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Evaluating Residence Time for SuperLig ® 644 Columns with Simulated LAW Envelope B Solution (U)

SAVANNAH RIVER TECHNOLOGY CENTER

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Abstract

The Hanford River Protection Project Waste Treatment Plant (RPP-WTP) will be performing cesium and technetium ion exchange using SuperLig® 644 and 639, respectively. Earlier work with LAW Envelope A (AN-105) simulant indicated that cesium adsorption by SuperLig® 644 and perrhenate (pertechnetate analog) adsorption by SuperLig® 639 are dependent on liquid volumetric flow rate during column loading. Acceptable lead column operation for both resins was attained (50% breakthrough at 100 column volumes) at maximum RPP-WTP design basis superficial velocities, but these results indicate that sorption kinetics could be limiting. As a follow-up to this previous work, LAW Envelope B (AZ-102) simulant was tested to verify column operability within the design basis. The simulant mimics the composition of low-activity waste solution from Tank 241-AZ-102 supernate in the Hanford waste tanks, which has higher cesium concentration than Envelopes A and C.

Batch contact tests were all performed with dry resin in the hydrogen form. The SuperLig® 644 resin batch # 991022SMC-IV29 was oven-dried and the "50 Liter"batch was air-dried. Results indicated that the equilibrium K_d values for cesium decrease steeply with increasing initial concentration. A 10-fold increase of initial cesium concentration in AZ-102 simulant (i.e. from 64 to 635 mg/L) reduced the cesium K_d values from 430 to 53 mL/g for IV29 resin batch. For the "50 Liter batch", the K_d values decreased from 675 to 83 mL/g in the same concentration range. The maximum loading capacity of cesium for oven-dry, hydrogen form SuperLig® resin batch #991022SMC-IV29 and air-dry "50 Liter" batch was ~ 0.17 and 0.22 mmole/g-resin, respectively. The cesium capacity for SuperLig® 644 resin as stated by the vendor was 0.33 mmole/g resin.

A series of four column tests were performed to evaluate the effect of volumetric flowrate on cesium sorption on SuperLig® 644 resin. A single column (2.7-cm i.d.) containing 100 mL (~18.64 g) of of oven dry, hydrogen form resin was used in these column tests. The tests were performed in the following: Test #1 at 1.3 BV/h, Test # 2 at 8.2 BV/h, Test # 3 at 0.64 BV/h, and Test # 4 at 1.3 BV/h. Each test consisted of loading, elution, and regeneration cycles. In the experimental conditions employed, the saturation capacity of cesium was 0.094, 0.097, and

0.081-mmole/g of resin at superficial velocities 0.21, 0.4, and 2.7 cm/min, respectively. The approximate (relative) residence times corresponding to the superficial velocities of 0.21, 0.4, and 2.7 cm/min were 83, 44, and 6.45 minutes at 100 ml bed. The lowest flow rate of 0.64 BV/h was selected to evaluate less than optimal flow conditions in the plant. The relative residence time of the carousel columns (three-bed in series) containing 415-gallon resin per bed baseline plant design is 83 minutes.

The cesium breakthrough curves were generally sigmoid (S-shaped), indicating that channeling did not occur during the column loading. The breakthrough curve of iron (minor competitor) was gradual, but the scatter of the data was significant at high superficial velocity. Elution of the resin with 0.5M nitric acid was effective, requiring 14 BV of eluent to reduce cesium concentration to below 1% of initial feed concentration. Iron elution exhibited a sharp peak after 1-3 BV of eluent had passed through the resin. Long and persistent elution tailing followed this elution peak.

Nomenclature

AZ-102	Hanford Site Tank 241-AZ-102
ADS	Analytical Development Section
BV	Bed volume
C/Co	Metal concentration in the column effluent divided by the metal concentration in feed
DF	Decontamination factors
DI	De-ionized water
F-Factor	Mass of oven-dry resin divided by the mass of air-dry resin
IV29	SuperLig® 644 batch # 991022SMC-IV29
IC	Ion chromatography
ICP-AES	Inductively coupled plasma/atomic emission spectroscopy
ICP-MS	Inductively coupled plasma/mass spectroscopy
K_d	Equilibrium distribution coefficient
PNNL	Pacific Northwest National Laboratory
RPP-WTP	River Protection Project – Waste Treatment Plant
RSD	Relative standard deviation
SRTC	Savannah River Technology Section
TAV	Total apparatus volume
TIC	Total inorganic carbon
TOC	Total organic carbon

1.0 Summary of Results

1.1 Objectives

The objective of this test was to:

- Determine the cesium loading profiles for LAW Envelope B simulant processed through SuperLig® 644 ion exchange columns that is operated at different residence times (flow rates). The cesium loading profiles will be used, along with other small-scale column test results, to update the cesium ion exchange column computer models

1.2 Conduct of Tests

The experimental investigations consisted of batch equilibration and column tests. Column tests were performed at three different flow rates (0.64, 1.3, and 8.2 BV/h) to examine the impact of residence time on the column performance. Experimental investigations were performed according to the "Task Technical and Quality Assurance Plan for Evaluating the Residence Time for SuperLig® 644 and SuperLig® 639 Columns with Simulated Envelope B Solution" (WSRC-TR-2001-00204, SRT-RPP-2001-00050, Rev. 0). The Task Plan was generated from the "Task Specification for Evaluating Residence Time for SuperLig® 639 and 644 Columns with Simulated Envelope B Solution" (TSP-W375-01-00021, Rev. 0).

1.3 Results and Performance against Objectives

The objective of this testing for the ion exchange column tests with simulated low-activity waste Envelope B solution was to evaluate the effect of residence time on cesium adsorption on SuperLig® 644 resin. The RPP-WTP design currently assumes that a minimum of 50 BV of waste can be processed while achieving a Cs-137 decontamination factor of ~ 6000. This DF is based on Cs-137 exit concentration of 0.185 μCi/mL from the lag column. The results we obtained for the lead column loading showed that 43 to 58 BV of AZ-102 simulant preceeded 50% breakthrough when the flow rate was varied from 0.64 to 8.2 BV/h.

1.4 Quality Requirements

This work was conducted in accordance with the RPP-WTP QA requirements specified for work conducted by SRTC as identified in DOE IWO MOSRLE60. SRTC has provided matrices to WTP demonstrating compliance of the SRTC QA program with the requirements specified by WTP. Specific information regarding the compliance of the SRTC QA program with RW-0333P, Revision 10, NQA-1 1989, Part 1, Basic and Supplementary Requirements and NQA-2a 1990, Subpart 2.7 is contained in these matrices. The QA requirements were provided under the Task Technical and Quality Assurance Plan for Evaluating the Residence Time for SuperLig® 644 and SuperLig® 639 Columns with Simulated Envelope B Solution" (WSRC-TR-2001-00204, SRT-RPP-2001-00050, Rev.0). Data verification was conducted through independent technical review of the final data report.

2.0 Introduction

The River Protection Project Waste Treatment Plant (RPP-WTP) has identified a process to pretreat and vitrify Hanford tank waste into a low activity and high level waste glass. The pretreatment unit-operations of the RPP-WTP process are sludge washing, filtration, precipitation, and ion exchange. Certain process units remove a portion of some radionuclides from the bulk of the waste and produce a relatively small volume of high level waste (HLW) sludge. This sludge is vitrified with glass forming compounds as high activity level glass. The decontaminated aqueous Low Activity Waste (LAW) phase contains the bulk of the waste volume and is vitrified as a low activity glass. The RPP has classified the LAW feed to the WTP into three envelopes: A, B, and C. Extensive testing with both radioactive and simulated waste for Envelopes A, B, and C was conducted for all unit processes.

The cesium removal is to be accomplished using SuperLig® 644 (Trademark of IBC Advanced Technologies, American Fork, Utah). This resin has been selected as the baseline ion exchange material for cesium removal from Hanford Site tank waste solutions. The resin contains proprietary polymerized ligands that have a high affinity for cesium ions even in the presence of highly alkaline conditions with sodium and potassium. Extensive experimental investigations

conducted at Savannah River Technology Center (SRTC) and Pacific Northwest National Laboratory (PNNL) over the last several years examined the resin capability for cesium removal from Hanford Site waste tank solutions. In experiments performed with simulated waste solutions, results suggest that SuperLig® 644 has an adequate density and low-cycle physical durability[1], sufficient chemical stability[2], sufficient cesium sorption capacity and selectivity[3] to justify its use in the WTP pretreatment facility. Experiments with actual radioactive Hanford tank waste samples AN-103 (Envelope A)[4] and AN-102 (Envelope C) [5,6] generally verified the simulant results, although performance with AZ-102 (Envelope B) was unexpectedly poor.[7] The objective of this study was to evaluate SuperLig® 644 ion exchange column performance with simulated Envelope B salt solution at different residence times (flow rates).

In this work, experimental investigations were performed according to the "Task Technical and Quality Assurance Plan for Evaluating the Residence Time for SuperLig® 644 and SuperLig® 639 Columns with Simulated Envelope B Solution" (WSRC-TR-2001-00204, SRT-RPP-2001-00050, Rev. 0).[8] The Task Plan was generated from the "Task Specification for Evaluating Residence Time for SuperLig® 639 and 644 Columns with Simulated Envelope B Solution" (TSP-W375-01-00021, Rev. 0).[9] The experimental investigations consisted of batch equilibration and column tests. Column tests were performed at three diffrerent flow rates (0.64, 1.3, and 8.2 BV/h) to examine the impact of residence time on the column performance.

3.0 Experimental

3.1 Materials*:* Envelope B simulant mimics the composition of Tank 241-AZ-102 at the Hanford Site. Forty-five liters of the simulant at 5.0M sodium concentration was prepared following the instructions provided by Eibling.[10] The simulant was allowed to stand for 24 hours and then filtered through a 0.45-μm filter. Duplicate sub-samples of the simulant were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) to determine the concentrations of metal constituents. The AZ-102 simulant composition is shown in Table 1.

The ion exchange resin used for cesium removal from Envelope B (AZ-102) simulant in column tests was SuperLig® 644 (batch # 991022SMC-IV29). This resin is a polymerized proprietary organic material supplied by IBC Advanced Technologies, American Fort, Utah. This resin batch was received in potassium form as 20-70 mesh granules. It was pretreated to remove potassium and other impurities that may have been left from the resin manufacturing process. The resin was then converted into hydrogen form. A mass correction factor (F-factor) was determined for the oven-dried hydrogen form of the resin. A second batch designated as the "50-Liter batch" was also used in batch contact tests to compare the data from the IV29 batch. The "50-Liter" batch was received in hydrogen form and stored wet in de-ionized water. The resin was in air-dried form prior to the K_d tests. F-factor determination of both resin batches was performed as prescribed by the "Task Technical and Quality Assurance Plan for Evaluating the Residence Time for SuperLig® 639 and 644 Columns with Simulated Envelope B Solution (U)" (WSRC-TR-2001-00204, SRT-RPP-2001-00050, Rev. 0).[8]

3.2 Equipment

The equipment used for batch contact and equilibration tests consisted of a bench top incubator shaker (model C24) supplied by New Brunswick Scientific Co., Edison New Jersey, Nalgene® filter units supplied by Nalgene Nunc International, Rochester, New York, and an analytical balance, (model AG285) obtained from Mettler Toledo. The analytical balance was accurate to ± 0.001 g. A high precision (0.01 ^{o}C) thermometer traceable to NIST calibration was mounted in polyethylene bottles containing de-ionized water to record the temperature in the incubator shaker environment. A house-supplied vacuum and a trap assembly were used during sample filtration. All experiments were performed in a chemical hood.

