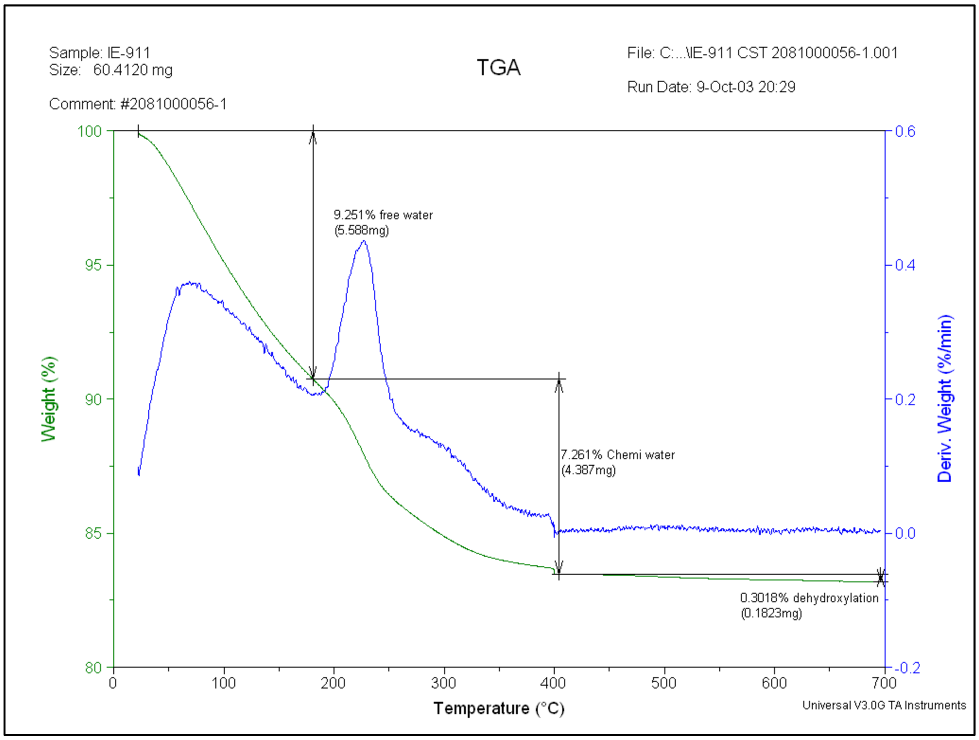

Figure 3-4. Thermal Gravimetric Analysis Results for IE-911 CST Media

Table 3.4. Thermal Gravimetric Analysis Results for IE-911 Media.

	CST Sample 1	CST Sample 2
	Wt. % Loss	
Free Water Mass Loss (20-200 °C)	9.251	8.877
Chemisorbed Water Mass Loss (200-400 °C)	7.261	7.123
Cumulative Total Mass Loss (20-400 °C)	16.512	16.000
Average Total Mass Loss (20-400 °C)	16.256	
	Hydrated CST Mass Correction	
F-factor	0.8349	0.8400
Average F-factor	0.8374	

The bulk density of a packed cylinder of the as-received IE-911 material was determined to be 1.227 g/mL. The initial bed density prior to tapping/packing was 1.186 g/mL. This density is slightly higher than in many historical batches and is partially attributed to moisture and to the fact that these earlier batches were not converted to the sodium form. The sodium form would be expected to be ~5% denser than the hydrogen form of the IE-911.

3.2 CST Loading Batch Contact Tests with SRS Average Simulant

Cesium loading batch contact tests were conducted using IE-911 media and SRS Average Simulant spiked to various total cesium concentrations. It is known from prior work that cesium sorption to CST media is essentially complete within 4 days with continuous agitation [King, 2018b]. Equilibrium cesium loading (mmol total Cs/g dry IE-911) and distribution coefficients ($K_d = [(C_i/C_f)-1][V/M*F]$; where C_i and C_f correspond to initial and final cesium concentrations, V = liquid volume, M = IE-911 reference state mass, and F is the F-factor mass correction for IE-911 water content) were calculated based on analytical results and sample masses for simulant samples spiked to the three total cesium levels provided in Table 3-5. Cesium loading on IE-911 exhibited a linear relationship (R^2 = 99.9%) with respect to the final cesium concentration when plotted on a log-log scale.

Table 3.5. Cesium Loading Batch Contact Test Results (96-hour contact) with IE-911 and SRS Average Simulant.

Sample	CST (g)	Simulant (g)	Initial Cs^+ (M)	Final Cs^+ (M)	K_d mL/g*	% Cs^+ Removal	Cs^+ Loading "Q" (mmol/g)*
A/B	0.10800	12.44506	1.67E-05	7.24E-07	2423	95.7	1.75E-03
A/B replicate	0.10289	12.44647		8.13E-07	2253	95.1	1.83E-03
B	0.10058	12.44716	1.44E-04	7.18E-06	2247	95.0	1.61E-02
B replicate	0.10363	12.42421		6.91E-06	2264	95.2	1.57E-02
C	0.10368	12.41637	1.05E-03	4.36E-05	2626	95.8	1.15E-01
C replicate	0.10042	12.42028		4.36E-05	2712	95.8	1.18E-01

* dry CST mass basis and simulant density of 1.251 g/ml

Evaluation of the cesium loading kinetics was necessary to verify the timescale required to confirm that the cesium loading kinetics performance was comparable to previous results. Replicate batch contact slurries of simulant and IE-911 beads were prepared for each time period to be measured, and the mixtures were removed from the shaker at the specified time, immediately filtered, and analyzed.

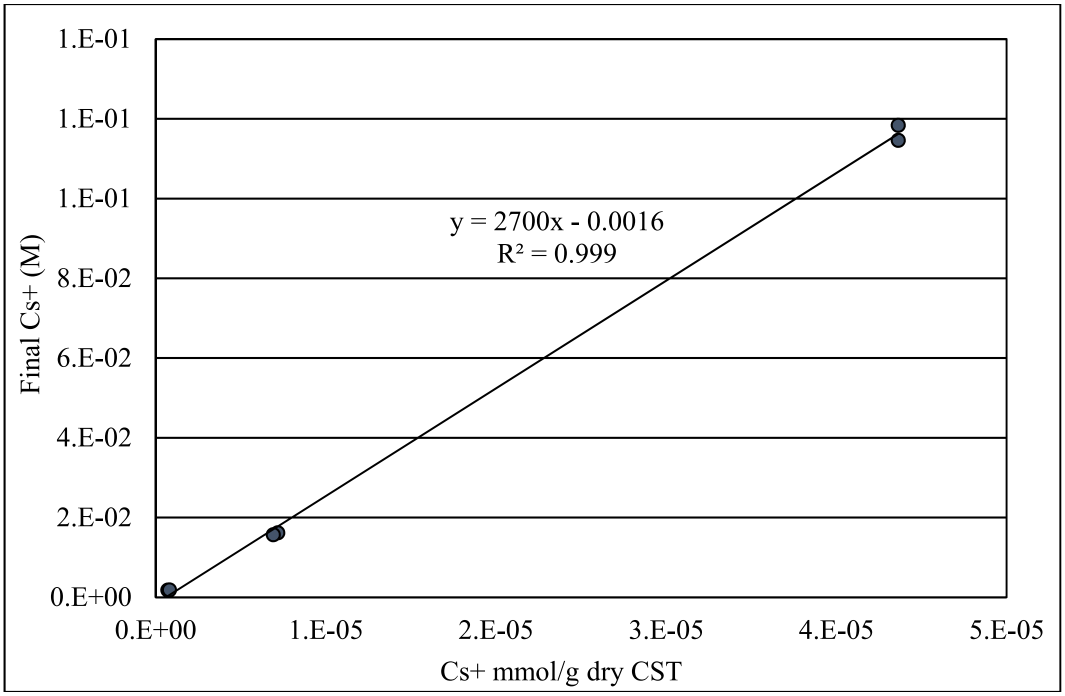

Figure 3-5. Cesium Equilibrium Loading (dry CST basis) from SRS Average Simulant on CST at 23°C.

