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Ion Exchange Column Tests Supporting Technetium Removal Resin Maturation

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December, 2013

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REVISION SUMMARY

Revision Summary		
Revision number	Summary of Changes	Date
0	Initial Issue	September, 2013
1	Add results from elevated temperature (45˚C) loading run; include results of computer modeling at both temperatures	December, 2013

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EXECUTIVE SUMMARY

The primary treatment of the tank waste at the DOE Hanford site will be done in the Waste Treatment and Immobilization Plant (WTP) that is currently under construction. The baseline plan for this facility is to treat the waste, splitting it into High Level Waste (HLW) and Low Activity Waste (LAW). Both waste streams are then separately vitrified as glass and sealed in canisters. The LAW glass will be disposed onsite in the Integrated Disposal Facility (IDF). There are currently no plans to treat the waste to remove technetium, so its disposition path is the LAW glass. Due to the soluble properties of pertechnetate and long half-life of ^{99}Tc, effective management of ^{99}Tc is important to the overall success of the Hanford River Protection Project mission. Options are being explored to immobilize the supplemental LAW portion of the tank waste, as well as to examine the volatility of ^{99}Tc during the vitrification process. Removal of ^{99}Tc, followed by off-site disposal, would eliminate a key risk contributor for the IDF Performance Assessment (PA) for supplemental waste forms, and has potential to reduce treatment and disposal costs. Washington River Protection Solutions (WRPS) is developing some conceptual flow sheets for supplemental LAW treatment and disposal that could benefit from technetium removal. One of these flow-sheets will specifically examine removing ^{99}Tc from the LAW feed stream to supplemental immobilization. To enable an informed decision regarding the viability of technetium removal, further maturation of available technologies is being performed.

This report contains results of experimental ion exchange distribution coefficient and column resin maturation kinetics testing using the resin SuperLig® 639[a] to selectively remove perrhenate from simulated LAW. This revision includes results from testing to determine effective resin operating temperature range. Loading tests were performed at 45˚C, and the computer modeling was updated to include the temperature effects.

SuperLig® 639 is an elutable ion exchange resin available from a vendor. In the tank waste, ^{99}Tc is predominantly found in the tank supernate as pertechnetate (TcO_4^-). Perrhenate (ReO_4^-) has been shown to be a good non-radioactive surrogate for pertechnetate in laboratory testing for this ion exchange resin, and the performance bias is well established. Removal of pertechnetate from tank waste samples using SuperLig® 639 has been demonstrated many times, but the current tests examine removal using new batches of resin and a substantially different tank waste composition that represents the model-generated average of the entire tank waste inventory after processing in the WTP.

Equilibrium contact testing indicated that this batch of SuperLig® 639 resin has good performance, with an average perrhenate distribution coefficient of 291 mL/g at a 100:1 phase ratio. This slightly exceeds the computer-modeled equilibrium distribution. Column testing at 24˚ ±1°C and 45˚ ±1°C (two campaigns) and ~3.2 BV/hr examined performance of the resin for perrhenate removal. Three columns were run in series to achieve a high decontamination factor, while maximizing loading of the first column. At 24°C the first column reached 65% Re breakthrough at 155 bed volumes (BV), while also maintaining <1% Re breakthrough on the third column through approximately 140 bed volumes. At 45°C, the first column reached 73% breakthrough at 106 bed volumes (BV), while maintaining better than 96% Re removal after the third column through approximately 87 bed volumes. The perrhenate was then stripped from the resin beds by elution with warm water. Since this resin has even higher selectivity for pertechnetate than perrhenate, this performance indicates that a viable ^{99}Tc-removal process

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[a] SuperLig is a trademark of IBC Advanced Technologies, Inc., American Fork, UT

could be developed that would remove 99% of the pertechnetate from the LAW. In that conceptualized process, the ^{99}Tc could then be eluted and sent for separate immobilization, while the resin bed is returned to service for multiple cycles.

The modeling agreed well with the experimental data for perrhenate removal with minor adjustments. Predicted breakthrough performance was on average within about 20% of measured values. For the full-scale system, modeling was used to predict the ^{99}Tc removal performance. For a flow rate of ~3.3 BV/hr and 1.37 m^3 of resin at 25˚C, three columns in series will process 207 BV (75,000 gallons) of LAW prior to an accumulated breakthrough of 1%. At 45˚C, the quantity of waste processed per cycle drops by ~50%. Operationally, this means that to achieve the same decontamination at 45˚C, the elution would occur twice as often, generating twice as much eluate that would need to be evaporated or disposed.