The equipment for ion exchange column tests included a single glass column, positive displacement pump, automatic fraction collector, and a water circulator. The column was constructed from borosilicate glass tubing with a 2.7-cm i.d., and a total length of 30 cm. The outside of the column walls was coated with a layer of clear polyvinylchloride to reduce hazards associated with potentially pressurizing the apparatus. The column top assemblies had a fill

reservoir, a pressure gauge, a pressure relief valve, and a feed inlet port. The fill reservoir through the column also served as a vent. The top assembly was connected to the lower section by a glass ground joint and was tightly fitted by a screw cap. A ruler affixed to the column wall was used to allow observation of resin bed height and liquid level changes. All tubing connections were made of polypropylene lines that had Teflon® quick-connect fittings attached to each end. A 3-way, 6 mm bore Teflon® stopcock was attached to the bottom of the column. The column head was attached to the column using a Rudivis ground-glass joint. Two 2-way, 6 mm bore stopcocks were attached on opposite sides of the column head to serve as feed ports. The column head also contained a pressure gauge, a pressure relief valve, and a fill reservoir that also served as a vent. All solutions were passed as down flow through the column using a Fluid Metering Incorporated (FMI) positive displacement pump. Scilog Inc. Middletown, Wisconsin supplied the pump head (model RH00). It was made of a stainless steel (1/8" i.d.) piston that is displaced by a 450 rpm optically encoded, servo-controlled motor. The flow rate range for the pump head/piston configuration was 0-23 mL/min. Samples were collected either manually or using a Spectrum Chromatography IS-95 Interval Sampler.

3.3 Procedure

3.3.1 Resin Pretreatment & F-factor determination: To remove any water-soluble residues, or undesired cations remaining on the resin after the manufacturing process, the resin samples were subjected to pre-treatment. For this purpose the resin was converted by acid-caustic cycles from sodium or potassium to hydrogen form. Approximately 50 grams (± 0.01 g) of SuperLig® 644 (batch # 991022SMC-IV29) was weighed in a high density polyethylene (HDPE) bottle and soaked in a 10:1 phase ratio of 1.0M sodium hydroxide solution for 2 hrs. The resin and sodium hydroxide solution mixture was gently swirled several times. No magnetic bar or mechanical stirrer was used to shake the mixture. The sodium hydroxide solution and resin mixture was slurried into a 1-inch diameter glass column. The excess sodium hydroxide solution was drained and discarded. The resin in the column was washed with 3 bed volumes (BVs) of de-ionized water, followed by 15 BVs of 0.5M nitric acid and 10 BVs of de-ionized water. The resin

was removed from the column and dried in a vacuum oven at 45 ± 5 ^{o}C and 24 in Hg. The dry mass of the pretreated resin in hydrogen form was approximately ~ 20 grams.

3.3.2 Batch Equilibration Tests: A known volume (~10 ml) of simulated Envelope B (AZ-102) solution was added into polyethylene bottles containing a known quantity (~0.10 g) of pretreated, oven-dried, SuperLig® 644 resin in hydrogen form. The batch equilibration tests were conducted in duplicate at 25 ^{o}C using SuperLig® 644 resin, batch # 991022SMC-IV29. The tests were all conducted in duplicate for 48 ± 1 hr. Laboratory control samples (~ i.e. 10 mL of simulant solution in which no resin was added) were treated in identical process steps as the simulant test samples. The concentrations of cesium in the control samples were used as initial concentrations for determination of equilibrium distribution coefficient (K_d values). Sub-samples of the simulant in contact with the resin were removed from the solution after 48 hours and filtered using a 0.45-micron filter. The samples were analyzed by ICP-MS to determine the concentration of total cesium and by ICP-AES to determine the concentrations of metal cations.

Table 1. Composition of Simulant (AZ-102)

Analyte	avg. value
Cs, mg/L	46.35
Total carbon, mg/L	22650
TIC, mg/L	10450
TOC, mg/L	12200
Free OH^-, M	0.32
Carbonate (M)	0.83
IC (anions), M	
Cl^-	5.71E-04
F^-	2.04E-01
$HCOO^-$	1.13E-01
NO_3^-	4.55E-01
NO_2^-	1.09E+00
$H(COO)_2^-$	1.70E-02
PO_4^-	1.13E-02
SO_4^-	1.61E-01
specific gravity	1.23
ICP-ES (mg/L)	
Al	1315
B	9.07
Ba	0.30
Ca	69.1
Cd	<0.028
Co	<0.088
Cr	1351
Cu	<0.1
Fe	0.99
Li	<0.5
Mg	<0.168
Mn	0.043
Mo	102
Na	114500
Ni	<0.5
P	291
Pb	<1.38
Si	3.4
Sn	<0.52
Sr	0.58
Ti	<0.28
V	<0.26
Zn	<0.74
Zr	<0.096
La	<1.4
K	5800
Re	<0.1
S	9505

Additional tests were conducted with SuperLig® 644 batch designated as "50 liter batch". IBC Advanced Technologies prepared this batch in May-August 2000 as part of a 150-liter production-scale batch. The bottles containing the solution and the resin were placed in an incubator- shaker. Approximately 18 mL of the simulant was contacted with ~0.18 g of air -dried form resin. The batch tests were all conducted in duplicate for 48 ± 1 hr. Laboratory control samples (~ i.e. 18 mL simulant), which contained no resin, were treated in identical process steps as the simulant test samples.

Sequential batch contact tests were also performed on the "50 Liter" batch to obtain more data on the isotherm curve. The sequential contact tests were conducted using fresh resin (in each new contact) with filtrate that had been separated from the resin in the preceding test. After the first contact, approximately 12 mL of the filtrate that had been separated from the resin was re-contacted with fresh resin (~0.12 g). The resin and the filtrate were gently shaken for 48 ±1 hours. The solutions were then separated from the resin using a 0.45-micron nylon filter unit. The third contact was carried in the same manner as the second contact test, except ~10 mL sample of the filtrate from the second test and ~ 0.1 g of fresh resin were equilibrated for 48 ±1 hours. After equilibration, the solutions were again separated from the resin by filtration unit. Sub-samples (~ 1-mL) of the filtrate were analyzed by ICP-MS and ICP-AES.

3.3.3 Small-Scale Column Tests: A known mass (~ 18.6 g) of pretreated SuperLig® 644 (batch # 991022SMC-IV29) resin was slurried into a 2.7 cm (~1-inch) i.d. glass column using de-ionized water. The outside walls of the column were tapped while the resin was being slurried into column to ensure uniform packing of the resin bed. The initial height of the resin bed in de-ionized was approximately 8.7-cm (~3.4-inches), yielding a column that contains ~50-mL of resin in hydrogen form. The temperature of the water-bath circulator and the column jacket were adjusted to 25 ^{o}C. The temperature of the liquid above the resin bed was periodically measured and recorded during the tests. Twelve bed volumes (BVs) of 0.25M sodium hydroxide solution was pumped as down flow into the column at approximately 3 bed volumes per hour (BV/h). The resin was stored overnight in the sodium hydroxide solution to allow maximum swelling of the

resin bed. After overnight storage, the NaOH liquid level was adjusted so that the volume of liquid above the resin bed was approximately 2 cm. The height of the resin bed was approximately 25.7-cm (8.57-inches), yielding a column that contained ~ 147-mL of swollen resin in sodium form. The preconditioning solution (0.25M NaOH) that remained above the resin bed and in the feed tubing was approximately 1 BV; the total apparatus volume (TAV) was, therefore, equal to 2 BV. Thus, the first 111-mL of simulant that was fed into the column at the beginning of the loading cycle was to be displaced, yet some unknown portion is mixed with incoming simulant. Likewise, the post-feed water wash and the eluting solutions were allowed to mix with the liquid head left above the resin from the previous cycle. No attempt was made to correct for mixing of solutions in the column headspace when calculating the number of bed volumes of feed, wash, or eluate processed.

The loading cycle was carried out at 25 ^{o}C. The loading cycle was considered to start at the moment that the AZ-102 simulant contacted the resin bed. The simulant was pumped as down flow through the column at ~ 1.3 BV/h. The first 3 BV of effluent was discarded to prevent dilution of the effluent by residual sodium hydroxide solution. Sub-samples of the column effluent were collected after 5 BV of solution had passed through the column and at intervals of approximately 10 BVs, until approximately 150-BVs of simulant had been processed. The samples were collected using a Spectrum Chromatography IS-95 Interval Sampler. Periodically (during sample collection except off-shift hours), the heights of the resin bed and the liquid above the resin were recorded. Similarly, the temperatures of the water-bath circulator and the resin bed were measured and recorded. Each of the column effluent samples was analyzed to determine the concentrations of Na, K, and Cs.

At the conclusion of the first loading cycle at 1.3 BV/h, the simulant was displaced from the column using 6 BVs (2 total apparatus volumes) of 0.1M sodium hydroxide solution. The dilute sodium hydroxide solution was pumped as down flow into the column at 3 BV/hr. The resin bed was then flushed with 6 BVs (2 total apparatus volumes) of de-ionized water at a flow rate of 3 BV/h. The dilute sodium hydroxide was used in order to prevent aluminum hydroxide precipitation that could foul the resin bed and the water rinse served to displace residual sodium hydroxide solution from the columns prior to elution. The column was eluted using 16BV of

0.5M nitric acid solution at 1.0 BV/hr. Sub-samples of the column eluate were collected in 2-BV increments. ICP-MS and ICP-AES were used to analyze the sub-samples for total cesium and elemental (metal) constituents, respectively. Composite elute solutions were also analyzed for total cesium (ICP-MS), elemental constituents (ICP-AES), anions (IC), and total organic and inorganic carbon (TIC/TOC). Upon conclusion of the elution cycle, the residual nitric acid solution was displaced from the column by pumping 6 BVs (2 total apparatus volumes) of de-ionized water through the column at 1.0 BV/hr. The column was stored in the de-ionized water for 2 days before the second column test at 8.2 BV/h was initiated.

The second column test was carried out at ~ 8.2 BV/h using a fresh batch of the AZ-102 simulant. The column was regenerated using a 0.25M NaOH solution. The resin was regenerated at 25 ^{o}C by pumping as down flow 12 BVs of 0.25M sodium hydroxide solution at 3.0 BV/hr through the column. The simulant was pumped as down flow through the column at ~ 8.2 BV/h and the first 3 BV of the effluent was discarded. Sub-samples of the column effluent were collected after 5 BVs of solution was processed and at intervals of approximately 10 BVs, until approximately of 100-BVs of the simulant had been processed.

Upon completion of the second loading cycle, 6 BVs of 0.1M sodium hydroxide at 3 BV/h was used to displace the simulant from column. The dilute sodium hydroxide was rinsed from the column with 6 BVs of de-ionized water at 3 BV/h. The column was eluted using 16 BV of 0.5M nitric acid solution at 1 BV/hr. Sub-samples of the column eluate were collected in 1-BV increments for the first 8 BVs and 2-BV increments, thereafter until 16 BVs of eluent had been processed. The eluate sub-samples were analyzed for total cesium and the eluate composite solution was analyzed for both cesium and metal constituents. The column was stored in de-ionized water at ambient temperature for 2 days before a third column test was initiated.

The third column test was carried out at 0.64 BV/h. The column was first regenerated (i.e. resin converted to sodium form) by transferring 12 BVs of 0.25M sodium hydroxide solution through the column at 3 BV/hr. The simulated Envelope B solution was then pumped as down flow through the column at 0.64 BV/h. After discarding the first 3 BVs of the effluent, sub-samples were collected after 5 BVs of solution was processed, and at intervals of approximately

10 BVs thereafter, until approximately 100 BVs of simulant had been processed. At the conclusion of the loading cycle, the simulant was displaced from column by transferring 6 BVs of 0.1M sodium hydroxide at 3 BV/h, followed by 6 BVs of de-ionized water to rinse the dilute sodium hydroxide off the resin. The column was eluted using 16 BVs of 0.5M nitric acid solution at 1 BV/hr. Sub-samples of the column eluate were collected in 1-BV increments for the first 18 BVs and in 2-BV increments thereafter until a total of 16 BVs of eluent had passed through the column.