Cesium loading kinetics results are provided in Figure 3-5 and Table 3-6. The 96-hour loading data points in the figure are from Table 3-5. Based on the results, cesium loading on the solid phase is essentially complete within 24 hours. However, the distribution coefficients, which are more responsive to the removal of the final amounts of cesium from the liquid phase, continue to change significantly between 24 and 96 hours. The average cesium K_d after 96 hours was 2296 mL/g (95% Cs^+ removal) versus the average 24-hour K_d of 1421 mL/g (92% Cs^+ removal).

Table 3.6. Cesium Loading Versus Time Test Results with IE-911 and SRS Average Simulant B at 23°C.

Sample	CST (g)	Simulant (g)	Initial Cs^+ (M)	Final Cs^+ (M)	K_d mL/g*	% Cs^+ Removal	Cs^+ Loading "Q" (mmol/g)*
1.5 hour	0.10008	12.51260	1.44E-04	4.88E-05	232	66.0	1.13E-02
1.5 hour replicate	0.10057	12.50274		4.66E-05	248	67.6	1.15E-02
5.5 hour	0.10073	12.50242		2.01E-05	729	86.0	1.46E-02
5.5 hour replicate	0.10005	12.50921		2.16E-05	675	85.0	1.46E-02
24 hour	0.10009	12.51170		1.10E-05	1442	92.4	1.58E-02
24 hour replicate	0.10011	12.50793		1.13E-05	1400	92.1	1.58E-02

* dry CST mass basis and simulant density of 1.251 g/ml

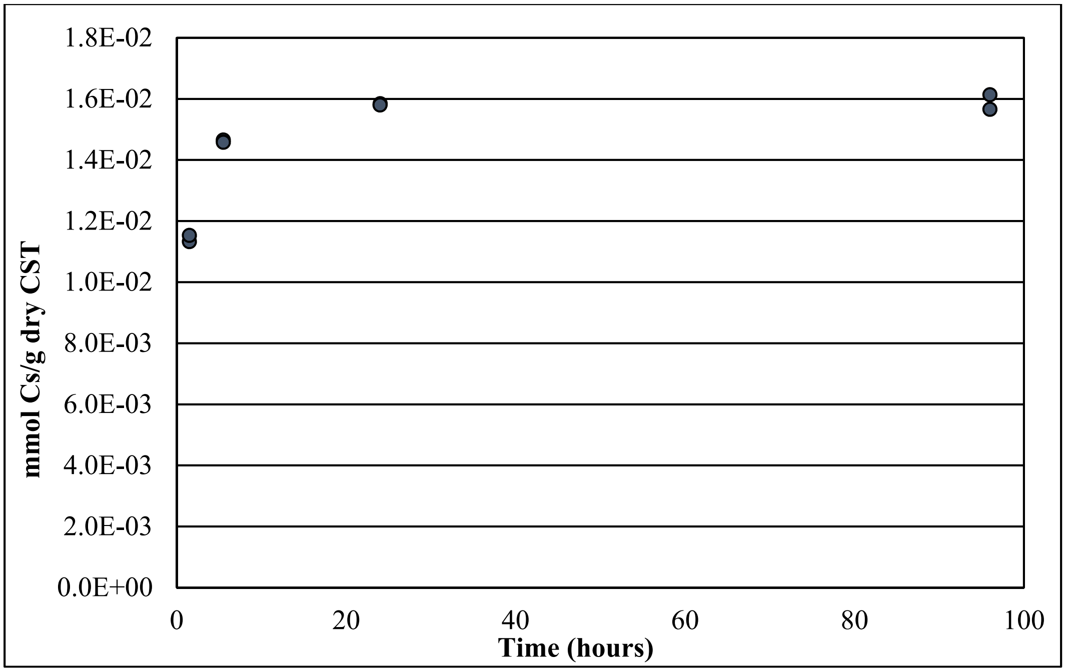

Figure 3-6. Cesium Loading (dry CST basis) Versus Time from SRS Average Simulant B on CST at 23 °C.

Strontium analysis results for all of the solutions (feed, batch contact equilibrium, and batch contact kinetics) are provided in Table 3-7. Detectable strontium was present in the simulant solutions as a reagent impurity at low levels, averaging 4.84E-7 M, and it was adsorbed from the solutions by the CST (final concentrations ≤1.5E-7 M). Although Sr, as the $SrOH^+$ ion, is a very strong competitor for ion exchange sites on CST, its initial concentration in this simulant is more than 30X lower than the lowest initial Cs concentration, so its effect would not measurably impact the Cs loading and it was not included in the modeling calculations.

Table 3.7. Strontium Analysis Results for Feed and Batch Contact Solutions.

Sample	Average Initial Sr^{2+} (M)	Final Sr^{2+} (M)
A/B	4.84E-07	<1.14E-07
A/B replicate		<1.14E-07
B		<1.14E-07
B replicate		<1.14E-07
C		<1.14E-07
C replicate		<1.14E-07
1.5 hour		1.34E-07
1.5 hour replicate		1.48E-07
5.5 hour		<1.14E-07
5.5 hour replicate		<1.14E-07
24 hour		<1.14E-07
24 hour replicate		<1.14E-07

3.3 Test Result Comparison with Modeling

A comparison of measured versus ZAM predicted isotherm behavior for this CST media (i.e., three separate batches are shown) is provided in Figure 3.7. These IE-911 loading test results for this 17-year old batch in Average SRS simulant (red diamonds) are compared to ZAM model predictions and to previously reported results [Beasley, et al., 2000; and King, et al., 2018b] in Figure 3-7. The loading levels observed for this CST batch are higher than the most recent testing but are virtually identical to historical samples. The results indicate essentially no correction for the IE-911 binder dilution factor, which is typically 0.68. In previous IE-911 performance modeling efforts [Hamm, et al., 2002], a dilution factor of 0.68 was selected as a conservatively low estimated value for the IE-911 engineered-form of CST when evaluating all available performance data. The historical results [Beasley, et al., 2000] were more consistent with the powdered form of CST (i.e., no binder), although IE-911 was utilized for all testing. This is partly because the ZAM model was based on the powdered form of CST (a.k.a. IE-910) and there was apparently no adjustment for moisture absorbed on the media. Since the original testing for the ZAM model development did not account for absorbed moisture, it is believed that the ZAM model would under-predict performance for moisture-corrected test data with IE-911, partially offsetting the calculated magnitude of the binder dilution factor. Regardless, based on the results it appears that this batch of IE-911 has very good performance compared to previous batches, indicating that the ~17 years of storage has had no measurable effect on the Cs absorption performance.