Depending on the selection of deployment options, additional work is needed to examine other conditions for treatment of the LAW, such as higher liquid density. If operation at 45˚C is desired, resin stability testing would be needed as well.

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LIST OF ABBREVIATIONS

ASTM	American Society of Testing and Materials
BV	Bed Volumes
°C	Celsius
C	Concentration
DI	Deionized
DOE	U.S. Department of Energy
DST	Double Shell Tank
F	resin dry weight correction Factor
g	Gram
HLW	High Level Waste
hr	Hour
HTWOS	Hanford Tank Waste Operations Simulator
ICP-ES	Inductively Coupled Plasma Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
ID	Internal Diameter
IDF	Integrated Disposal Facility
IX	Ion Exchange
K_d	Distribution Coefficient
L	Liter
LAW	Low Activity Waste
M	Molarity
m	meter
mg	milligram
min	minute
mL	milliliter
PA	Performance Assessment
SRNL	Savannah River National Laboratory
SST	Single Shell Tank
V	Volume of liquid (mL)
WRPS	Washington River Protection Solutions
WTP	Waste Treatment and Immobilization Plant

1.0 Introduction

Savannah River National Laboratory (SRNL) is performing studies on behalf of WRPS to support the disposition of tank waste at the DOE Hanford site near Richland, Washington. The primary treatment of the tank waste will be done in the WTP that is currently under construction. The baseline plan for this facility is to treat the waste, splitting it into HLW and LAW. Both waste streams are then separately vitrified as glass and sealed in canisters. The LAW glass is the disposition path for the soluble ^{99}Tc, and it will be disposed onsite in the IDF. Because ^{99}Tc has a very long half-life (211,000 years) and is highly mobile [Icenhower, 2008, 2010], it has potential to be a major dose contributor to the PA of the IDF [Mann, 2003]. Due to the soluble properties of pertechnetate, and the potential for impact to the PA, effective management of ^{99}Tc is important to the overall success of the River Protection Project mission. Options are being explored to immobilize the LAW portion of the tank waste, as well as to examine the volatility of technetium during the vitrification process. Removal of ^{99}Tc, followed by off-site disposal of technetium from the supplemental LAW, would eliminate a key risk contributor for the IDF PA for supplemental waste forms, and has potential to reduce treatment and disposal costs. WRPS is developing some conceptual flow sheets for supplemental LAW treatment and disposal that could benefit from technetium removal. One of these flow-sheets will specifically examine removing ^{99}Tc from the LAW feed stream to supplemental immobilization. To enable an informed decision regarding the viability of technetium removal, further maturation of available technologies is being performed.

Technetium in the tank waste is predominantly found in the tank supernate as pertechnetate (TcO_4^-), although there is also a soluble non-pertechnetate, and some insoluble technetium, which is presumably Tc(IV) oxide. Technology development for ^{99}Tc removal has focused on pertechnetate separations. No methods have been identified that can remove the soluble non-pertechnetate specie(s) unless first destroyed and converted to pertechnetate. The insoluble technetium oxide is removed by filtration.

This report contains results of experimental ion exchange column testing using the resin SuperLig® 639 to selectively remove perrhenate from simulated supplemental LAW and modeling of the column performance. SuperLig® 639 is an elutable ion exchange resin available from a vendor. This document summarizes the testing performed to further mature the technical readiness of SuperLig® 639 for treatment of LAW at Hanford, and operation at elevated temperature. The WTP baseline flow-sheet condition for supplemental LAW feed that exits the pretreatment facility is at 45˚C. Removal of pertechnetate from tank waste samples using SuperLig®639 has been demonstrated many times [McCabe, 2013], but the current tests examine removal using new batches of resin and a substantially different tank waste composition that represents the entire tank waste inventory, and extends operation to 45˚C. The new batches of resin were produced to meet a specification defined as part of this program and manufactured by the vendor [Bruening, 2013]. Prior work had focused on individual Double-Shell Tank (DST) wastes, and did not encompass the high nitrate-containing feeds expected from dissolution of saltcake in Single Shell Tanks (SST). The simulant formulation was derived from a computer model of the WTP LAW composition that accounts for the tank retrieval schedule, internal recycle streams, and composition changes due to pretreatment processing, and was mathematically averaged. This composition (Table 1-1) was based on Hanford Tank Waste Operations Simulator (HTWOS) model, and adjusted to create an entirely soluble aqueous simulant [Russell, PNNL-22352, 2013]. In the current tests, perrhenate (ReO_4^-) is used as a non-radioactive substitute for pertechnetate. This has been shown to be a good substitute, once adjusted for the difference in performance [Hamm, 2013]. Testing examined performance of SuperLig®639 for perrhenate removal using three columns in series to achieve a high decontamination factor, while maximizing loading of the first column. The conceptual flowsheet is to remove the ^{99}Tc by loading it onto the resin, then eluting it for separate disposal, and returning the resin bed to service for additional cycles.