The fourth column test was carried out at 1.3 BV/h and it was similar to the first column test. This test was done to compare the performance of the resin before and after the resin was exposed to a high flow condition. In this test, the column was regenerated by transferring 12 BVs of 0.25M sodium hydroxide as down flow at 3 BV/h. The conditions (i.e. flow rate, temperature) during column loading, displacement, rinsing, and elution were identical to that of the first column test at 1.3 BV/h. Sub-samples of the column effluent were collected after processing 5 BVs of simulant, and at intervals of approximately 10 BVs thereafter, until approximately 100 BVs of simulant have been processed.

4.0 Results and Discussion

Batch contact tests were based on the measurement of the distribution coefficient or K_d value of cesium at various equilibrium concentrations. The K_d value was defined as the ratio of the molal concentration of cesium in the resin to the molar concentration in the solution. The distribution coefficient (K_d value) was calculated using the following equation:

$$K_d = \left[\left(\frac{C_{init}}{C_{final}}\right) - 1\right]\left[\frac{V}{M * F}\right] \qquad \textbf{(1)}$$

where C_{init} and C_{final} are the cesium concentration in the AZ-102 simulant before and after contacting with resin, V is the volume of solution used, M is the mass of resin used (pre-treated

here), and F is the resin dry weight correction factor (F-factor). Typically distribution coefficients are measured at equilibrium so the data represents one point on the equilibrium isotherm. For this work, the distribution coefficients were obtained at three different levels of cesium concentration, namely 64, 140, 653 mg/L (i.e. 4.8E-05, 1E-03, and 4.9E-03M, respectively). The lowest concentration (64 mg/L or 4.8E-05M) represents the nominal concentration of cesium in the AZ-102 Hanford tank waste solution. The high concentrations (140 and 650 mg/L) were selected with the purpose of promoting particle diffusion control. All K_d measurements were performed in duplicate. The K_d values reported are the average of two separate measurements. Tables 2 (a) and 2 (b) show the average K_d values and percent relative standard deviation for the fresh, air-dried "50 Liter" batch, and the oven-dried batch 991022SMC-IV29, respectively. Table 2 (c) presents the data (K_d values and percent relative standard deviation) for spent resin from AZ-101 simulant column tests.

Table 2 (a): Cesium Batch Contact Results for Air-Dried "50 Liter batch"

Expt. #	phase ratio	$[Cs]_o$, mg/L	$[Cs]_{eq}$, mg/L	avg. K_d, mL/g	% RSD
1	100	64	8.81	675	1.79
2	10	64	1.17	578	0.27
3	99	142	31.3	379	1.08
4	99	653	370	83	0.89

Table 2 (b): Cesium Batch Contact Results for Oven-Dried " IV29 batch"

Expt. #	phase ratio	$[Cs]_o$, mg/L	$[Cs]_{eq}$, mg/L	avg. K_d, mL/g	% RSD
1	96	64	11.8	430	2.03
2	96	142	43.5	221	3.05
3	96	653	431	52	1.99

Table 2 (c): Cesium Batch Contact Results for Oven-Dried "Spent IV29 batch"

Expt. #	phase ratio	$[Cs]_o$, mg/L	$[Cs]_{eq}$, mg/L	avg. K_d, mL/g	% RSD
1	98	64	10.6	490	1.30
2	98	142	46.9	208	6.22
3	98	653	444	53	12.92

Figure 1 shows the equilibrium distribution coefficients (K_d values) of cesium for oven-dried batch #991022SMC-IV29 before (symbol: pink triangle) and after use in column tests (symbol: blue diamond), and the air-dried "50 Liter batch" (symbol: open red circle). It can be seen that the cesium K_d values decreased steeply with increasing cesium concentration. For example, the cesium K_d values for the AZ-102 simulant containing initial cesium concentrations of 64, 142, and 653 mg/L after contact with spent oven-dried form resin (#991022SMC-IV29 batch) for 48 hours were 490, 208, and 53 mL/g, respectively. The K_d values for the air-dried form of the "50 Liter" batch resin contacted with the AZ-102 simulant at the same time and in the same concentration range were 675, 379, and 83 mL/g, respectively. The reason for the difference in the K_d values between the two resin batches is unknown. However, it could be due to batch-to-batch variability of the resin. In addition, the resin batch #991022SMC-IV29 was oven-dried at 45 ± 5 ^oC (under vacuum) and stored in hydrogen form for several days prior to the batch contact tests. The "50 Liter batch" resin was simply air-dried form.

Battelle Pacific Northwet National Laboratory (PNNL) recently conducted batch contact tests with AZ-102 actual Hanford waste tank sample and SuperLig® resin batch # 010319SMC-IV-73 found cesium K_d values of 221, 63, and 47 mL/g for initial cesium concentrations of 22, 376, and 665 mg/L, respectively. The Cs K_d values obtained at Battelle using actual AZ-102 are in good agreement with our Cs K_d results as shown in Fig. 1 (symbol: green triangle).

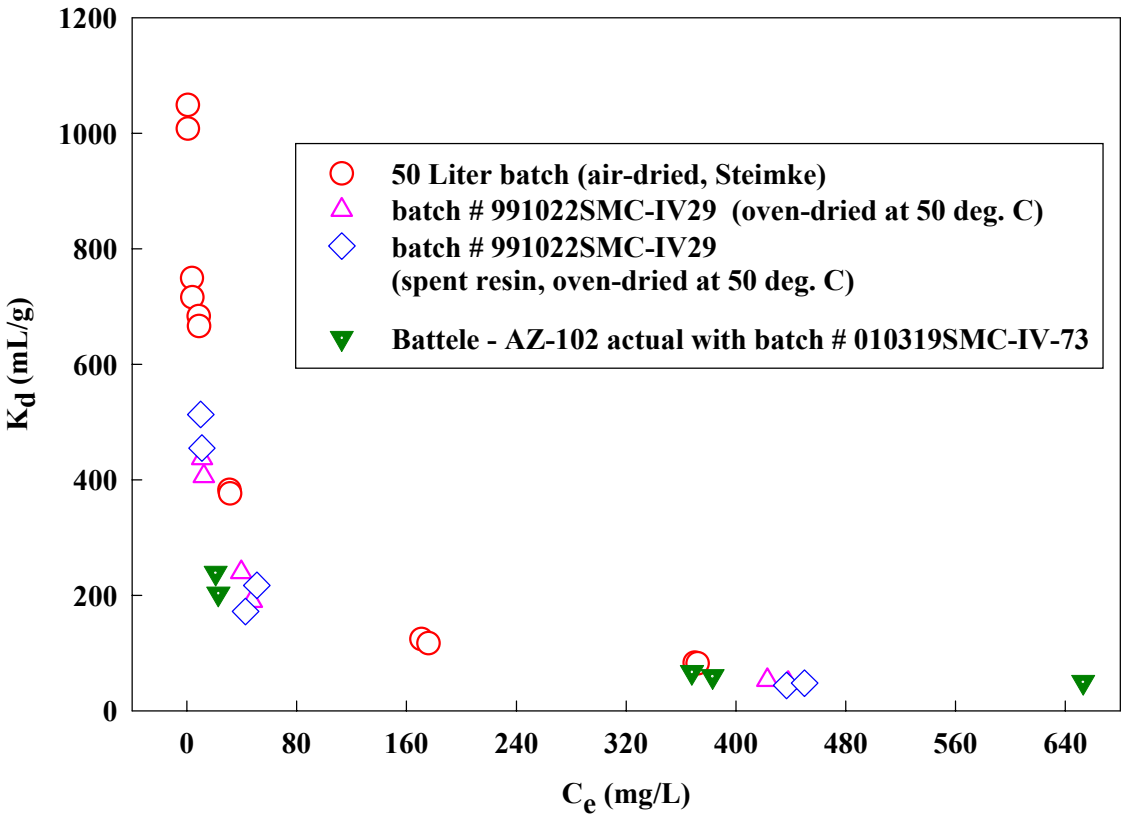

Figure 1. Plot of cesium K_d Values vs. equilibrium concentration

Figure 2 shows the isotherm curves for cesium sorption on SuperLig 644 resin. The development of the isotherm depicts that the loading increased with increasing concentration in the simulant. Near, but not yet at the Cs capacity of the resin, a loading of ~ 0.17 mmole/g was observed for resin batch #991022SMC-IV29 vs. 0.22 mmole/g for "50 Liter" resin batch. These values are significantly lower than the capacity (0.33-mmole/g resin) stated by the vendor.

The column performance tests with Envelope B (AZ-102) simulant were carried out at three different flow rates (0.64, 1.3, and 8.2 BV/h) or superficial velocities (0.21 0.4, and 2.7 cm/min). A single-column (2.7-cm inside diameter) containing ~ 100 mL (18.64 g) of hydrogen form SuperLig® 664 resin was used. The simulant mimics the composition of low-activity waste solution from Tank 241-AZ-102 supernate in the Waste Treatment Plant. Envelope B –

sometimes referred to as Neutralized Current Acid Waste (NCAW)- is high in cesium (~ order of magnitude higher than other Hanford waste tanks) and glass limiting constituents such as sulfate, phosphate, and halides. Consequently, columns must be operated at low flow rate to achieve acceptable column performances. Table 3 shows a summary of column performance results for AZ-102 simulant. There seems to be a 26% difference in the number of BVs processed at 50% breakthrough between Test 1 and Test 2 (Table 3, column 5). This suggests that there is a dependence of resin performance on the feed flow rate. This behavior is generally expected when the feed solution is concentrated and the loading process is controlled by mass transfer from the mobile to the resin phase.