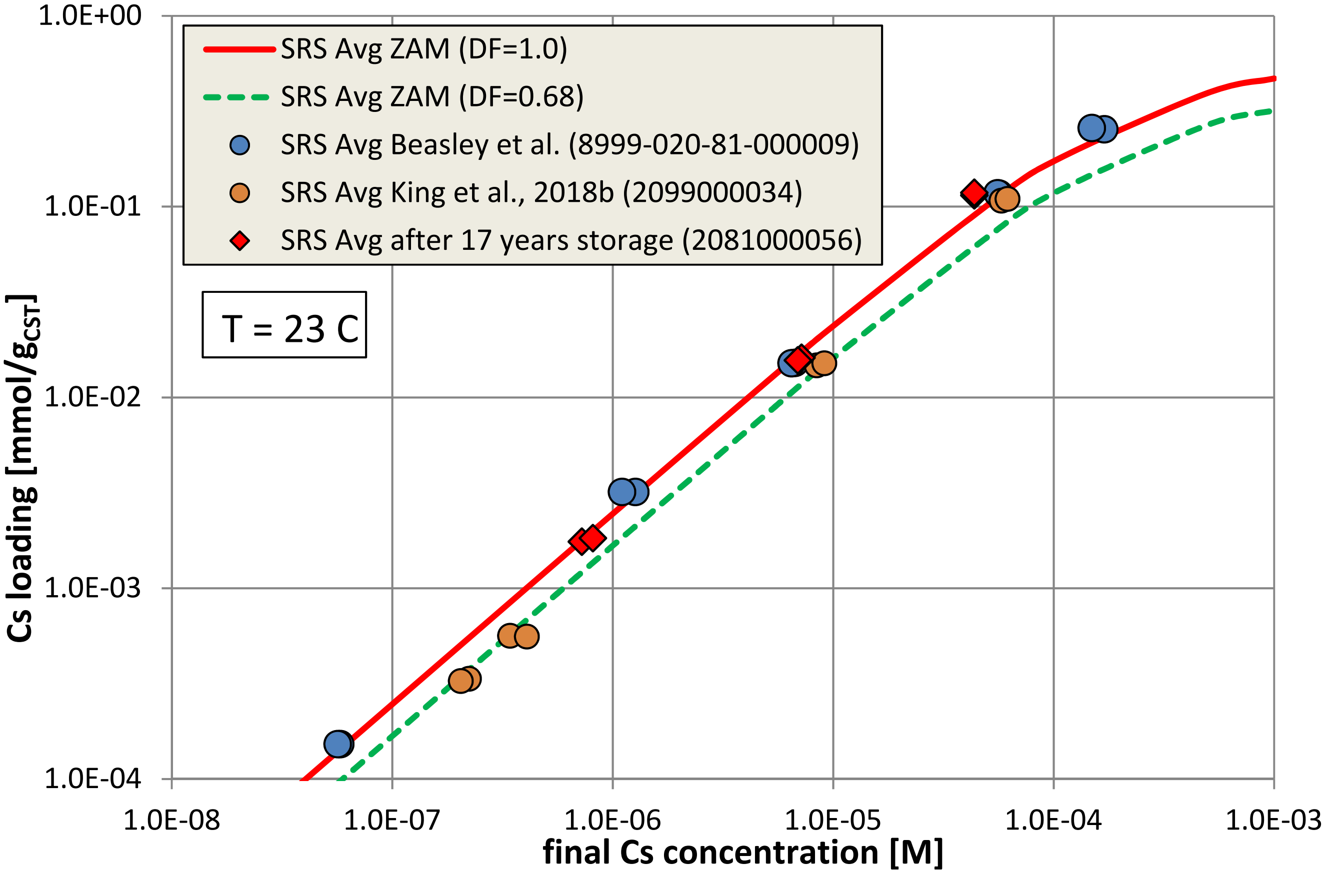

Figure 3-7. Comparison of Observed and Predicted (ZAM Model) Cesium Equilibrium Loading Isotherm with SRS Average Simulant and IE-911 at 23 °C (CST Batch indicated in parenthesis).

Figure 3-8 shows the measured cesium equilibrium loading and kinetic data versus the calculated equilibrium isotherm data. The red lines shown in Figures 3-7 and 3-8 are identical, but Figure 3-8 is focused only on the range of data created within this report. This figure also illustrates the approach to equilibrium during the kinetics testing, with the blue circles advancing in time from right to left along an operating line (i.e., essentially a simple mass balance relationship).

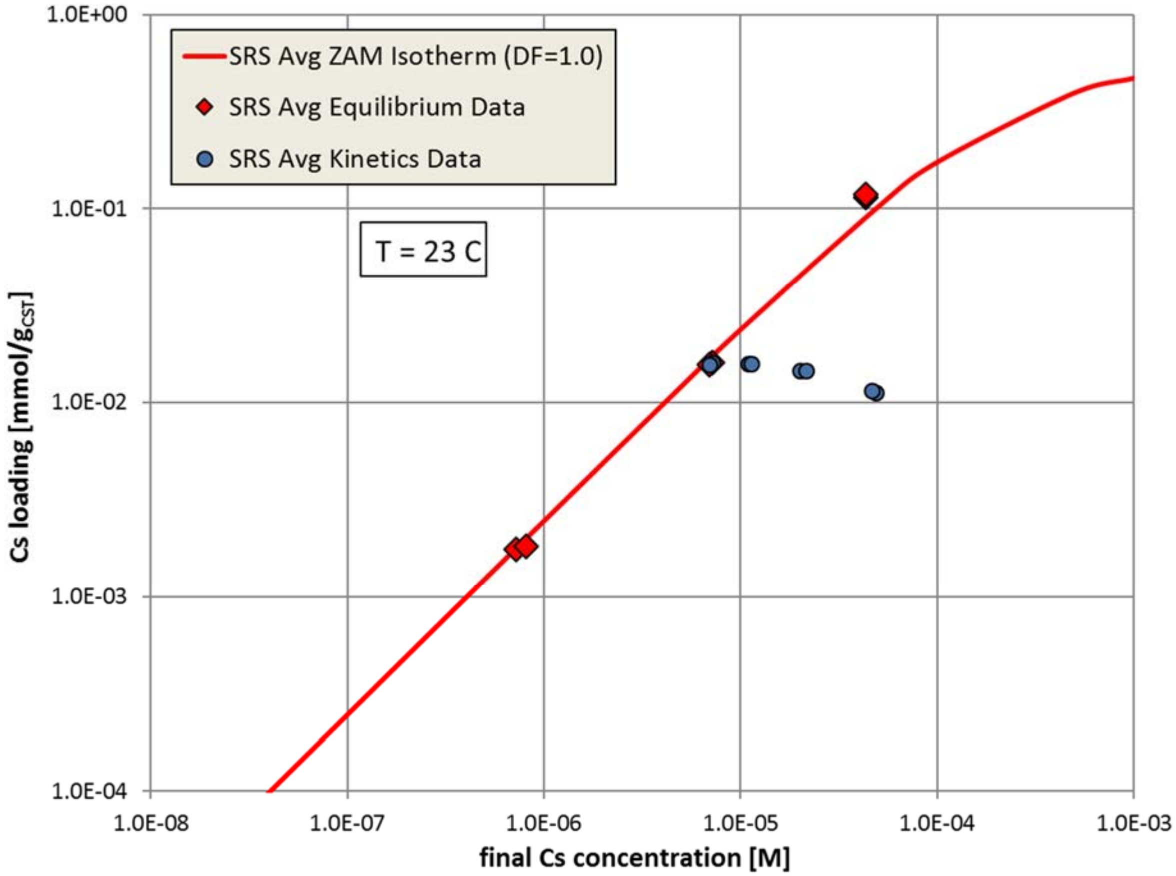

Figure 3-8. Comparison of Kinetics and Equilibrium Data versus Predicted (ZAM Model) Cesium Equilibrium Loading Isotherm with SRS Average Simulant and IE-911 at 23 °C.