Table 1-1. HTWOS Average 5 M Simulant Target Molar Composition

Ion	Molarity (M)
NO_3^-	1.60
OH^-	1.611
SO_4^{-2}	0.086
$Al(OH)_4^-$	0.307
NO_2^-	0.565
CO_3^{-2}	0.274
K^+	0.0328
Acetate	0.0385
F^-	0.0316*
HPO_4^{-2}	0.049
Cl^-	0.042
ReO_4^-	4.5E-05
Total [Na+]	5.0

*Fluoride was omitted from the preparation

2.0 Experimental Procedure

2.1 Ion Exchange Resin

The resin for batch contacts and in the ion exchange columns was SuperLig® 639 resin from lot # 130611552-56, manufactured by IBC Advanced Technologies, Inc., in American Fork, Utah in May, 2013 [Bruening, 2013].

Figure 2-1 shows an optical micrograph of the as-received resin. It is generally spherical and some particle size variation is clear. The beads are porous despite the glossy solid appearance of the surface of the beads, with a mean wet particle diameter of approximately 774 microns. The resin was not observed to shrink or swell appreciably (≤10%) under any condition during this testing.

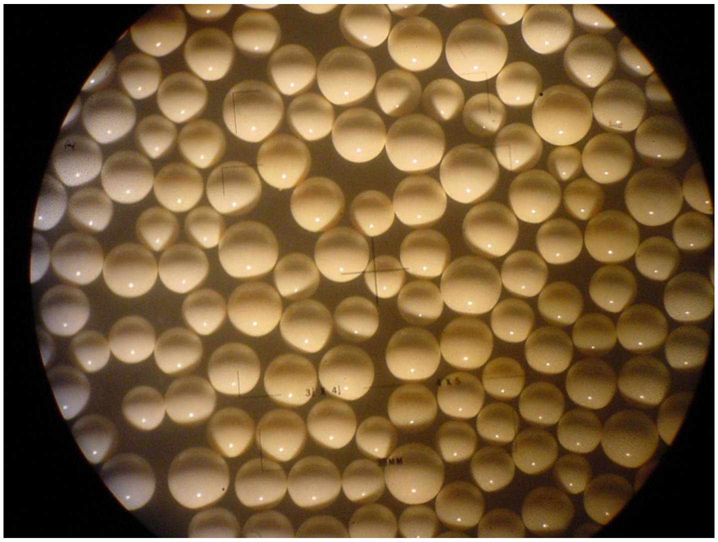

Table 2-1. Optical Micrograph of SuperLig® 639 Beads.

The pretreatment procedure for the as-received resin involved two stages: soaking the resin in ~65°C Deionized (DI) water followed by a 0.25 M NaOH flush to displace the water. Specifically, resin was measured into individual vials filled with DI water, shaken vigorously to displace air within the beads and discourage floating, and placed in a water bath. The bath was heated to 65˚ ±7°C for 3 hours. The resin beads were left in the bath for another 21 hours at room temperature. The resins were then shaken in a shaker for an hour before being transferred to their respective columns with 0.25 M NaOH. Column 1 had 4.9001 grams of resin while column 2 had 4.899 grams, and column 3 had 4.902 grams (resin weight as received and before pretreatment).