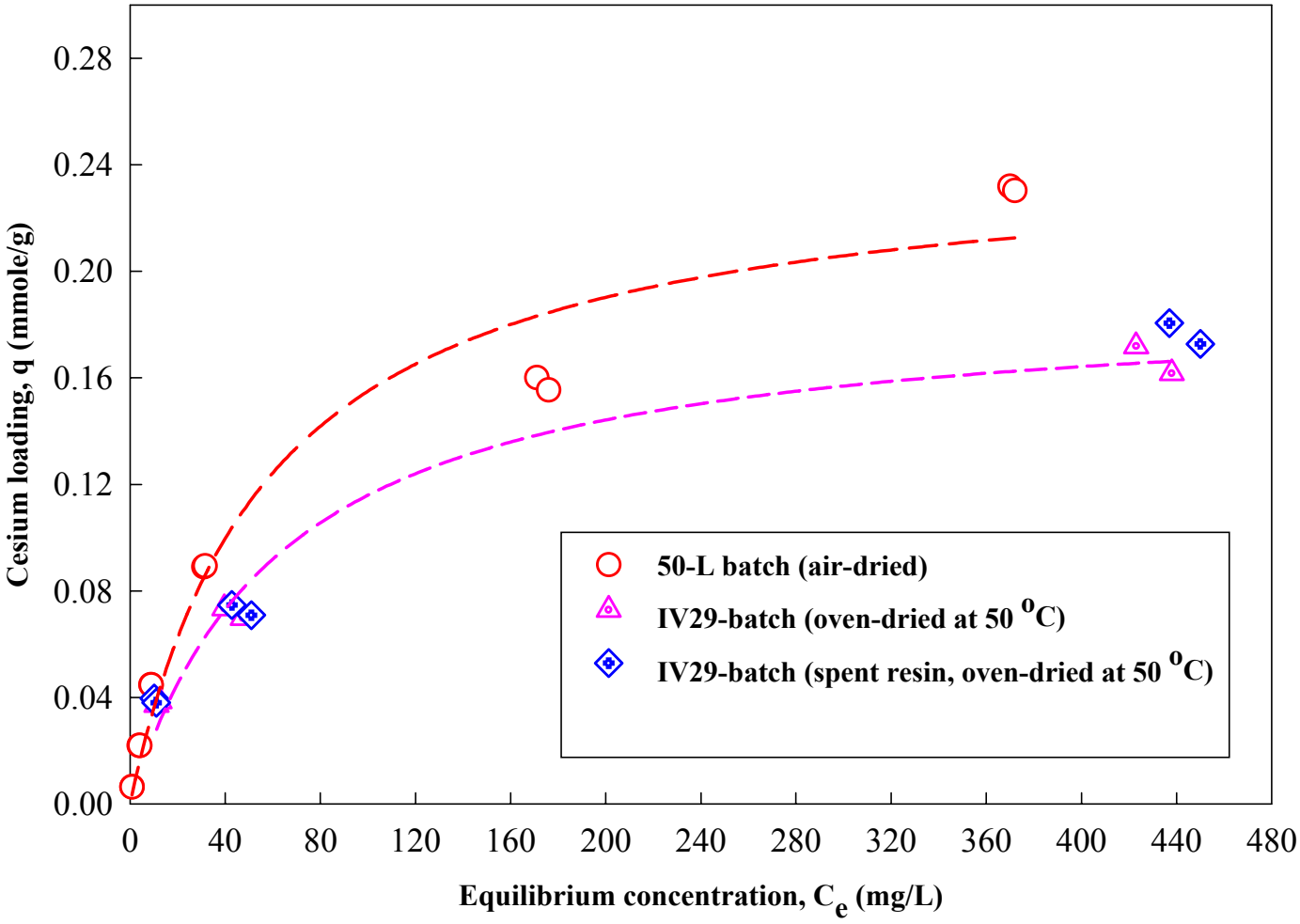

Figure 2. Plot of cesium loading vs. equilibrium concentration

Table 3. Summary of Column Performance Tests

	Height/Dia.	Flowrate		Elution	Breakthrough
Test #	(cm/cm)	BV/h	cm/min	(BV/h)	# BV @ 50%
1	19.5/2.7	1.3	0.4	0.94	58
2	19.4/2.7	8.2	2.7	0.89	43
3	19.5/2.7	0.64	0.21	0.9	53
4	19.5/2.7	1.3	0.4	0.9	50

Initial mass of resin packed into the column = 18.64 g

Table 4 shows the breakthrough capacities of cesium and minor competitors (i.e. chromium, cadmium, iron, and calcium) as calculated from composite effluent solutions and mass of resin bed. Generally speaking, the capacity of the metals increased in the following order: cesium > chromium > calcium > iron, except in the first test run. A high loading capacity for chromium was observed, but the mechanism by which it is adsorbed onto the resin is unknown. The cesium capacity obtained from the column data (~0.094 mmole/g) was within 5% of the maximum capacity (~0.17 mmole/g) observed in batch equilibrium tests. The saturation capacities of the minor competitors (iron, chromium, and calcium) were significantly lower than that of cesium.

Table 4. Breakthrough Capacities of Cesium and Minor Competitors from Column Data (mmole/g)

Test #	Flow rate	Cesium	Chromium	Iron	Calcium
1	1.3	1.05E-01	4.03E-03	4.49E-03	8.49E-03
2	8.2	9.08E-02	2.45E-02	6.31E-03	2.45E-03
3	0.64	7.03E-02	2.83E-02	2.74E-03	4.33E-04
4	1.3	9.01E-02	2.39E-02	4.86E-03	5.54E-03

Table 5 shows a summary of the swelling and shrinking history of the resin bed during the column tests. When the resin was first slurried into the column, the volume of the resin bed was 50 mL. After passing 12 BV of 0.25M NaOH through the resin bed at 3 BV/h and allowing it to soak overnight, the fully swollen resin bed volume was 147 mL. Thus, based on an initial 18.64 g mass of pretreated (hydrogen form) IV29 resin, the specific volume of the resin bed after initial

preconditioning was 7.9 mL/g resin. Data collected on the height of resin bed during column tests show that the average specific volume during regeneration, loading, and elution cycles was ~ 7.3, 6.0, and 4.5 ml/g, respectively. Thus, the percent volume change of the resin bed between elution and regeneration cycles was ~ 62% vol. It was noted that the bed had shrunk about 18% vol. during column loading with simulant containing ~ 5M Na^+. The volume reduction during loading is probably due to exchange of large hydrated sodium ions on the solid phase (resin) with smaller hydrated cesium ions from the liquid phase (simulant). During this exchange, the resin loses significant amounts of water associated with hydrated sodium ions into the solution, and, thus begins to contract. Generally, some swelling of the resin is desirable for the ion exchange process to take place. When the resin is swollen, it allows faster mass transfer by reducing intraparticle resistance. Resin swelling and shrinking, however, can become undesirable from operation's point of view since excessive swelling could potentially cause hydraulic problems and channeling. The swelling and shrinking behavior of this resin batch was essentially invariant with superficial velocity under present experimental conditions

Table 5. Resin Bed Swelling and Shrinking History (bed volume in mL)

Test #	Flow rate (BV/h)	0.25M NaOH	5M Na^+ Simulant	0.1M NaOH	0.5M HNO3
1	1.3	137	112	137	85
2	8.2	137	111	141	83
3	0.64	138	112	139	80
4	1.3	135	112	141	78

Figure 3 shows the breakthrough curves of cesium from AZ-102 simulant at three different flow rates. The plots show the cesium concentration profile (i.e. cesium concentration in the effluent divided by the concentration in the feed) as a function of the number of bed volumes (BVs) of simulant processed. A plot of Cs-137 (radioisotope) breakthrough data for AZ-102 sample of actual Hanford tank waste was also presented in Figure 3. Characteristic sharp breakthrough curves (S- shapes) were obtained for the low superficial velocity (i.e. 0.21 to 0.4 cm/min) tests with AZ-102 simulant and actual sample test conducted at Battelle, Pacific Northwest National Laboratory. Low superficial velocity or flow rate generally causes a decrease in the slope of the initial part of the breakthrough curves and hence an increase in the

breakthrough capacity. The breakthrough capacity was calculated from the amount of cesium loaded onto the resin just before being detected in the column outlet divided by mass of the resin bed. At superficial velocities of 0.21, 0.4, and 2.7 cm/min, we found the breakthrough capacity of the resin was 0.094, 0.097, and 0.081-mmole/g resin, respectively. Slightly higher capacity observed at lower superficial velocities is mainly due to an increase in the residence time.

At a superficial velocity of 0.21 cm/min (0.64 BV/h), the cesium breakthrough was observed after processing approximately 40 BV of the feed solution and a 50% breakthrough occurred after processing 53 BV. Further increasing the superficial velocity to 0.4 cm/min (1.3 BV/h), cesium was detected in the column effluent after processing 35 BV of simulant and a 50% breakthrough occurred after 58 BV of simulant had passed through the column. Thus, there was some, but marginal, improvement in the number of bed volumes of feed processed when the flow rate was reduced from 1.3 to 0.64 BV/h. In this range, it appears that film diffusion is not sensitive to the flowrate.

The sharp breakthrough curves observed for low superficial velocity are desirable in order to achieve efficient use of the resin. Although time is often an important consideration in process throughput and it is desirable to use as high flow rate as possible, the column performance of the high superficial velocity test (2.7 cm/min) declined significantly as compared to the test performed at 0.21 cm/min (0.64 BV/h). This is probably due to the fact that for the higher flow rate, the residence time is correspondingly shorter (6.5 min vs. 83 min).

Figure 4 shows the elution curves of cesium from SuperLig® 644 resin using 0.5M nitric acid solution. It can be seen that the elution curve for each test consists of three sections. The first section corresponds to the initial portion of the elution and includes the displacement of the liquid in the bed from the previous water rinse cycle. The next section contains a sharp peak where the major portion of the cesium is eluted from the resin. In this section, the cesium concentration in the eluate reached its maximum. The sharp peak was observed after 3 to 4 BV of nitric acid (0.5 M) had passed through the column. The last section of the curve shows the short tail of the elution that followed the elution peak. The cesium concentration after transferring 14

BVs of eluent into the column was less than 1% of its concentration in the feed. The elution was performed at constant flow rate despite the fact that the resin bed was shrinking during the elution cycle. The shrinking of the resin during elution did not seem to affect the shape of the elution profiles.