Similarly, Figure 3-9 shows the same data as Figure 3-8, but focused to a narrower range of compositions and on a log-linear scale to better highlight the approach to equilibrium. The dashed line shows the change in concentration as the Cs absorbs onto the solids during the kinetics (i.e., the operating line), and the arrow indicates the progression of time. This information provides insight into the Cs diffusion rate within the beads, since the IE-911 is pore diffusion limited. From that data, we can derive the "tortuosity factor" or "τ" (tau), which is a measure of the Cs^+ diffusion within the pores versus free diffusion in the liquid [Hamm, et.al., 2002]. Although the tortuosity factor can also be determined from dynamic column tests, this method requires less simulant and considerably less experimental effort. This method also is more focused on the kinetic aspects allowing the analysis effort to better uniquely identify this tortuosity factor.

The data plotted in Figure 3-9 were all taken from separate batch contact tests where varying contact times were tested (i.e., 1.5, 5.5, 24, and 96 hours). All of the blue circle data started with the same initial Cs^+ liquid-phase concentration, shown as the green square in the bottom right corner. If the phase ratios for all of these batch contact tests were the identical value, then all of this data would have fallen somewhere along one unique operating line. Due to slight variations in phase ratios (i.e., dry mass of material versus simulant volume) each test had its own unique operating line. However, the variation in most of the tests were sufficiently close to view this data as one aggregate kinetics test operating along a single operating line as shown.

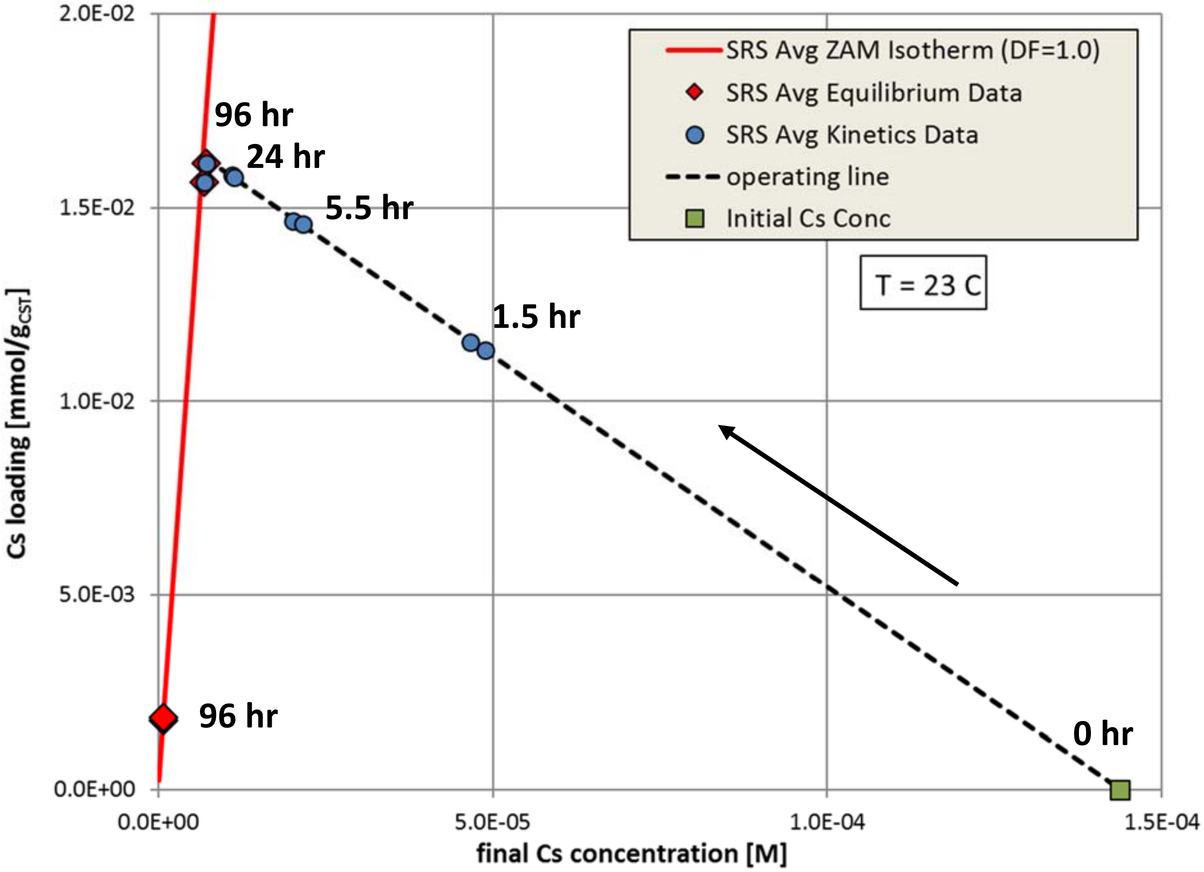

Figure 3-9. **Comparison of Kinetics and Equilibrium Data versus Predicted (ZAM Model) Cesium Equilibrium Loading Isotherm with SRS Average Simulant and IE-911 at 23°C.**

Figure 3-10 shows the results of the kinetics test along with several VERSE runs at varying tortuosity factor values. The use of VERSE to perform kinetic test assessments was discussed in Hamm et al. (2002). In Hamm et al. (2002) a detailed discussion was provided as to how VERSE can be employed to back out a tortuosity factor when a series of batch contact tests, such as the ones presented above, are available. Although VERSE is designed to compute sorbate loading in a flowing system, it was used in this case to estimate the tortuosity factor by mimicking a static system using a column configuration but with minimal liquid flow but with a very high fixed value for the film diffusion coefficient (i.e., see Chapter 7 of Hamm et al. [2002] for the details).