2.2 Simulant Feed Composition

HTWOS 5M Average [Na] Mass Based Simulant spiked with perrhenate was used for loading. Sodium perrhenate (0.0489 g) was added to the 4.0 L of premixed simulant to achieve a concentration of 8.33 mg/L of Re (4.48×10^{-5} M [ReO_4^-]). Detailed simulant information can be found in Appendix A. Sodium fluoride was omitted from the simulant preparation procedure. This is not expected to impact the perrhenate removal results because the fluoride ion does not appreciably interact with the resin, as evidenced by good agreement with modeling results when only sodium, potassium, nitrate, and ionic strength are considered [Hamm, 2013]. Detailed analysis results can also be found in Laboratory Notebook WSRC-NB-2001-00063.

For computer modeling, a best value of the rhenium concentration in the simulant is needed. Table 2-1 shows the actual mass measurement of sodium perrhenate added to 4.0 Liter (L) of simulant, which should be the most accurate individual value. The next four rows contain four analytical measurements from column samples obtained by Inductively Coupled Plasma – Emission Spectroscopy (ICP-ES) and Inductively Coupled Plasma –Mass Spectroscopy, respectively. The sixth row shows the measurement #3 that was made for the batch contact sample set using ICP-ES. The last row shows the average of the analytical measurements and one standard deviation. Calculations of removal fraction (Concentration/initial concentration i.e., C/C_0) were made using the control sample concentration within each sample set to reduce analytical bias. The result of measurement #3 is anomalously low for unknown reasons. The mass measurement during the simulant preparation, averaged with equal weighting of the average of the analytical measurements was recommended for modeling use (8.0 mg/L Re ($4.3x10^{-5}$ M)).

Table 2-2. Rhenium Concentration Measurements.

Method	Re Concentration, mg/L
Simulant Prep. Batching	8.33
ICP-ES Measurement #1	7.46
ICP-ES Measurement #2	7.57
ICP-MS Measurement #1	8.05
ICP-MS Measurement #2	9.04
ICP-ES Measurement #3	5.91
Average of analytical measurements	7.7 +/- 1.1
Average of both methods (used for modeling) (7.7 + 8.3)/2	8.0

2.3 Ion Exchange Equipment

Three ion exchange columns as shown in Figure 2-2 were connected in series as lead, lag, and polish with sampling points for the effluent of each. Custom-made, jacketed borosilicate columns (1.56 cm internal diameter), shown in Figure 2-3, were used to contain the resin beds.

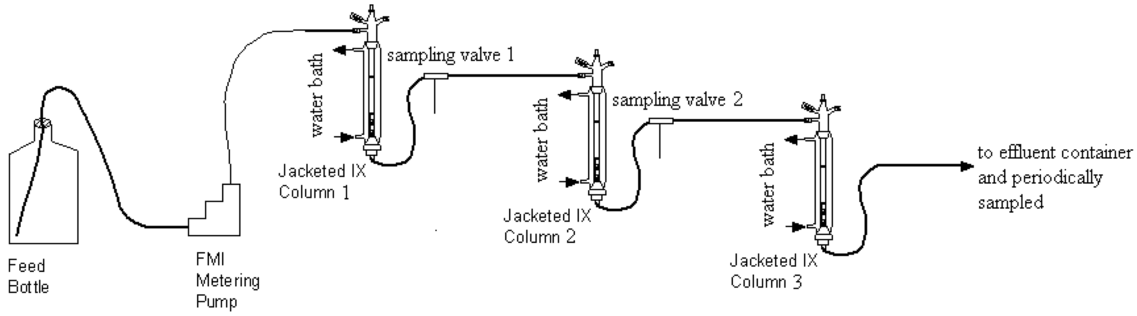

Figure 2-1. Series of Three Small Columns and Sampling Points.

The total height of the resin bed reservoir scale was approximately 10 cm, marked in millimeters. Each resin bed rested on top of a 200 mesh stainless steel screen tack-welded to a stainless steel ring and fitted with an O-ring seal at the 1 cm mark in the column. The empty space between the screen and the Teflon® plug in the bottom of each column was filled with 3 mm diameter glass beads to minimize dead space in the flow path.

The columns were connected by 1/16" internal diameter (ID) fluorinated ethylene propylene tubing. Lines entering the columns were secured by Swagelok® Ultra Torr Straight fittings mounted to removable glass heads that allowed the line to be quickly removed and reinserted by loosening the nut. The glass heads were connected to the column by a conical ground glass fitting with a plastic screw tight nut. The tubing was fed out of the columns through Swagelok® fittings mounted in a Teflon® plug. Column headspaces were vented so that atmospheric pressure was always present. Liquid flow was always driven by gravity after being pumped to the top of the first column. Liquid levels were controlled by elevation of the downstream tubing and the drip point at the top of the next column or over the collection jar.