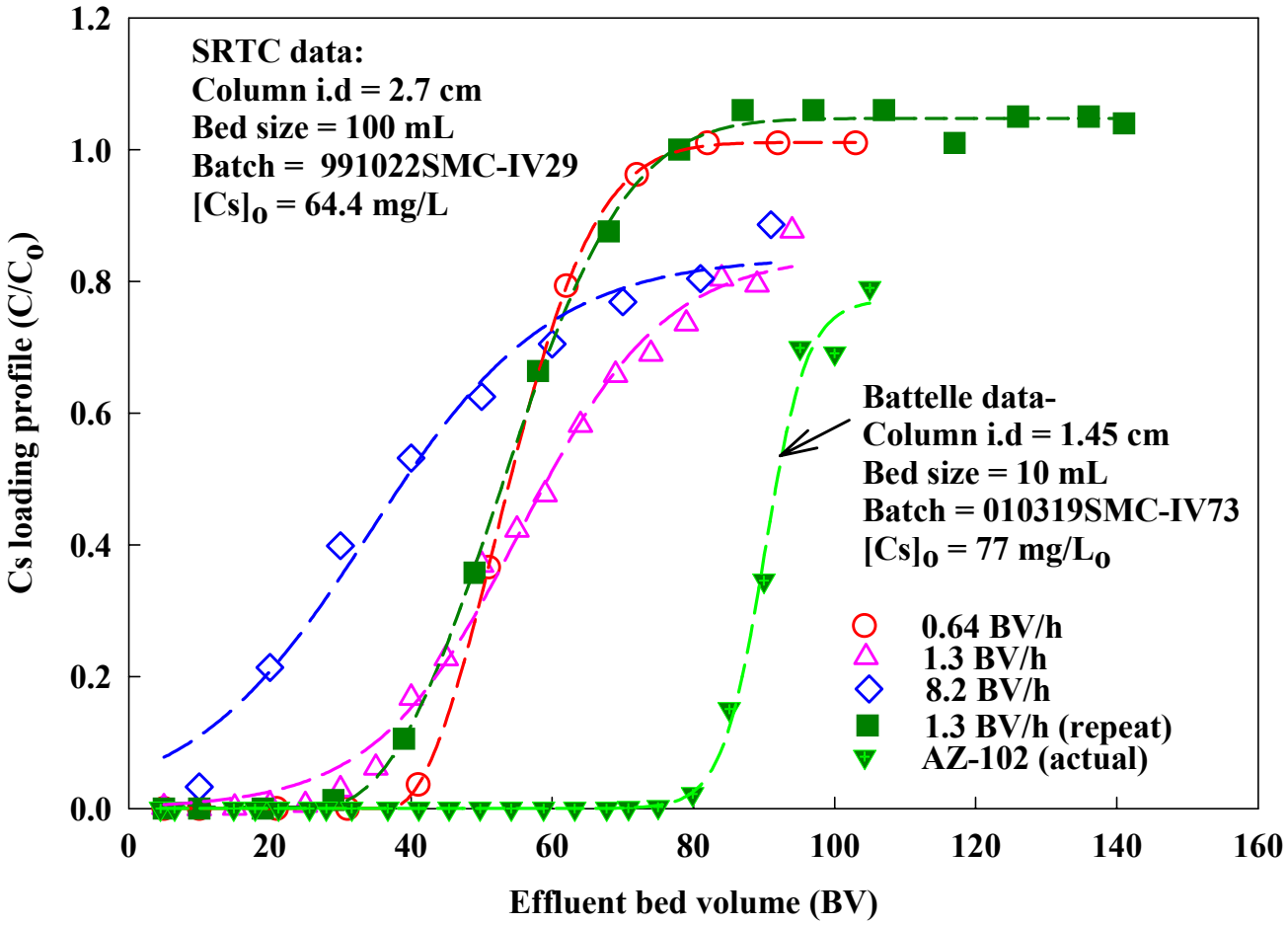

Figure 3. Cesium breakthrough curves at different flow rates

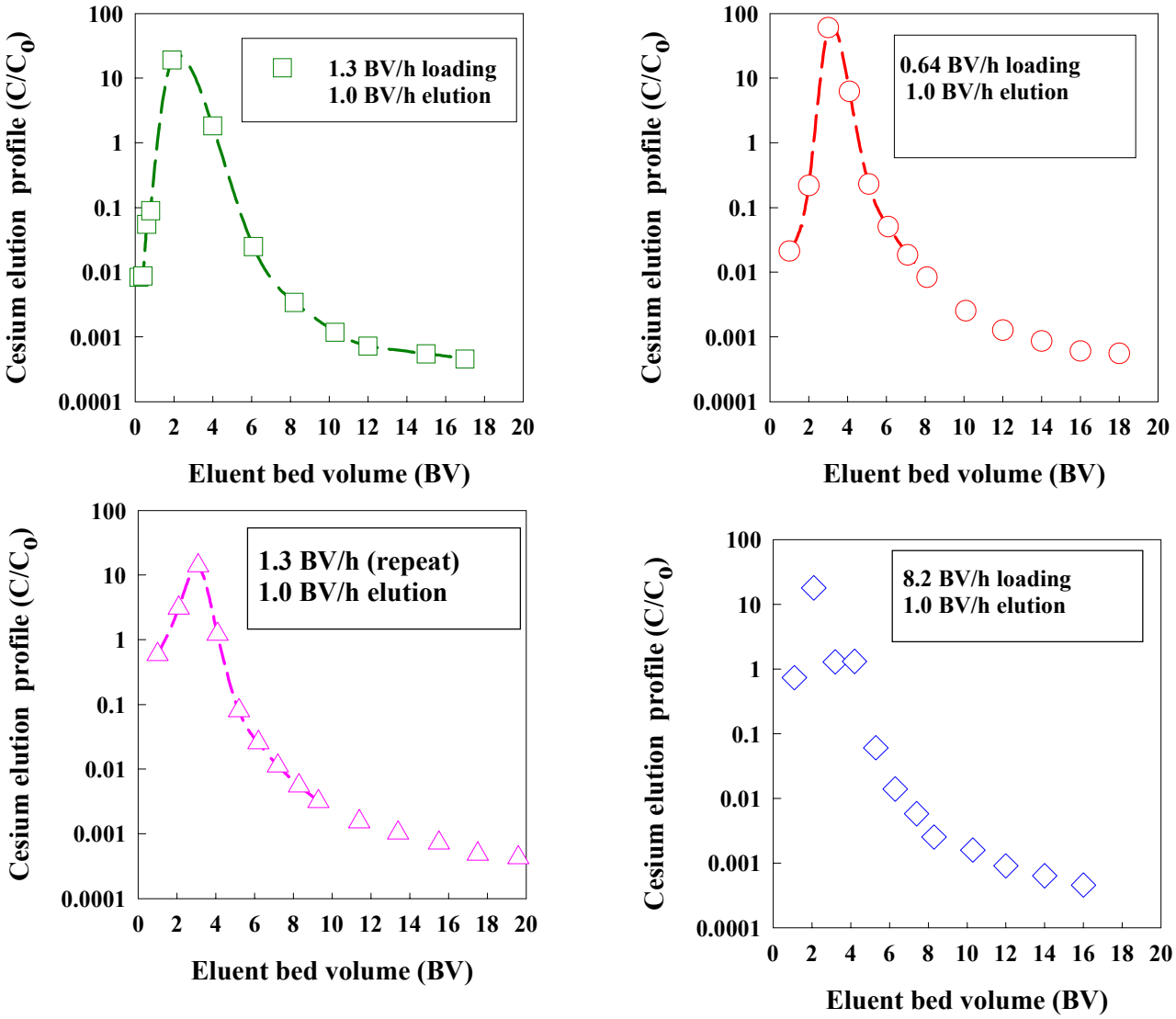

Figure 4. Cesium elution profiles for SuperLig 644 and AZ-102 Simulant

Figure 5 shows the loading and elution profiles of iron at various superficial velocities. At low superficial velocities (0.21-0.4 cm/min), 50% breakthrough of iron occurred after processing ~ 40 BVs and the shape of the breakthrough curves was generally linear. At higher superficial velocity (2.7 cm/min), 50% breakthrough of iron occurred after processing only 20 BVs of AZ-

102 simulant and the breakthrough point was observed after only 5 BVs of simulant had passed through the column. The early breakthrough of iron could be due to poor diffusion-controlled column kinetics. Elution Peaks (Figure 5, left and top axis) which correspond to maximum iron concentration in the eluate, were observed after 1-3 BVs of eluent (0.5M HNO_3) had passed through the resin bed. The elution tailing was very long and persistent, indicating that iron elution from the resin was not complete. It should be noted that more than 10% of iron remained on the resin bed after 16 BVs of eluent had passed through the column.

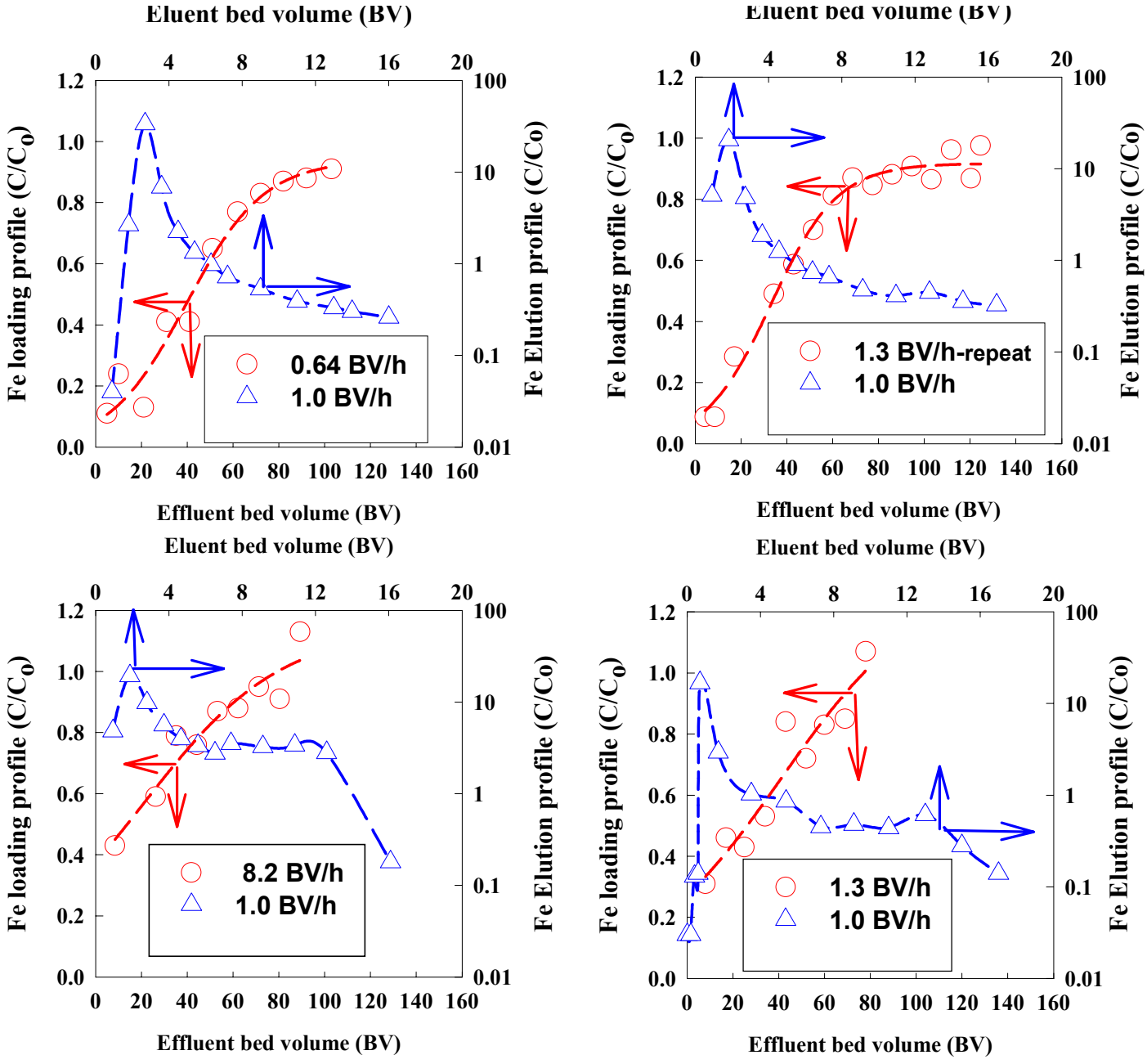

Figure 5. Iron breakthrough and elution curves

5. Conclusion

A series of batch tests were conducted with AZ-102 simulant using two batches of SuperLig® 644 resin. The results show a drop in K_d results when the capcaity of the resin is reached and the solution concentration continues to increase. K_d is defined as the molal concentration of the solute in the resin divided by the molar concentration of the solute in the liquid phase. Therefore, K_d will decrease to zero after the resin capacity is reached and the solution concentration continues to increase. The maximum loading capacity for cesium was calculated from the equilibrium isotherm curves and the values obtained were 0.17 and 0.22 mmole/g for the oven-dried batch #991022SMC-IV29 and air-dried "50-Liter" batch, respectively.

Four column loading and elution tests were performed to evaluate the effects of flow rate (residence time) on cesium sorption from AZ-102 (Envelope B) simulant using a single-column (2.7 cm i.d.) containing ~ 100 mL of SuperLig 644® resin. Column breakthrough and elution profiles were obtained at three different flow rates: 0.64, 1.3, and 8.2 BV/h (i.e. superficial velocities, 0.21, 0.4, and 2.7 cm/min). The results of column loading tests revealed that there was marginal improvement in the number of bed volumes of feed processed when the flow rate was reduced from the nominal plant flow rate of 1.3 BV/h to 0.64 BV/h. However, A significant reduction in the column performance was observed at higher flow rate (8.2 BV/h).

Cesium elution from SuperLig® 644 resin was accomplished using 0.5M nitric acid at ~ 1BV/h. Elution peaks for cesium were found between 3 to 4 BVs, followed by short elution tailing. Elution was complete after passing ~14 BV of 0.5M nitric acid into the columns.

The column tests revealed that iron is being loading onto the SuperLig® 644 resin from AZ-102 simulant. The elution profile of iron showed a sharp peak and a long elution tailing. Although iron is present in AZ-102 simulant as trace quantity (<1 ppm) and the mechanism of its uptake by the resin is unknown, further investigation is needed to understand the long-term impact of residual iron on resin stability. Trace metals such as iron and copper act as catalysts for oxidative degradation of organic resin.