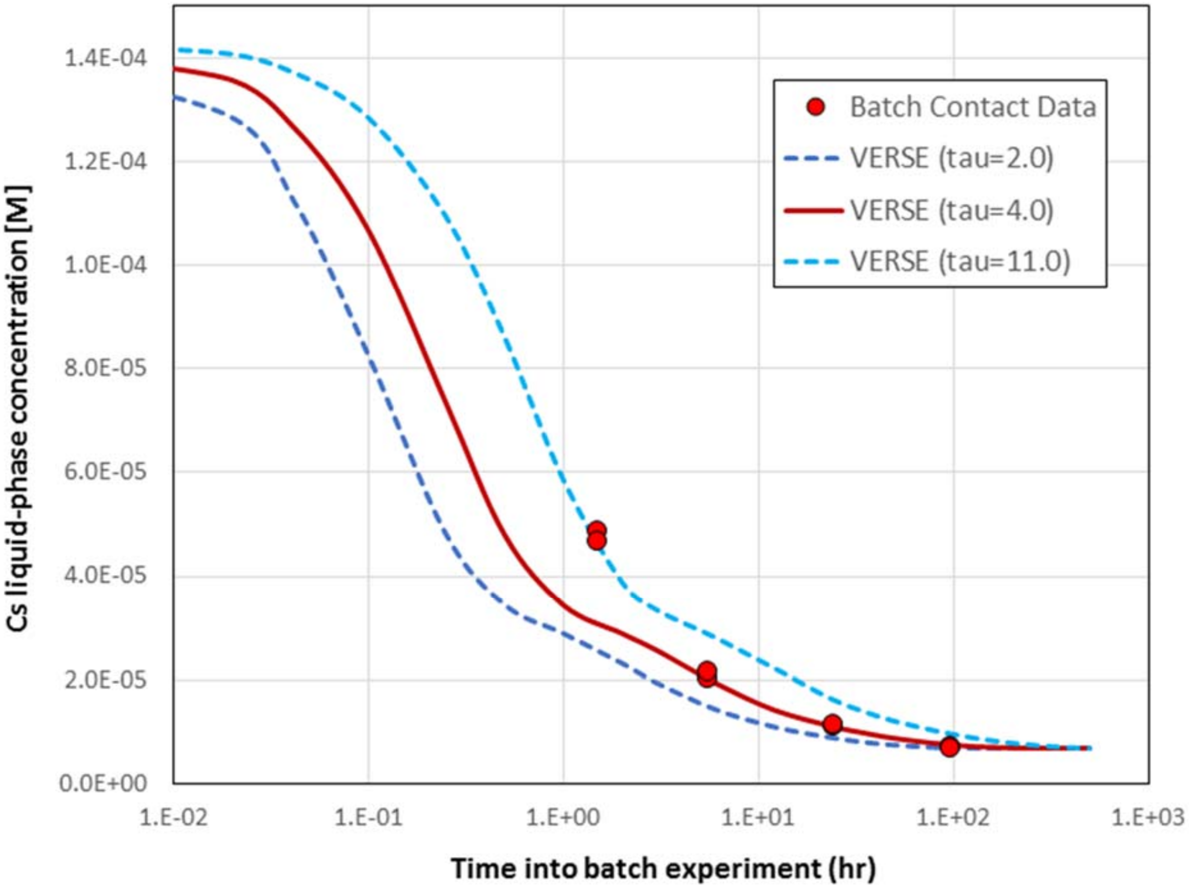

Figure 3-10. Estimate of Tortuosity Factor (tau).

The results of the estimation of tortuosity factor from this test indicates that the shortest duration data, 1.5 hours, indicates that τ = 11, but for all other data τ = 4. A τ of 4 is comparable to that obtained from several column tests [Hamm, et.al., 2002]. The τ of 11 at short duration is tentatively attributed to the effect of adding the dry IE-911 to the liquid at the beginning of the experiment. Initially, the pores of the IE-911 are filled mostly with air, and the wetting of the pores with simulant likely takes some time, which would increase the apparent τ value.

VERSE input and output files for the tortuosity factor of 4.0 are provided in Appendix C.

4.0 Conclusions

Based on the test results and associated ZAM modeling the following conclusions can be made about the batch of IE-911 that had been stored for ~17 years:

- The physical property measurements were consistent with historical results.
- The Cs absorption isotherms were very good compared to historical results.
- The kinetics of Cs absorption were consistent with historical results.

Additionally, it was found that the various methods of measuring the particle size of the IE-911 agree reasonably well. The sieve method yields a slightly smaller size than the Microtrac laser method but are within one standard deviation. It was found that it is critical to obtain representative sub-samples for the Microtrac method, and multiple samples should be analyzed in order to ensure an accurate measurement. It is advisable to use the results from the sieve analysis for computer modeling because it is the small dimension that will dominate the kinetics and because the sieving is done at larger scale with a more representative sample than the Microtrac. However, both are important methods to perform on future batches so that comparisons across laboratories can be made and to ensure subsampling of large containers is representative of the entire batch.

Overall then, the results indicate that the ~17 years of storage had no impact on the properties or performance of IE-911, both from a static and a kinetic perspective, and it is acceptable for use.

5.0 Recommendations

Note: these recommendations are limited to verifying acceptability, consistency, and stability of IE-911, and do not represent overall program recommendations.

A more standardized and documented batch contact equilibrium test procedure and physical property measurement protocol is needed to ensure consistency in acceptance testing.

Resolution is needed regarding the apparent inconsistency in “dilution factor” from the CST binder; i.e., variability in adjusting the ZAM modeling to the test results. This would involve ensuring a consistent preconditioning procedure, drying procedure, F-factor measurement, and test procedure (mentioned above).

There is currently no requirement or plan to check the kinetics of a batch of CST material, but this is a vitally important parameter since it directly ties to the ability to achieve a target Decontamination Factor during column operations. It would be useful to establish a routine protocol to check the kinetics of the IE-911 using a series of batch contact approach tests so that the kinetics performance can be evaluated without performing column tests. This may include pre-wetting the CST media so that pore diffusivity is not impacted by using dry material.

Consistent preparation and use of simulants is recommended and should include the analysis suite. Measurement of all competing species in tank waste samples and those present as impurities in the simulants used for any testing, particularly strontium.

Resolution is needed regarding the higher than expected distribution coefficients at high Cs concentrations which has been observed several times. This may be due to a difference in drying procedures or testing methods used throughout the different laboratories and over the years of testing that leads to a difference in the apparent total capacity of IE-911.

6.0 References

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Hamm, L.L., Hang, T., McCabe, D.J., King, W.D., "Preliminary Ion Exchange Modeling for Removal of Cesium from Hanford Waste Using Hydrous Crystalline Silicotitanate Material", WSRC- TR-2001-00400, SRT-RPP-2001-00134, Rev. 0, July 2002.

King, W.D., "Task Technical and Quality Assurance Plan for Batch Contact Sorption and Desorption Testing to Support Tank Closure Cesium Removal Operations", SRNL-RP-2017-00536, Rev. 1, January 2018a.

King, W. D., Hamm, L. L., Coleman, C. J., Fondeur, F. F., Reboul, S. H., Crystalline Silicotitanate (CST) Ion Exchange Media Performance Evaluations in SRS Average Supernate Simulant and Tank 10H Waste Solution to Support TCCR, SRNL-STI-2018-00277, Revision 0. June 2018b

Walker, D.D., "Preparation of Simulated Waste Solutions", WSRC-TR-99-001 16, Rev. 0, April 1999.

Wilmarth, W. R., J. T. Mills, V. H. Dukes, and F. F. Fondeur, "Effect of Sodium Hydroxide Pretreatment of UOP IONSIV IE-911 Crystalline Silicotitanate Sorbent" WSRC-TR-2000-00167, Rev. 0, 2000

Wilmarth, W.R., Walker, D.D., Fondeur, F.F., Fink, S.D., Nyman, M. Krumhansel, J., Mills J.T., Dukes V.H., Croy, B.H., Examination of Pre-Production Samples of UOP Ionsiv® IE-910 and IE-911, WSRC-MS-2001-00733, September 2001

Zheng, Z., R. G. Anthony, and J. E. Miller, 1997. "Modeling Multicomponent Ion Exchange Equilibrium Utilizing Hydrous Crystalline Silicotitanates by a Multiple Interactive Ion Exchange Site Model," Ind. Eng. Chem. Res., Vol. 36, No. 6, pp. 2427-2434.

7.0 Appendices

Appendix A. Microtrac Particle Size Analysis Results

Five subsamples from the bottle of IE-911 retrieved from the drum were analyzed by suspending the samples in water and the particle size was determined by Microtrac S3500. Results are shown in Table A-1. The Standard Deviation shown for each sample is that calculated by the Microtrac and is a representation of the width of the particle distribution, not an indication of the error of the mean. The average of the five Mean Area measurements is 433 µm, with a standard deviation of 28.