Fluid Metering (Fluid Metering, Inc.) pumps provided controlled flow rates. Two different pumps were used for fast and slow steps in the campaign. Flow calibrations for the pumps are in Appendix B. Feed temperatures were monitored with three type-T thermocouples, inserted through a port in the heads, read by a 12 channel, DigiSense® scanning thermometer. The temperature was ambient room temperature during loading and displacement for the first test and heated during the second. All elutions were heated to 65˚C. A Neslab® RTE-111 water bath kept the column temperature constant during elution. Teflon® quick-connect fittings and flexible Polyvinyl chloride tubing were used to connect the water bath to the column jackets.

Figure 2-2. Photograph of a Column with Bed of SuperLig® 639 Resin

Water displacement measurements were made to estimate dead volumes in the apparatus. Liquid first saw a liquid headspace in column 1, then the first resin bed (down-flow), then a glass bead-filled volume below the screen, then tubing/sample valve to the top of column 2. The liquid then encountered the same series of volumetric spaces for columns 2 and 3.

Estimated volume of the liquid space above each bed was about 1.8 cm times the column internal flow area (volume = 3.4 mL). This fluctuated during the run/sampling by as much as 2 mL (but the bed remained submerged in liquid at all times). The column bottoms were filled with glass beads, with liquid volumes of about 7 mL each. Tubing from the bottom of column 1 to the top of column 2 was about 1.65 mL (about 2.7 feet of 1/16" ID tubing). Similar tubing from bottom of column 2 to top of column 3 was 1.86 mL. The tubing from column 3 to the drip point was 1.91 mL. Sampling valves were equidistant between columns. No volume leading to the column 1 headspace is relevant because that line was flushed with simulant before starting the campaign.

Table 2-3. Estimated Dead Volumes in the Apparatus

Dead Space	Approximate measured volume, mL
1 foot of tubing	0.62
Bead-filled space at the bottom of a column	7.46
Liquid above resin*	3.4 ± 2
Tubing from column 1 to 2	1.65
Tubing from column 2 to 3	1.86
Tubing from column 3 to drip point	1.91

*varied to accommodate liquid density while maintaining flow rate

2.4 Operation for the Three-Column Campaigns

The first 2-day loading campaign was planned to provide at least 150 bed volumes of feed to the first column at 25°C. The second loading campaign at 45°C loading was shortened to 106 BV because results from the first campaign gave assurance that the shorter second campaign would still see at least 50% breakthrough in the first column. The steps for the cycle are provided in Table 2-3. The ion exchange treatment took place in four stages: pretreatment, loading, displacement, and elution. During the first two stages, liquid was pumped to the lead column only and gravity fed to the other columns. Pretreatment (6 BV of 0.25 M NaOH) was followed by simulant loading.

Table 2-4. Steps for Ion Exchange Operation

Treatment Stage	Rate (BV/hour)	Rate (mL/min)	Duration (hours)	Temperature (°C)	Volume (mL)
Pretreatment	1.0	0.1667	6	25	53*
1st Loading campaign	3.2-3.4	0.5667	48	24 +/- 1	1698*
2nd loading campaign	3.2-3.4	0.5667	33.6	45 +/- 1	1150*
Displacement	3.0	0.5000	1	25	See tables 3-3 & 3-6
Elution	1.0	0.1667	20	65	

*pumped to 3 columns in series

For the next two steps, the columns were disconnected from each other, displaced with dilute caustic (0.1 M), and eluted with warm water separately. The test matrix of Table 2-3 was developed for 65% breakthrough on the lead column and a bed volume of 10 mL, but the actual reported results are based on the measured bed volume. The second loading campaign with 45°C loading still followed the program of Table 2-3 except for the temperature and feed volume.

Sampling events occurred approximately every three hours, with the first 13 hours being unattended operation overnight (unattended span for the first loading campaign only). Sampling thus commenced early the next day, through the next night, and through the second day, ending the 48-hour loading campaign. The second loading campaign with the 45 °C loading was sampled every 3 hours.