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Appendix-A

Tank 241-AZ-102 (Envelope B) Simulant

Appendix A-1: Composition of Tank AZ-102 Simulant (at 5 M Na)

Compounds	Formula	Formula, wt.	Grams/Liter
Aluminum Nitrate	$Al(NO_3)_3 \bullet 9H_2O$	371.15	18.823
Boric Acid	H_3BO_3	61.83	0.05
Calcium Nitrate	$Ca(NO_3)_2 \bullet 4H_2O$	434.23	0.359
Cesium Nitrate	$CsNO_3$	194.02	0.074
Potassium Molybdate	K_2MoO_4	238.14	0.263
Potassium Nitrate	KNO_3	101.1	14.503
Strontium Nitrate	$Sr(NO_3)_2$	211.65	0.0009
Sodium Acetate	$NaCH3COO \bullet 3H_2O$	136.08	2.756
Disodium EDTA	$Na_2C_{10}H_{14}N_2O_8 \bullet 2HO$	372.24	0.515
N-(2-HEDTA)	$C_{10}H_{18}N_2O_7$	278.26	0.153
Iminodiacetic acid	$HN(CH_2CO_2H)_2$	131.08	0.422
Citric acid	$C_6H_8O_7 \bullet H_2O$	210.14	8.611
Sodium Fluoride	NaF	41.99	4.05
Sodium Sulfate	Na_2SO_4	142.04	44.095
Sodium Hydroxide	NaOH	40	21.372
Sodium Formate	HCOONa	68.01	12.51
Sodium Glycolate	$HOCH_2COONa$	98.03	20.176
Sodium Oxalate	$Na_2C_2O_4$	134	7.777
Sodium Phosphate	$Na_3PO_4 \bullet 12H_2O$	380.12	3.685
Sodium Chromate	Na_2CrO_4	161	4.33
Sodium Carbonate	Na_2CO_3	105.99	92.846
Sodium Nitrate	$NaNO_3$	84.99	16.602
Sodium Nitrite	$NaNO_2$	69	82.086
Water	H_2O	18	880.94

Appendix A-2: Composition of AZ-102 Simulant Solution

Analyte	ADS # 3-173799	ADS # 3-173800	avg. value
Cs, mg/L	63.8	63.9	64
Total carbon, mg/L	22800	22500	22650
TIC, mg/L	10400	10500	10450
TOC, mg/L	12400	12000	12200
Free OH^-, M	0.31	0.33	0.32
IC (anions), M			
Cl^-	5.71E-04	5.71E-04	5.71E-04
F^-	2.05E-01	2.03E-01	2.04E-01
$HCOO^-$	8.64E-02	1.39E-01	1.13E-01
NO_3^-	4.82E-01	4.27E-01	4.55E-01
NO_2^-	1.16E+00	1.02E+00	1.09E+00
$H(COO)_2^-$	1.70E-02	1.70E-02	1.70E-02
PO_4^-	1.16E-02	1.11E-02	1.13E-02
SO_4^-	3.06E-01	1.57E-02	1.61E-01
ICP-ES, mg/L			
Al	1290	1340	1315
B	8.55	9.59	9.1
Ba	0.29	0.30	0.3
Ca	69.3	68.9	69.1
Cd	<0.028	<0.028	<0.028
Co	<0.088	<0.088	<0.088
Cr	1330	1371	1351
Cu	<0.1	<0.1	<0.1
Fe	1.07	0.92	1
Li	<0.5	<0.5	<0.5
Mg	<0.168	<0.168	<0.168
Mn	0.032	0.043	0.037
Mo	101	104	102
Na	114000	115000	114500
Ni	<0.5	<0.5	<0.5
P	294	289	291
Pb	<1.38	<1.38	<1.38
Si	2.6	4.2	3
Sn	<0.52	<0.52	<0.52
Sr	0.58	0.58	1
Ti	<0.28	<0.28	<0.28
V	<0.26	<0.26	<0.26
Zn	<0.74	<0.74	<0.74
Zr	<0.096	<0.096	<0.096

Appendix-B

Cesium Batch Contact Data

Appendix B-1:Cesium Batch Data
Envelope B (Tank 241-AZ-102) simulant
Resin batch # 991022smc-IV29
Fresh pretreated, oven-dry (H-form)

Sample ID	LIMS #	Solution mass (g)	Resin mass (g)	Solution vol. (mL)	phase ratio	F-factor	$[Cs]_e$ (mg/L)	uptake, K_d (mL/g)	loading, q (mmole/g)
AZ102-SL644IV-1E-04-1	3-174411	12.2752	0.1077	9.98	93	0.983	11.10	437	3.64E-02
AZ102-SL644IV-1E-04-1D	3-174412	12.3227	0.1015	10.02	99	0.983	12.40	406	3.78E-02
AZ102-SL644IV-1E-03-1	3-174413	12.3179	0.1032	10.01	97	0.983	47.40	190	6.76E-02
AZ102-SL644IV-1E-03-1D	3-174414	12.3525	0.1065	10.04	94	0.983	39.60	240	7.13E-02
AZ102-SL644IV-5E-03-1	3-174415	12.2953	0.1033	10.00	97	0.983	438.00	48	1.58E-01
AZ102-SL644IV-5E-03-1D	3-174416	12.3313	0.1042	10.03	96	0.983	423.00	53	1.69E-01
AZ102-1E-04, control #1	3-174417	11.9567	na	9.72	na	na	63.6	na	na
AZ102-1E-04,control #1D	3-174418	12.3901	na	10.07	na	na	63.5	na	na
AZ102-1E-03, control #1	3-174419	12.9433	na	10.52	na	na	141	na	na
AZ102-1E-03,control #1D	3-174420	12.329	na	10.02	na	na	142	na	na
AZ102-5E-03, control #1	3-174421	12.382	na	10.07			660		
AZ102-5E-03, ontrol #1D	3-174422	12.3443	na	10.04	na	na	653	na	na

Appendix B-2: Cesium Batch Data

Envelope B (Tank 241-AZ-102) simulant

Batch # 991022smc-IV29

Spent resin, oven-dry (H-form)

Sample ID	LIMS #	Solution mass (g)	Resin mass (g)	Solution vol. (mL)	phase ratio	F-factor	$[Cs]_e$ (mg/L)	uptake, K_d (mL/g)	loading, q (mmole/g)
AZ102-SL644SP-1E-04-1	3-174910	12.3619	0.1019	10.050	99	0.98	10.1	519	3.91E-02
AZ102-SL644SP-1E-04-1D	3-174911	12.2924	0.1037	9.994	96	0.98	11.0	460	3.76E-02
AZ102-SL644SP-1E-03-1	3-174912	12.3343	0.1008	10.028	99	0.98	51.0	185	6.60E-02
AZ102-SL644SP-1E-03-1D	3-174913	12.3122	0.1038	10.010	96	0.98	42.8	232	6.99E-02
AZ102-SL644SP-5E-03-1	3-174914	12.2862	0.1017	9.989	98	0.98	450	51	1.50E-01
AZ102-SL644SP-5E-03-1D	3-174915	12.2216	0.1022	9.936	97	0.98	437	55	1.58E-01
AZ102-IVSP, LCS #1E-04	3-174916	12.3569	na	10.05	na		63.1		
AZ102-IVSP, LCS #1E-03	3-174917	12.326	na	10.02	na		145		
AZ102-IVSP,LCS #5E-03	3-174918	12.3201	na	10.02	na		682		

Appendix B-3: Cesium Batch Data

Envelope B (Tank 241-AZ-102) simulant

Resin batch # 50 Liter

50-Liter batch, air-dry (H-form)

Sample ID	LIMS #	Solution mass (g)	Resin mass (g)	Solution vol. (mL)	phase ratio	F-factor	$[Cs]_e$ (mg/L)	uptake, K_d (mL/g)	loading, q (mmole/g)
AZ102-SL50L-nomCs-1	3-176458	18.5396	0.151	15.07	100	0.92	8.90	666	4.46E-02
AZ102-SL50L-nomCs-1D	3-176459	18.4574	0.1501	15.01	100	0.92	8.72	683	4.48E-02
AZ102-SL50L-1E-03-1	3-176460	18.5898	0.1518	15.11	100	0.92	31.60	376	8.94E-02
AZ102-SL50L-1E-03-1D	3-176461	18.4658	0.1522	15.01	99	0.92	31.00	382	8.91E-02
AZ102-SL50L-5E-03-1	3-176462	18.5897	0.1526	15.11	99	0.92	372.00	82	2.30E-01
AZ102-SL50L-5E-03-1D	3-176463	18.4957	0.1518	15.04	99	0.92	370.00	83	2.32E-01
AZ102-SL50L-nomCs-2	3-176464	12.2202	1.0033	9.94	10	0.92	1.16	579	5.05E-03
AZ102-SL50L-nomCs-2D	3-176465	12.3546	1.0006	10.04	10	0.92	1.18	577	5.12E-03
AZ102-1E-04, LCS #1	3-174417	11.9567	na	9.72	na	na	63.60	na	na
AZ102-1E-04, LCS #1D	3-174418	12.3901	na	10.07	na	na	63.50	na	na
AZ102-1E-03, LCs #1	3-174419	12.9433	na	10.52	na	na	141	na	na
AZ102-1E-03, LCS#1D	3-174420	12.329	na	10.02	na	na	142	na	na
AZ102-5E-03, LCS#1	3-174421	12.382	na	10.07	na	na	660	na	na
AZ102-5E-03, LCS #1D	3-174422	12.3443	na	10.04	na	na	653	na	na

Appendix-C

Cesium Column Loading and Elution data

Appendix C-1: Cesium Column Loading

Flow rate = 0.64 BV/h

Envelope B (Tank 241-AZ-102) simulant

Resin batch # 991022smc-IV29

Column size = 2.7 cm

Sample ID	ADS #	Resin bed height (cm)	Flow rate (mL/min)	Flow rate (BV/h)	# BV processed	$[Cs]_{eff}$ (ug/L)	Cs profile [C/Co]
CR0.64-L5	3-174187	19.7	1.19	0.64	5	0.002	3.90E-05
CR0.64-L10	3-174188	19.7	1.19	0.64	10	0.0036	7.01E-05
CR0.64-20	3-174189	19.7	1.19	0.64	19	0.002	3.90E-05
CR0.64-L30	3-174190	19.7	1.19	0.64	29	0.002	3.90E-05
CR0.64-L40	3-174191	19.7	1.19	0.64	38	1.86	3.62E-02
CR0.64-L50	3-174192	19.7	1.19	0.64	48	18.8	3.66E-01
CR0.64-L60	3-174193	19.7	1.19	0.64	57	40.7	7.93E-01
CR0.64-L70	3-174194	19.7	1.19	0.64	67	49.4	9.62E-01
CR0.64-L80	3-174195	19.7	1.19	0.64	76	51.7	1.01E+00
CR0.64-L90	3-174196	19.7	1.19	0.64	86	51.9	1.01E+00
CR0.64-L100	3-174197	19.7	1.19	0.64	95	51.9	1.01E+00

Appendix C-2: Cesium Column Elution

Envelope B (Tank 241-AZ-102) simulant

Resin batch # 991022smc-IV29

Column size = 2.7 cm

Sample ID	ADS #	Resin bed height (cm)	Flow rate (mL/min)	Flow rate (BV/h)	# BV processed	$[Cs]_{eff}$ (ug/L)	Cs profile [C/Co]
CR0.64-E1	3-174208	19.5	1.67	0.9	0.9	1.08	2.10E-02
CR0.64-E2	3-174209	nm	1.67	0.9	1.8	11.2	2.18E-01
CR0.64-E3	3-174210	nm	1.67	0.9	2.7	3080	6.00E+01
CR0.64-E4	3-174211	nm	1.67	0.9	3.6	320	6.23E+00
CR0.64-E5	3-174212	15.3	1.67	0.9	4.5	11.8	2.30E-01
CR0.64-E6	3-174213	15.3	1.67	0.9	5.4	2.59	5.04E-02
CR0.64-E7	3-174214	nm	1.67	0.9	6.3	0.946	1.84E-02
CR0.64-E8	3-174215	14.6	1.67	0.9	7.2	0.428	8.34E-03
CR0.64-E10	3-174216	14.6	1.67	0.9	9.0	0.13	2.53E-03
CR0.64-E12	3-174217	14.6	1.67	0.9	10.8	0.0654	1.27E-03
CR0.64-E14	3-174218	14	1.67	0.9	12.6	0.0442	8.61E-04
CR0.64-E16	3-174219	14	1.67	0.9	14.4	0.0308	6.00E-04
CR0.64-E18	3-174220	13.8	1.67	0.9	16.2	0.0284	5.53E-04