Table A.1 Particle Size Analysis Results from Microtrac S3500

Data item	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**
Mean Volume (diameter) (µm)	457.8	439	445.4	506.1	436.5
Mean Number (diameter) (µm)	395.1	376.7	382.7	438.1	373.3
Mean (diameter) Area (µm)	432.8	416	421.7	480.2	412.6
Calculated (exterior) Surface area (m^2/mL)	1.39E-2	1.44E-2	1.42E-2	1.25E-2	1.45E-2
Standard deviation	93.92	95.85	95.02	108.7	94.71

Appendix B. ZAM Summary

The following are the ZAM input and output files for a subset of the batch contact cases considered. The replicate test cases are not being shown here. All ZAM runs made during this effort have been saved and archived onto SRNL servers that can be retrieved at a later date, if requested.

The isotherm for the SRS Avg simulant at 23 ^{o}C was created by running a series of ZAM numerical batch contact cases and then fitting a binary Langmuir isotherm to the results:

$$Q_{Cs} = \frac{\eta_{df}\overline{C}_T c_{Cs}}{c_{Cs} + \beta} \quad [\text{mmole/g}_{\text{dry-CST}}]$$

For this application (i.e., assessment of kinetics data) the fitting process focused in on a beta factor that was weighted in favor of the isotherm closest to the test sample B provided in Table 3-5. The computed beta factor employed, and isotherms plotted in the main body of this report, has the value:

$$\beta = 2.350\text{x}10^{-4} \quad [\text{M}]$$

The presence of Sr within the simulant was not considered in these analyses.

The following sections contain the input and output files for the ZAM runs made for the three main batch contact equilibrium (i.e., 96 hr) tests listed in Table 3-5.

Input: 23°C – (Sample A/B of Table 3-5)

```
1, 296.15                                                   Activity Coeff. Model, Temperature
Storage Impact Performance 23.0C                                           Title
7, 10                                                               Number of Cations & Anions
1228                                                                Density(kg/m3) OLI based
 3, 6,  1,  5,  4, 40, 13                                                  Names of Cations
13, 9, 27, 15, 19,  2, 20, 28, 25  1                        Names of Anions (Add COOH-, C2O4--)
96.0107                                                                    C2O4-- MW
5.6    1.6666E-05  1.0E-14  0.0  0.015  0.0  0.0                    Concentrations of Cations
1.91   2.14  0.52  0.15  0.16 0.037017  0.01 0.31  0.008  0.032        Concentrations of Anions
0.0099495, 0.09044352                                                      Liquid (L), Solid (g)
0                                                           Initial Solid Form (Na+ (0); H- (1))
.9                                                                         Calculation Adjustment
```

Output: 23°C – (Sample A/B of Table 3-5)

```
   Solution:  Storage Impact Performance 23.0C
  **********************INPUT***********************

    Density=  .1228E+04 kg/m3

               Molecular Wt.    Valance    Molarity(mol/L)
  Na+.....        22.9898         1.        .5600E+01
  Cs+.....       132.9054         1.        .1667E-04
  H+......         1.0079         1.        .1000E-13
  Rb+.....        85.4678         1.        .0000E+00
  K+......        39.0983         1.        .1500E-01
  SrOH+...       105.0000         1.        .0000E+00
```

```
  Sr++....         87.6200          2.       .0000E+00
  OH-.....         17.0073         -1.       .1910E+01
  NO3-....         62.0049         -1.       .2140E+01
  NO2-....         46.0000         -1.       .5200E+00
  SO4--...         96.0636         -2.       .1500E+00
  CO3--...         60.0092         -2.       .1600E+00
  Cl-.....         35.4527         -1.       .3702E-01
  PO4---..         94.9712         -3.       .1000E-01
  Al(OH)4-         95.0000         -1.       .3100E+00
  Other--.         96.0107         -2.       .8000E-02
  F-......         18.9984         -1.       .3200E-01

  Liquid(L)= .9950E-02   Solid(g)= .9044E-01

   Material: Na Form



  **********************OUTPUT***********************

   Ionic Strength=           7.239483796648766 mol/kg

          Q (mmol/gCST)    C (mmol/L)    Kd (ml/gCST)
  Cs        .1755E-02      .7085E-03      .2478E+04
  Rb        .0000E+00      .0000E+00      .0000E+00
  Sr        .0000E+00      .0000E+00      .0000E+00
  K         .9994E-01      .1409E+02      .7093E+01
```

Input: 23°C – (Sample B of Table 3-5)

```
1, 296.15                                                   Activity Coeff. Model, Temperature
Storage Impact Performance 23.0C                                           Title
7, 10                                                              Number of Cations & Anions
1228                                                               Density(kg/m3) OLI based
 3, 6,  1,  5,  4, 40, 13                                                  Names of Cations
13, 9, 27, 15, 19,  2, 20, 28, 25  1                        Names of Anions (Add COOH-, C2O4--)
96.0107                                                                    C2O4-- MW
5.6    1.4371E-04     1.0E-14 0.0     0.015  0.0     0.0           Concentrations of Cations
1.91   2.14    0.52  0.15  0.16  0.037144  0.01  0.31  0.008  0.032 Concentrations of Anions
0.0099512, 0.084229715                                                     Liquid (L), Solid (g)
0                                                           Initial Solid Form (Na+ (0); H- (1))
.9                                                                         Calculation Adjustment
```

Output: 23°C – (Sample B of Table 3-5)

```
   Solution:  Storage Impact Performance 23.0C
  **********************INPUT***********************

    Density=  .1228E+04 kg/m3

              Molecular Wt.    Valance    Molarity(mol/L)
  Na+.....         22.9898          1.       .5600E+01
  Cs+.....        132.9054          1.       .1437E-03
  H+......          1.0079          1.       .1000E-13
  Rb+.....         85.4678          1.       .0000E+00
  K+......         39.0983          1.       .1500E-01
  SrOH+...        105.0000          1.       .0000E+00
  Sr++....         87.6200          2.       .0000E+00
  OH-.....         17.0073         -1.       .1910E+01
  NO3-....         62.0049         -1.       .2140E+01
  NO2-....         46.0000         -1.       .5200E+00
  SO4--...         96.0636         -2.       .1500E+00
  CO3--...         60.0092         -2.       .1600E+00
  Cl-.....         35.4527         -1.       .3714E-01
  PO4---..         94.9712         -3.       .1000E-01
```

```
  Al(OH)4-         95.0000         -1.       .3100E+00
  Other--.         96.0107         -2.       .8000E-02
  F-......         18.9984         -1.       .3200E-01

  Liquid(L)= .9951E-02   Solid(g)= .8423E-01

   Material: Na Form



  **********************OUTPUT***********************

   Ionic Strength=           7.239878629424939 mol/kg

         Q (mmol/gCST)    C (mmol/L)    Kd (ml/gCST)
  Cs        .1619E-01      .6704E-02      .2415E+04
  Rb        .0000E+00      .0000E+00      .0000E+00
  Sr        .0000E+00      .0000E+00      .0000E+00
  K         .9904E-01      .1416E+02      .6994E+01
```