Sampling was done in a way to minimize flow disturbances in the apparatus. At the appointed sample times, column 3 was sampled first by placing a sample vial under its output drip point for 10 minutes. This did not impose any flow disturbance upstream. It allowed flow rate measurement by weight of sample for the 10 minutes. Column 2 was sampled next, with the operation of its sample valve stopping flow to column 3. The sample point at the outlet of column 1 was sampled last. Sample points were flushed by the discharge of a few mL of liquid into a spare vial before fresh sample liquid was actually collected in the sample vial. All sample masses were recorded, and sampling in each case was controlled to be 10 or 11 minutes.

Feed flowrate was measured by averaging the sample volumes collected at column 3 (collection time was known). An alternative method was to measure the feed mass pumped out of the feed bottle in the whole campaign. Flow results are given in Sections 3.2.1 and 3.3.1 below.

2.5 Batch Contact Tests

Batch Contact tests were performed using as-received SuperLig® 639 Lot #130611552-56, manufactured by IBC Advanced Technologies, Inc., in American Fork, Utah in May, 2013. Dry resin was weighed and placed in plastic bottles. Simulant was added to achieve either ~20:1 or 100:1 volume:resin phase ratios for contact batches. The precise ratios were based on mass measurements of simulant and resin beads. The bottles were agitated on a shaker for 51 hours at 26.6 °C. After contact, the liquids were submitted for Re analysis by ICP-ES.

2.6 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. Completion of this work fulfills the requirements of Tasks 4.2 and 4.5 of the Task Technical and Quality Assurance Plan for Technetium Ion Exchange Resin Manufacturing Maturation, SRNL-RP-2012-00708, Revision 1. (IEWO M0SRV00074 Tasks 3.5 and 3.8)

3.0 Results and Discussion

3.1 Batch Contacts

Batch contacts were performed with fresh subsamples of the same batch of resin as the column tests, but it was not pre-conditioned (resin wetting is not usually an issue with agitated batch contacts). Results of the Re batch contacts are shown in Tables 3-1 and 3-2. Distribution Coefficient was performed utilizing Equation 1:

$$K_d = [(C_0/C_f)-1][V/M*F] \qquad \text{(Eqn. 1)}$$

where

C_0 = initial concentration
C_f = final concentration
V = Volume of liquid (mL)
M = mass of resin (g)
F = resin dry weight correction factor (F = 1 due to <0.2 wt% moisture as measured by vendor)

Table 3-1. Perrhenate Distribution Coefficient Results at 100:1 Phase Ratio

Parameter	Sample 1	Sample 2	Sample 3
Resin (g)	0.2000	0.2001	0.2002
Liquid (mL)	19.93	19.91	19.93
Initial [Re] (mg/L)	5.92	5.92	5.92
Final [Re] (mg/L)	1.49	1.53	1.51
K_d (mL/g)	297	285	291
Average K_d (mL/g)	291		
Standard Deviation	5.8		

Table 3-2. Perrhenate Distribution Coefficient Results at 20:1 Phase Ratio

Parameter	Sample 1	Sample 2	Sample 3
Resin (g)	1.0013	1.0007	1.0008
Liquid (mL)	19.93	19.92	19.94
Initial [Re] (mg/L)	5.92	5.92	5.92
Final [Re] (mg/L)	0.410	0.324	0.553
K_d (mL/g)	268	344	193
Average K_d (mL/g)	268		
Standard Deviation	75		

Data from the distribution coefficient measurements were used to benchmark the computer model parameters for this particular batch of resin (Appendix C). Only a slight adjustment of the modeling parameters were needed to match this particular batch of resin (Table C-1).

3.2 Three Column Campaign at ~25 °C

3.2.1 *Loading*

The loading phase flow rates were adjusted to fit the swelled resin bed volume of 10.89 mL. Loading took place at an average flow rate of 3.22 BV/hr. The effluent from the first 17 hours of the loading stage, diluted by initial liquid in the beds, was discarded. Effluent from the remainder of the run was retained for future use. The two flow results were 0.59 +/- 0.02 mL/min for 12 samples and 0.58 mL/min for the campaign average. Data were processed using recorded time and a flow rate of 0.585 mL/min. The feed pump ran for 48 hours, 22 minutes.

Sampling of the loading stage was conducted approximately every 10 BV except for the 13 hour initial overnight operation. When a column output was to be sampled, liquid was collected for 10 or 11 minutes per column. Collection began with a sample from column 3 and continued upstream so that sampling did not affect the function of columns not yet sampled. Beginning with the second sampling set, the sampling valves for columns 1 and 2 were allowed to drain into a beaker before samples were collected to displace any residual fluid from the last sample. During each sampling set, column parameters were also collected, including temperature, bed heights, and liquid levels.