Appendix C-3: Cesium Column Loading
Flow rate = 1.3 BV/h
Envelope B (Tank 241-AZ-102) simulant
Resin batch # 991022smc-IV29
Column size = 2.7 cm

Sample ID	ADS #	Resin bed height (cm)	Flow rate (mL/min)	Flow rate (BV/h)	# BV processed	$[Cs]_{eff}$ (ug/L)	Cs profile [C/Co]
CR1.3-L5	3-173912	20.2	2.43	1.3	5	0.098	1.91E-03
CR1.3-L10	3-173913	20.2	2.43	1.3	10	0.006	1.17E-04
CR1.3-L20	3-173915	19.9	2.43	1.3	20	0.284	5.53E-03
CR1.3-L30	3-173917	19.9	2.43	1.3	30	1.5	2.92E-02
CR1.3-L40	3-173919	19.9	2.49	1.3	40	8.61	1.68E-01
CR1.3-L50	3-173921	19.9	2.49	1.3	50	19	3.70E-01
CR1.3-L60	3-173923	19.9	2.39	1.3	60	24.5	4.77E-01
CR1.3-L70	3-173925	19.9	2.39	1.3	70	33.8	6.58E-01
CR1.3-L80	3-173927	19.9	2.39	1.3	80	37.8	7.36E-01
CR1.3-L90	3-173929	19.9	2.39	1.3	90	40.8	7.95E-01
CR1.5-L95	3-173930	19.5	2.45	1.5	94	45	8.77E-01

Appendix C-4: Cesium Column Elution
Envelope B (Tank 241-AZ-102) simulant
Resin batch # 991022smc-IV29
Column size = 2.7 cm

Sample ID	ADS #	Resin bed height (cm)	Flow rate (mL/min)	Flow rate (BV/h)	# BV* processed	$[Cs]_{eff}$ (ug/L)	Cs profile [C/Co]
CR1.3-E1-1		19.5	1.75	1.06	0.2	0.43	8.34E-03
CR1.3-E1-2		nm	1.73	1.05	0.4	0.45	8.77E-03
CR1.3-E1-3		nm	1.73	1.05	0.6	2.83	5.51E-02
CR1.3-E1-4		nm	1.73	1.05	0.8	4.58	8.92E-02
CR1.3-E2	3-174175	15.3	1.73	1.05	1.9	981	1.91E+01
CR1.3-E4	3-174176	15.3	1.73	1.05	4.0	94.1	1.83E+00
CR1.3-E6	3-174177	nm	1.73	1.05	6.1	1.28	2.49E-02
CR1.3-E8	3-174178	nm	1.73	1.05	8.2	0.175	3.41E-03
CR1.3-E10	3-174179	nm	1.73	1.05	10.3	0.0604	1.18E-03
CR1.3-E12	3-174180	nm	1.73	1.05	12	0.037	7.21E-04
CR1.3-E12	3-174181	14.8	1.79	1.09	15	0.0282	5.49E-04
CR1.3-E16	3-174182	14.8	1.79	1.09	17	0.0233	4.54E-04
CR1.3-E18	3-174183	14.8	1.79	1.09	19	0.0063	1.23E-04
CR1.3-E20	3-174184	14.8	1.79	1.09	21	0.0032	6.23E-05

Appendix C-5: Cesium Column Loading
Flow rate = 8.2 BV/h
Envelope B (Tank 241-AZ-102) simulant
Resin batch # 991022smc-IV29
Column size = 2.7 cm

Sample ID	ADS #	Resin bed height (cm)	Flow rate (mL/min)	Flow rate (BV/h)	# BV processed	$[Cs]_{eff}$ (ug/L)	Cs profile [C/Co]
CR8-L5	3-174095	20	15.1	7.9	5	nm	nm
CR8-L10	3-174096	19.8	14.39	7.6	10	1.7	3.31E-02
CR8-L20	3-174098	19.8	15.2	8.0	20	11	2.14E-01
CR8-L30	3-174100	19.8	15.2	8.0	30	20.5	3.99E-01
CR8-L40	3-174102	19.5	15.2	8.2	40	27.3	5.32E-01
CR8-L50	3-174104	19.4	15.2	8.2	50	32.1	6.25E-01
CR8-L60	3-174106	19.4	15.2	8.2	60	36.2	7.05E-01
CR8-L70	3-174108	19.4	15.2	8.2	70	39.5	7.69E-01
CR8-L80	3-174110	19.4	15.2	8.2	80	41.3	8.04E-01
CR8-L90	3-174112	19.4	15.2	8.2	90	45.5	8.86E-01
CR8-L100	3-174114	19.4	15.2	8.2	100	53	1.03E+00

Appendix C-6: Cesium Column Elution
Envelope B (Tank 241-AZ-102) simulant
Resin batch # 991022smc-IV29
Column size = 2.7 cm

Sample ID	ADS #	*Resin bed* height (cm)	Flow rate (mL/min)	Flow rate (BV/h)	# BV processed	$[Cs]_{eff}$ (ug/L)	Cs profile [C/Co]
CR8-E1	3-174120	19.5	1.75	1.06	1.1	37.9	7.38E-01
CR8-E2	3-174121	nm	1.73	1.05	2.1	923	1.80E+01
CR8-E3	3-174122	nm	1.73	1.05	3.2	66.2	1.29E+00
CR8-E4	3-174123	nm	1.73	1.05	4.2	67.2	1.31E+00
CR8-E5	3-174124	nm	1.73	1.05	5.3	3.13	6.10E-02
CR8-E6	3-174125	nm	1.73	1.05	6.3	0.719	1.40E-02
CR8-E7	3-174126	nm	1.73	1.05	7.4	0.298	5.80E-03
CR8-E8	3-174127	14.6	1.62	0.98	8.3	0.13	2.53E-03
CR8-E10	3-174128	14.6	1.62	0.98	10.3	0.0824	1.60E-03
CR8-E12	3-174129	14.6	1.62	0.98	12	0.0468	9.12E-04
CR8-E14	3-174130	14.6	1.62	0.98	14	0.0329	6.41E-04
CR8-E16	3-174131	14.6	1.62	0.98	16	0.0236	4.60E-04
CR8-E18	3-174132	14.6	1.62	0.98	18	0.001	1.95E-05

Appendix C-7: Cesium Column Loading
Flow rate = 1.3 BV/h –Repeat Test
Envelope B (Tank 241-AZ-102) simulant
Resin batch # 991022smc-IV29
Column size = 2.7 cm

Sample ID	ADS #	Resin bed height (cm)	Flow rate (mL/min)	Flow rate (BV/h)	# BV processed	$[Cs]_{eff}$ (ug/L)	Cs Profile [C/Co]
CR1.3R-L5	3-174569	19.5	2.4	1.3	5	0.005	9.69E-05
CR1.3R-L10	3-174570	19.5	2.4	1.3	10	0.0047	9.10E-05
CR1.3R-L20	3-174571	19.5	2.4	1.3	20	0.0054	1.05E-04
CR1.3R-L30	3-174572	19.5	2.4	1.3	30	0.669	1.30E-02
CR1.3R-L40	3-174573	19.5	2.4	1.3	40	5.45	1.06E-01
CR1.3R-L50	3-174574	19.5	2.4	1.3	50	18.5	3.58E-01
CR1.3R-L60	3-174575	19.5	2.4	1.3	60	34.3	6.64E-01
CR1.3R-L70	3-174576	19.5	2.4	1.3	70	45.2	8.76E-01
CR1.3R-L80	3-174577	19.5	2.4	1.3	80	51.6	1.00E+00
CR1.3R-L90	3-174578	19.5	2.4	1.3	90	54.5	1.06E+00
CR1.3R-L100	3-174579	19.5	2.4	1.3	100	54.9	1.06E+00
CR1.3R-L110	3-174580	19.5	2.4	1.3	110	54.9	1.06E+00
CR1.3R-L120	3-174581	19.5	2.4	1.3	120	52	1.01E+00
CR1.3R-L130	3-174582	19.5	2.4	1.3	130	54.4	1.05E+00
CR1.3R-L140	3-174583	19.5	2.4	1.3	140	54.2	1.05E+00
CR1.3R-L145	3-174584	19.5	2.4	1.3	145	53.8	1.04E+00

Appendix C-8: Cesium Column Elution
Envelope B (Tank 241-AZ-102) simulant
Resin batch # 991022smc-IV29
Column size = 2.7 cm

Sample ID	ADS #	resin bed height (cm)	Flow rate (mL/min)	Flow rate (BV/h)	# BV processed	$[Cs]_{eff}$ (ug/L)	Cs profile [C/Co]
CR1.3R-E1	3-174591	19.5	1.7	1.0	1.0	3.04E+01	5.92E-01
CR1.3R-E2	3-174592	nm	1.7	1.0	3.1	7.19E+02	1.40E+01
CR1.3R-E3	3-174593	nm	1.7	1.0	4.1	6.24E+01	1.22E+00
CR1.3R-E4	3-174594	nm	1.7	1.0	5.2	4.13E+00	8.04E-02
CR1.3R-E5	3-174595	nm	1.7	1.0	6.2	1.32E+00	2.57E-02
CR1.3R-E6	3-174596	nm	1.7	1.0	7.2	0.573	1.12E-02
CR1.3R-E7	3-174597	14.6	1.7	1.0	8.3	0.284	5.53E-03
CR1.3R-E8	3-174598	14.6	1.7	1.0	9.3	0.163	3.17E-03
CR1.3R-E10	3-174599	14.6	1.7	1.0	11.4	0.079	1.54E-03
CR1.3R-E12	3-174600	14	1.7	1.0	13.4	0.053	1.03E-03
CR1.3R-E14	3-174601	14	1.7	1.0	15.5	0.037	7.21E-04
CR1.3R-E16	3-174602	13.8	1.7	1.0	17.5	0.025	4.87E-04
CR1.3R-E18	3-174603	13.8	1.7	1.0	19.6	0.022	4.29E-04

Appendix-D

Iron Column Loading and Elution data

Appendix D-1: Iron Column Loading

Flow rate = 0.64 BV/h

Tank 241-AZ-102 (Envelope B) simulant

Resin batch # 991022smc-IV29

Column size = 2.7 cm

Sample ID	ADS #	Resin bed height (cm)	Flow rate (mL/min)	Flow rate (BV/h)	# BV processed	$[Fe]_{eff}$ (mg/L)	Fe profile [C/Co]
CR0.64-L5	3-174187	19.7	1.19	0.64	5	0.11	1.14E-01
CR0.64-L10	3-174188	19.7	1.19	0.64	10	0.24	2.54E-01
CR0.64-20	3-174189	19.7	1.19	0.64	19	0.13	1.38E-01
CR0.64-L30	3-174190	19.7	1.19	0.64	29	0.41	4.27E-01
CR0.64-L40	3-174191	19.7	1.19	0.64	38	0.41	4.28E-01
CR0.64-L50	3-174192	19.7	1.19	0.64	48	0.65	6.81E-01
CR0.64-L60	3-174193	19.7	1.19	0.64	57	0.77	8.06E-01
CR0.64-L70	3-174194	19.7	1.19	0.64	67	0.83	8.68E-01
CR0.64-L80	3-174195	19.7	1.19	0.64	76	0.87	9.02E-01
CR0.64-L90	3-174196	19.7	1.19	0.64	86	0.88	9.17E-01
CR0.64-L100	3-174197	19.7	1.19	0.64	95	0.91	9.48E-01