Input: 23°C – (Sample C of Table 3-5)

```
1, 296.15                                                          Activity Coeff. Model,
Temperature
Storage Impact Performance 23.0C                                           Title
7, 10                                                              Number of Cations & Anions
1228                                                               Density(kg/m3) OLI based
 3, 6,  1,  5,  4, 40, 13                                                  Names of Cations
13, 9, 27, 15, 19,  2, 20, 28, 25  1                        Names of Anions (Add COOH-, C2O4--)
96.0107                                                                    C2O4-- MW
5.6    1.0459E-03     1.0E-14 0.0     0.015  0.0     0.0           Concentrations of Cations
1.91   2.14   0.52  0.15  0.16  0.038046  0.01  0.31  0.008  0.032 Concentrations of Anions
0.0099266, 0.086825779                                                     Liquid (L), Solid (g)
0                                                           Initial Solid Form (Na+ (0); H- (1))
.9                                                                         Calculation Adjustment
```

Output: 23°C – (Sample C of Table 3-5)

```
   Solution:  Storage Impact Performance 23.0C
  **********************INPUT***********************

    Density=  .1228E+04 kg/m3

                 Molecular Wt.    Valance    Molarity(mol/L)
  Na+.....         22.9898         1.       .5600E+01
  Cs+.....        132.9054         1.       .1046E-02
  H+......          1.0079         1.       .1000E-13
  Rb+.....         85.4678         1.       .0000E+00
  K+......         39.0983         1.       .1500E-01
  SrOH+...        105.0000         1.       .0000E+00
  Sr++....         87.6200         2.       .0000E+00
  OH-.....         17.0073        -1.       .1910E+01
  NO3-....         62.0049        -1.       .2140E+01
  NO2-....         46.0000        -1.       .5200E+00
  SO4--...         96.0636        -2.       .1500E+00
  CO3--...         60.0092        -2.       .1600E+00
  Cl-.....         35.4527        -1.       .3805E-01
  PO4---..         94.9712        -3.       .1000E-01
  Al(OH)4-         95.0000        -1.       .3100E+00
  Other--.         96.0107        -2.       .8000E-02
  F-......         18.9984        -1.       .3200E-01

  Liquid(L)= .9927E-02   Solid(g)= .8683E-01

   Material: Na Form
```

```
**********************OUTPUT***********************

 Ionic Strength=           7.241373802069601 mol/kg

        Q (mmol/gCST)    C (mmol/L)    Kd (ml/gCST)
Cs        .1131E+00      .5660E-01      .1998E+04
Rb        .0000E+00      .0000E+00      .0000E+00
Sr        .0000E+00      .0000E+00      .0000E+00
K         .9030E-01      .1421E+02      .6354E+01
```

Appendix C. VERSE Analyses

The following are the VERSE input and output files for the case where a tortuosity factor of 4.0 was analyzed. All of the VERSE runs made in the course of this effort have been saved and archived onto SRNL servers that can be retrieved at a later date, if requested.

Note that for this kinetics simulation VERSE also requires an initialization input file that is also included below.

Input: 23°C – (tortuosity factor of 4.0; main input file)

```
Simulation of SRNL King (2018) Cs-CST batch kinetic test (SRS avg at 23C)
1 component (Cs) isotherm (1.4e-4 M initial Cs)
1, 1, 1, 6                       ncomp, nelem, ncol-bed, ncol-part
FUUNA                            isotherm,axial-disp,film-coef,surf-diff,BC-col  FCUNA
NNNYN                            input-only,perfusable,feed-equil,datafile.yio
MM                               comp-conc units
1.970206, 2.54, 0.000000001, 0.0 Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
204.0, 0.995781, 0.24,  0.0      part-rad(um), bed-void, part-void, sorb-cap()
  0.0                            initial concentrations (M)
S                                COMMAND - conc step change
1, 0.0, 1.43857d-4, 1, 0.0       spec id, time(min), conc(M), freq, dt(min)
V                                COMMAND - viscosity/density change
0.0255, 1.251                    fluid viscosity(posie), density(g/cm^3) [OLI=1.228, King=1.251]
h                                COMMAND - effluent history dump
2, 1.0, 1.0, 0.25, 0.1           unit op#, ptscale(1-4) filtering
D
-1, 0.0000016667, 1, 0.0
D
-1,  1.0, 1, 0.0
D
-1,  2.5, 1, 0.0
D
-1,    6, 1, 0.0
D
-1,   15, 1, 0.0
D
-1,   30, 1, 0.0
D
-1,   60, 1, 0.0
D
-1,  120, 1, 0.0
D
-1,  180, 1, 0.0
D
-1,  360, 1, 0.0
D
-1,  720, 1, 0.0
D
-1, 1440, 1, 0.0
D
-1, 2160, 1, 0.0
D
-1, 2880, 1, 0.0
D
-1, 4320, 1, 0.0
D
-1, 4800, 1, 0.0
D
-1, 6000, 1, 0.0
D
-1, 8000, 1, 0.0
D
```

```
-1, 10000, 1, 0.0
D
-1, 12000, 1, 0.0
D
-1, 14000, 1, 0.0
D
-1, 16000, 1, 0.0
D
-1, 18000, 1, 0.0
D
-1, 20000, 1, 0.0
D
-1, 22000, 1, 0.0
D
-1, 24000, 1, 0.0
D
-1, 26000, 1, 0.0
D
-1, 28000, 1, 0.0
D
-1, 30000, 1, 0.0
-                                end of commands
30000.0, 1.0                      end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                   abs-tol, rel-tol
-                                non-negative conc constraint
1.0d0                            size exclusion factor
5.0                              bed dispersion coefficient (cm^2/min)
1.401d-4                         part-pore diffusivities (cm^2/min) tortuosity factor=4.0
5.604d-4                         Brownian diffusivities (cm^2/min)  OLI based
10.00                            specified film coefficient (cm/min)
4.8936d-3                        Freundlich/Langmuir Hybrid a    (moles/L B.V.) rhob=0.0084372
1.0                              Freundlich/Langmuir Hybrid b    (1/M)          ccap=0.580
1.0                              Freundlich/Langmuir Hybrid Ma   (-)            DF  =1.0
1.0                              Freundlich/Langmuir Hybrid Mb   (-)
2.3500d-4                        Freundlich/Langmuir Hybrid beta (-)
-----------------------------------------------------------------------------
2.802d-4                         part-pore diffusivities (cm^2/min) tortuosity factor=2.0
1.401d-4                         part-pore diffusivities (cm^2/min) tortuosity factor=4.0
9.340d-5                         part-pore diffusivities (cm^2/min) tortuosity factor=6.0
5.604d-5                         part-pore diffusivities (cm^2/min) tortuosity factor=10.0
5.095d-5                         part-pore diffusivities (cm^2/min) tortuosity factor=11.0
```

Input: 23°C – (tortuosity factor of 4.0; initialization input file)

```
 .00000000D+01, -.55671305D-13
 .00000000D+01, -.55676396D-13
 .00000000D+01, -.55684078D-13
 .00000000D+01, -.55695127D-13
 .00000000D+01, -.55699650D-13
 .00000000D+01, -.55700609D-13
 .00000000D+01, -.55700936D-13
 1.4385700D-04, -.55699991D-13
 .00000000D+01, -.55668219D-13
 .00000000D+01, -.55671145D-13
 .00000000D+01, -.55683769D-13
 .00000000D+01, -.55695324D-13
 .00000000D+01, -.55701254D-13
 .00000000D+01, -.55702074D-13
 .00000000D+01, -.55702728D-13
 1.4385700D-04, -.55702260D-13
 .00000000D+01, -.55667356D-13
 .00000000D+01, -.55677368D-13
 .00000000D+01, -.55689670D-13
 .00000000D+01, -.55698912D-13
 .00000000D+01, -.55705473D-13
 .00000000D+01, -.55706771D-13
 .00000000D-05, -.55702625D-13
```

```
 1.4385700D-04, -.55703848D-13
 1.4385700D-04,  .00000000D+00
 1.4385700D-04, -.55703848D-13
```