During loading of the columns, 155 BV were processed through the lead column. Reaching greater than 50% breakthrough was desired to demonstrate the full loading profile on the first column and a measureable profile on the third column. Column 1 exceeded that by reaching 65% breakthrough by the end of loading. ICP-ES analysis of column 3 data did not detect any measurable rhenium in any of the samples, so Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) was used to obtain more data from column 2 and 3 samples. Its detection limit of about 0.05 mg/L Re allowed some data to be measured for column 3, and a minimum measurable C/C_0 of 0.0063 was obtained. Detailed experimental results can be found in Appendix B. Note that fewer than 155 BV were processed through columns 2 and 3 because of the “loss” of effluent from column 1 during sampling. This loss is accounted for in the data presented below.

The breakthrough curves (Figure 3-1) have a gradual slope, indicating the mass transfer rate of the resin was quite slow, which is common. Contributing causes include the high concentration of nitrate and low concentration of potassium, and perhaps resin porosity. This combination of nitrate and potassium is challenging, since nitrate is the chief competitor to perrhenate/pertechnetate absorption.

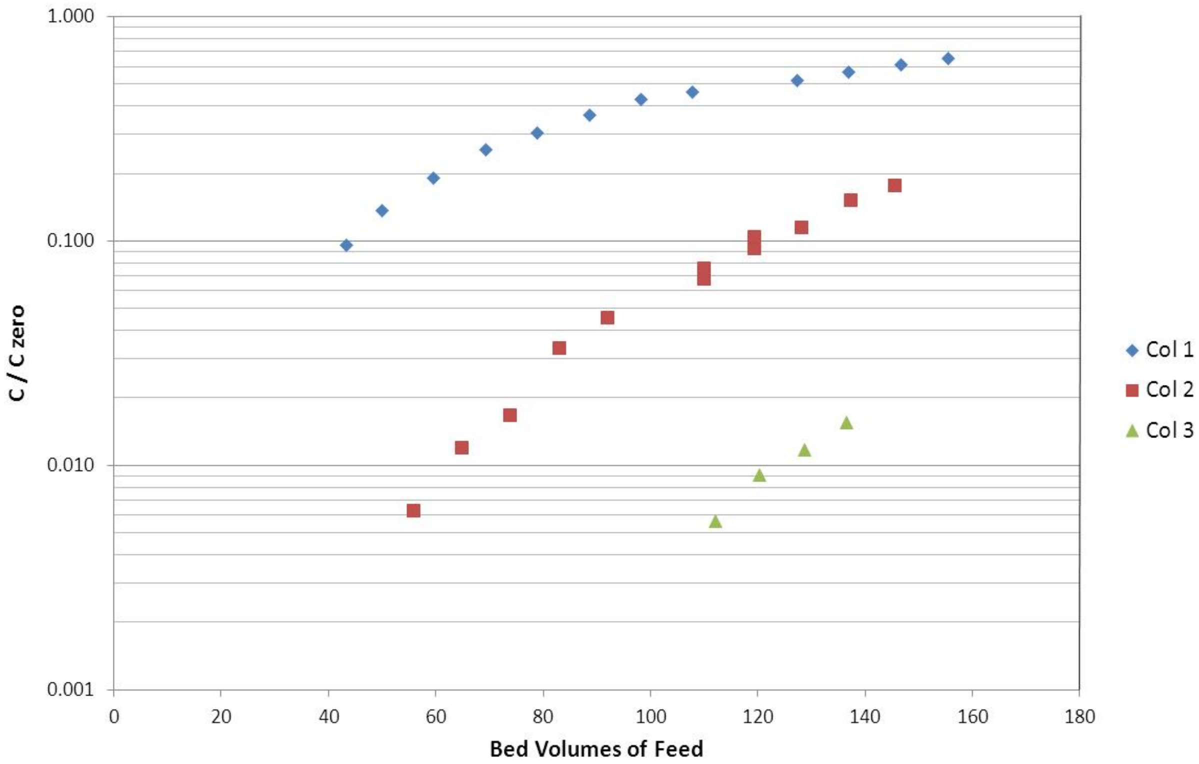

Figure 3-1. Rhenium Breakthrough Curves for the Three Columns

3.2.2 *Displacement*

The three columns were displaced separately using 0.1 M NaOH solution. The change in feed fluid densities, from 1.235 g/mL for simulant to 1 g/mL for eluent, required the exit lines to be adjusted lower than their loading positions. The pump was set to a slower flow rate for this displacement stage than for loading and connected to each column for one hour before they were eluted. Displacement effluent from each column was collected in one sample container per column.