Appendix D-2: Iron Column Elution

Tank 241-AZ-102 (Envelope B) simulant

Resin batch # 991022smc-IV29

Column size = 2.7 cm

Sample ID	ADS #	Resin bed height (cm)	Flow rate (mL/min)	Flow rate (BV/h)	# BV processed	$[Fe]_{eff}$ (mg/L)	Fe profile [C/Co]
CR0.64-E1	3-174208	19.5	1.67	0.9	0.9	0.04	0.05
CR0.64-E2	3-174209	nm	1.67	0.9	1.8	2.65	2.76
CR0.64-E3	3-174210	nm	1.67	0.9	2.7	33.60	35.00
CR0.64-E4	3-174211	nm	1.67	0.9	3.6	6.85	7.14
CR0.64-E5	3-174212	15.3	1.67	0.9	4.5	2.24	2.33
CR0.64-E6	3-174213	15.3	1.67	0.9	5.4	1.33	1.39
CR0.64-E7	3-174214	nm	1.67	0.9	6.3	0.98	1.02
CR0.64-E8	3-174215	14.6	1.67	0.9	7.2	0.72	0.75
CR0.64-E10	3-174216	14.6	1.67	0.9	9.0	0.53	0.55
CR0.64-E12	3-174217	14.6	1.67	0.9	10.8	0.39	0.41
CR0.64-E14	3-174218	14	1.67	0.9	12.6	0.33	0.35
CR0.64-E16	3-174219	14	1.67	0.9	14.4	0.30	0.31
CR0.64-E18	3-174220	13.8	1.67	0.9	16.2	0.26	0.27

Appendix D-3: Iron Column Loading
Flow rate = 1.3 BV/h
Tank 241-AZ-102 (Envelope B) simulant
Resin batch # 991022smc-IV29
Column size = 2.7 cm

Sample ID	ADS #	Resin bed height (cm)	Flow rate (mL/min)	Flow rate (BV/h)	# BV processed	$[Fe]_{eff}$ (mg/L)	Fe profile [C/Co]
CR1.3-L5	3-173912	20.2	2.43	1.3	5	nm	nm
CR1.3-L10	3-173913	20.2	2.43	1.3	10	0.31	3.23E-01
CR1.3-L20	3-173915	19.9	2.43	1.3	20	0.46	4.79E-01
CR1.3-L30	3-173917	19.9	2.43	1.3	30	0.43	4.48E-01
CR1.3-L40	3-173919	19.9	2.49	1.3	40	0.53	5.52E-01
CR1.3-L50	3-173921	19.9	2.49	1.3	50	0.84	8.75E-01
CR1.3-L60	3-173923	19.9	2.39	1.3	60	0.72	7.50E-01
CR1.3-L70	3-173925	19.9	2.39	1.3	70	0.83	8.65E-01
CR1.3-L80	3-173927	19.9	2.39	1.3	80	0.85	8.85E-01
CR1.3-L90	3-173929	19.9	2.39	1.3	90	1.07	1.11E+00
CR1.5-L95	3-173930	19.5	2.45	1.5	94	nm	nm

Appendix D-4: Iron Column Elution
Tank 241-AZ-102 (Envelope B) simulant
Resin batch # 991022smc-IV29
Column size = 2.7 cm

Sample ID	ADS #	Resin bed height (cm)	Flow rate (mL/min)	Flow rate (BV/h)	# BV* processed	$[Fe]_{eff}$ (mg/L)	Fe profile [C/Co]
CR1.3-E1-1		19.5	1.75	1.06	0.2	3.49E-02	3.64E-02
CR1.3-E1-2		nm	1.73	1.05	0.4	3.29E-02	3.43E-02
CR1.3-E1-3		nm	1.73	1.05	0.6	1.32E-01	1.38E-01
CR1.3-E1-4		nm	1.73	1.05	0.8	1.39E-01	1.45E-01
CR1.3-E2	3-174175	15.3	1.73	1.05	1.9	16.8	1.75E+01
CR1.3-E4	3-174176	15.3	1.73	1.05	4.0	2.94	3.06E+00
CR1.3-E6	3-174177	nm	1.73	1.05	6.1	1.03	1.07E+00
CR1.3-E8	3-174178	nm	1.73	1.05	8.2	0.86	8.98E-01
CR1.3-E10	3-174179	nm	1.73	1.05	10.3	0.45	4.67E-01
CR1.3-E12	3-174180	nm	1.73	1.05	12	0.48	5.02E-01
CR1.3-E12	3-174181	14.8	1.79	1.09	15	0.44	4.60E-01
CR1.3-E16	3-174182	14.8	1.79	1.09	17	0.61	6.39E-01
CR1.3-E18	3-174183	14.8	1.79	1.09	19	0.28	2.88E-01
CR1.3-E20	3-174184	14.8	1.79	1.09	21	0.14	1.47E-01

Appendix D-5: Iron Column Loading
Flow rate = 8.2 BV/h
Tank 241-AZ-102 (Envelope B) simulant
Resin batch # 991022smc-IV29
Column size = 2.7 cm

Sample ID	ADS #	Resin bed height (cm)	Flow rate (mL/min)	Flow rate (BV/h)	# BV processed	$[Fe]_{eff}$ (mg/L)	Fe profile [C/Co]
CR8-L5	3-174095	20	15.1	7.9	5	nm	nm
CR8-L10	3-174096	19.8	14.39	7.6	10	0.43	4.45E-01
CR8-L20	3-174098	19.8	15.2	8.0	20	0.81	8.41E-01
CR8-L30	3-174100	19.8	15.2	8.0	30	0.59	6.15E-01
CR8-L40	3-174102	19.5	15.2	8.2	40	0.79	8.20E-01
CR8-L50	3-174104	19.4	15.2	8.2	50	0.76	7.87E-01
CR8-L60	3-174106	19.4	15.2	8.2	60	0.87	9.06E-01
CR8-L70	3-174108	19.4	15.2	8.2	70	0.88	9.17E-01
CR8-L80	3-174110	19.4	15.2	8.2	80	0.95	9.89E-01
CR8-L90	3-174112	19.4	15.2	8.2	90	0.91	9.50E-01
CR8-L100	3-174114	19.4	15.2	8.2	100	1.13	1.18E+00

Appendix D-6: Iron Column Elution
Tank 241-AZ-102 (Envelope B) simulant
Resin batch # 991022smc-IV29
Column size = 2.7 cm

Sample ID	ADS #	*Resin bed* height (cm)	Flow rate (mL/min)	Flow rate (BV/h)	# BV processed	$[Fe]_{eff}$ (mg/L)	Fe profile [C/Co]
CR8-E1	3-174120	19.5	1.75	1.06	1.1	4.83	5.14
CR8-E2	3-174121	nm	1.73	1.05	2.1	19.3	20.5
CR8-E3	3-174122	nm	1.73	1.05	3.2	9.80	10.4
CR8-E4	3-174123	nm	1.73	1.05	4.2	5.61	5.97
CR8-E5	3-174124	nm	1.73	1.05	5.3	3.96	4.21
CR8-E6	3-174125	nm	1.73	1.05	6.3	3.35	3.56
CR8-E7	3-174126	nm	1.73	1.05	7.4	2.76	2.94
CR8-E8	3-174127	14.6	1.62	0.98	8.3	3.50	3.73
CR8-E10	3-174128	14.6	1.62	0.98	10.3	3.25	3.46
CR8-E12	3-174129	14.6	1.62	0.98	12	3.38	3.60
CR8-E14	3-174130	14.6	1.62	0.98	14	2.80	2.98
CR8-E16	3-174131	14.6	1.62	0.98	16	nm	nm
CR8-E18	3-174132	14.6	1.62	0.98	18	0.18	0.19

Appendix D-7: Iron Column Loading
Flow rate = 1.3 BV/h –Repeat Test
Tank 241-AZ-102 (Envelope B) simulant
Resin batch # 991022smc-IV29
Column size = 2.7 cm

Sample ID	ADS #	Resin bed height (cm)	Flow rate (mL/min)	Flow rate (BV/h)	# BV processed	$[Fe]_{eff}$ (mg/L)	Fe Profile [C/Co]
CR1.3R-L5	3-174569	19.5	2.4	1.3	5	0.09	9.17E-02
CR1.3R-L10	3-174570	19.5	2.4	1.3	10	0.09	9.17E-02
CR1.3R-L20	3-174571	19.5	2.4	1.3	20	0.28	2.97E-01
CR1.3R-L30	3-174572	19.5	2.4	1.3	30	0.73	7.66E-01
CR1.3R-L40	3-174573	19.5	2.4	1.3	40	0.49	5.11E-01
CR1.3R-L50	3-174574	19.5	2.4	1.3	50	0.59	6.12E-01
CR1.3R-L60	3-174575	19.5	2.4	1.3	60	0.70	7.29E-01
CR1.3R-L70	3-174576	19.5	2.4	1.3	70	0.81	8.46E-01
CR1.3R-L80	3-174577	19.5	2.4	1.3	80	0.87	9.07E-01
CR1.3R-L90	3-174578	19.5	2.4	1.3	90	0.85	8.82E-01
CR1.3R-L100	3-174579	19.5	2.4	1.3	100	0.88	9.18E-01
CR1.3R-L110	3-174580	19.5	2.4	1.3	110	0.91	9.46E-01
CR1.3R-L120	3-174581	19.5	2.4	1.3	120	0.86	9.01E-01
CR1.3R-L130	3-174582	19.5	2.4	1.3	130	0.96	1.00E+00
CR1.3R-L140	3-174583	19.5	2.4	1.3	140	0.87	9.04E-01
CR1.3R-L145	3-174584	19.5	2.4	1.3	145	0.98	1.02E+00

Appendix D-8: Iron Column Elution
Tank 241-AZ-102 (Envelope B) simulant
Resin batch # 991022smc-IV29
Column size = 2.7 cm

Sample ID	ADS #	resin bed height (cm)	Flow rate (mL/min)	Flow rate (BV/h)	# BV processed	$[Fe]_{eff}$ (mg/L)	Fe profile [C/Co]
CR1.3R-E1	3-174591	19.5	1.7	1.0	1.0	5.11	5.32
CR1.3R-E2	3-174592	nm	1.7	1.0	3.1	20.7	21.6
CR1.3R-E3	3-174593	nm	1.7	1.0	4.1	4.84	5.04
CR1.3R-E4	3-174594	nm	1.7	1.0	5.2	1.87	1.95
CR1.3R-E5	3-174595	nm	1.7	1.0	6.2	1.25	1.30
CR1.3R-E6	3-174596	nm	1.7	1.0	7.2	0.90	0.94
CR1.3R-E7	3-174597	14.6	1.7	1.0	8.3	0.74	0.77
CR1.3R-E8	3-174598	14.6	1.7	1.0	9.3	0.66	0.69
CR1.3R-E10	3-174599	14.6	1.7	1.0	11.4	0.47	0.49
CR1.3R-E12	3-174600	14	1.7	1.0	13.4	0.41	0.43
CR1.3R-E14	3-174601	14	1.7	1.0	15.5	0.45	0.47
CR1.3R-E16	3-174602	13.8	1.7	1.0	17.5	0.36	0.37
CR1.3R-E18	3-174603	13.8	1.7	1.0	19.6	0.33	0.34