Output: 23°C – (tortuosity factor of 4.0; main output file)

```
===============================================================================
 VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
 ===============================================================================
 Input file: case
 Simulation of SRNL King (2018) Cs-CST batch kinetic test (SRS avg at 23C)
 1 component (Cs) isotherm (1.4e-4 M initial Cs)
 Begin Run:  10:34:04 on 10-25-2018   running under Windows 95/8
 Finite elements    - axial:  1  particle: 1
 Collocation points - axial:  1  particle: 6 => Number of eqns:    26
 Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
 Use Profile File? Y   Generate Profile File? N
 Axial dispersion correlation:   User-specified
 Film mass transfer correlation: User-specified
 ===============================================================================
 SYSTEM PARAMETERS (at initial conditions):

 t(stop)        =  30000.00000 min         dtheta max     =      1.00000 BV
 abs. tol.      =       .10000E-06         rel. tol.      =       .10000E-03
 Total Length   =      1.97021 cm          D              =      2.54000 cm
 Tot. Capacity  =       .00000 eq/L solid  Col. Vol.      =      9.98318 mL
 F              =       .00000 mL/min      Uo (linear)    =       .00000 cm/min
 R              =    204.00000 microns     L/R            =     96.57873
 Bed Void frac. =       .99578             Pcl. Porosity  =       .24000
 Spec. Area     =       .62044 1/cm        Time/BV        =************* min
 Vol CSTRs      =       .00000 mL

 Component no.  =      1
 Ke  [-]        =  .10000E+01
 Eb  [cm2/min]  =  .50000E+01
 Dp  [cm2/min]  =  .14010E-03
 Doo [cm2/min]  =  .56040E-03
 kf  [cm/min]   =  .10000E+02
 Ds  [cm2/min]  =  .00000E+00

 Dimensionless Groups:
 Re             =  .65837E-11
 Sc(i)          =  .21824E+04
 Peb(i)         =  .78095E-10
 Bi(i)          =  .60671E+04
 Nf(i)          =  .61940E+11
 Np(i)          =  .80320E+09
 Pep(i)         =  .12024E-06

 Isotherm       =  Freundlich/Langmuir Hybrid
 Iso. Const. 1  =  .48936E-02
 Iso. Const. 2  =  .10000E+01
 Iso. Const. 3  =  .10000E+01
 Iso. Const. 4  =  .10000E+01
 Iso. Const. 5  =  .23500E-03
 Init. Conc.    =  .00000E+00
 Conc. at eqb.  =  .00000E+00
 Conc. units           M
 ===============================================================================
 COMMAND LIST:
   1: Step conc. of component 1 at .0000     min to .1439E-03 M
      Execute   1 times, every .0000     mins.
   2: User set viscosity to .2550E-01 poise and density to 1.251     g/cm3
   3: Monitor conc. history at stream  2.  Filename = case.h01
      Output density adjustments:
      1.0    *default abs conc delta,      1.0    *default rel conc delta,
      .25    *default force w/ conc delta, .10    *default force w/o conc delta
   4: Dump full profile file at  .1667E-05 min
```

```
      Execute   1 times, every .0000     mins.
   5: Dump full profile file at  1.000     min
      Execute   1 times, every .0000     mins.
   6: Dump full profile file at  2.500     min
      Execute   1 times, every .0000     mins.
   7: Dump full profile file at  6.000     min
      Execute   1 times, every .0000     mins.
   8: Dump full profile file at  15.00     min
      Execute   1 times, every .0000     mins.
   9: Dump full profile file at  30.00     min
      Execute   1 times, every .0000     mins.
  10: Dump full profile file at  60.00     min
      Execute   1 times, every .0000     mins.
  11: Dump full profile file at  120.0     min
      Execute   1 times, every .0000     mins.
  12: Dump full profile file at  180.0     min
      Execute   1 times, every .0000     mins.
  13: Dump full profile file at  360.0     min
      Execute   1 times, every .0000     mins.
  14: Dump full profile file at  720.0     min
      Execute   1 times, every .0000     mins.
  15: Dump full profile file at  1440.     min
      Execute   1 times, every .0000     mins.
  16: Dump full profile file at  2160.     min
      Execute   1 times, every .0000     mins.
  17: Dump full profile file at  2880.     min
      Execute   1 times, every .0000     mins.
  18: Dump full profile file at  4320.     min
      Execute   1 times, every .0000     mins.
  19: Dump full profile file at  4800.     min
      Execute   1 times, every .0000     mins.
  20: Dump full profile file at  6000.     min
      Execute   1 times, every .0000     mins.
  21: Dump full profile file at  8000.     min
      Execute   1 times, every .0000     mins.
  22: Dump full profile file at  .1000E+05 min
      Execute   1 times, every .0000     mins.
  23: Dump full profile file at  .1200E+05 min
      Execute   1 times, every .0000     mins.
  24: Dump full profile file at  .1400E+05 min
      Execute   1 times, every .0000     mins.
  25: Dump full profile file at  .1600E+05 min
      Execute   1 times, every .0000     mins.
  26: Dump full profile file at  .1800E+05 min
      Execute   1 times, every .0000     mins.
  27: Dump full profile file at  .2000E+05 min
      Execute   1 times, every .0000     mins.
  28: Dump full profile file at  .2200E+05 min
      Execute   1 times, every .0000     mins.
  29: Dump full profile file at  .2400E+05 min
      Execute   1 times, every .0000     mins.
  30: Dump full profile file at  .2600E+05 min
      Execute   1 times, every .0000     mins.
  31: Dump full profile file at  .2800E+05 min
      Execute   1 times, every .0000     mins.
  32: Dump full profile file at  .3000E+05 min
      Execute   1 times, every .0000     mins.
 ==============================================================================
 VERSE-LC finished in   329 steps.  Average step size 91.19     minutes
 End run:  10:34:04 on 10-25-2018
 Integrated Areas in History Files:
 case.h01                  .228428
```

Output: 23°C – (tortuosity factor of 4.0; history file)

```
History at exit of unit op          2
 .16667E-05,  .14386E-03
 1.0000    ,  .13663E-03
```

```
2.5000    ,  .12666E-03
6.0000    ,  .10696E-03
15.000    ,  .73552E-04
30.000    ,  .48031E-04
60.000    ,  .34413E-04
120.00    ,  .28857E-04
180.00    ,  .25654E-04
360.00    ,  .19383E-04
720.00    ,  .14185E-04
1440.0    ,  .10968E-04
2160.0    ,  .96201E-05
2880.0    ,  .87844E-05
4320.0    ,  .79274E-05
4800.0    ,  .77322E-05
6000.0    ,  .74046E-05
8000.0    ,  .70707E-05
10000.    ,  .69209E-05
12000.    ,  .68331E-05
14000.    ,  .67924E-05
16000.    ,  .67685E-05
18000.    ,  .67574E-05
20000.    ,  .67509E-05
22000.    ,  .67479E-05
24000.    ,  .67461E-05
26000.    ,  .67453E-05
28000.    ,  .67448E-05
30000.    ,  .67446E-05
```

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