Table 3-3 shows the as-measured conditions for the displacement step for each of the columns. In each case about three BV of 0.1 M NaOH was pumped through each column individually in one hour.

Table 3-3. Displacement Data for the 25 °C Campaign

Column	Mass Fed, g	Mass Collected, g	Average bed Volume, mL*	BV/hr for the one hour	Rhenium Concentration, mg/L
Column 1	32.85	34.50	10.5	3.12	6.32
Column 2	30.81	35.99	10.3	2.98	<1
Column 3	31.24	35.6	10.5	2.97	<1

*from bed level measurement

Masses collected in each case were higher than liquid masses pumped in because simulant of higher density (>1.23 g/ml) was being displaced and mixed with the 0.1 M NaOH. At room temperature 0.1 M NaOH has a density of 1.003 g/mL.

3.2.3 *Elution*

The primary focus of this program was to examine the loading profile with this waste composition, and eluate of the lead column was sampled to ensure the resin could be re-used in subsequent experiments. The columns were eluted immediately following their displacements, beginning with column 3. Columns were eluted separately with 65˚ ±3°C DI water for 20 hours at 0.95 BV/hr, 1.00 BV/hr, and 1.02 BV/hr, for columns 1, 2, and 3 respectively. Elution effluents for columns 2 and 3 were collected in a single container, but were not analyzed. However, column 1 effluent was routed to a fractional sampler, set to collect samples in ½ hour increments. All elutions were started in the afternoon and set to run overnight. The sampling mechanism for column 1 malfunctioned during the unsupervised night shift, presumably due to an air bubble caught in the line, and most of the elution samples were not collected.

Table 3-4 shows that only a cumulative volume of less than three bed volumes of eluate was collected (3 x BV = 32.7 mL). However, the sample results show that rhenium was concentrated almost 100 times over feed values. The elution data (Table 3-4) also show Na/K mole ratios of as little as 11.2, when the feed Na/K mole ratio is over 150. The eluate was enriched in potassium by 14-fold over the sodium level, in this case. This is consistent with past work showing the greatly increased affinity that the resin has for potassium over sodium [King, 2003b]. In that work potassium enrichments of 4 to 16-fold, compared to feed, were observed. This current result is within that range.

Table 3-4. Elution Data from Column 1

Sample	Volume mL	Cum. Vol. mL	$[K^+]$ mg/L	$[Na^+]$ mg/L	$[Re^{+7}]$ mg/L	$[Na^+]/[K^+]$ Mole ratio
1,2	2.7	2.7	268	3190	29.2	20.2
3	11.0	13.7	452	2730	170	12.3
4	0.3	14.0	360	2600	721	10.3
5	9.2	23.2	228	1540	452	11.5
6	2.0	25.2	85.4	596	677	11.9
7	0.3	25.5	77.2	509	636	11.2
8	0.6	26.1	69.1	459	637	11.3

The total volume of liquid used to elute the lead column (202 mL), was about 12% of the volume of feed processed (1698 mL), indicating good volume compression. The volume of eluate could be further decreased by evaporation of this dilute stream.

The volume of the resin columns during various operations is shown in Table 3-5. Minimal shrinking or swelling was observed, and no floating of resin was observed.

Table 3-5. Resin Bed Heights

Condition	Column 1 Height (cm) (± 0.1 cm)	Column 2 Height (cm) (± 0.1 cm)	Column 3 Height (cm) (± 0.1 cm)
Preconditioning	5.5	5.2	4.9
Feed Loading	5.7	5.6	5.6
Displacement	5.5	5.3	5.4
Elution	5.5	5.3	5.3

3.3 Three Column Campaign at 45 °C

The same ion exchange setup and resin beds were used for a second campaign where loading was to be performed at nominally 45 °C. This section gives the results of that work.

3.3.1 *Loading*

Measurement of resin bed volumes for the loading phase flow averaged 10.55 mL. The two measured flow results were 0.55 +/- 0.08 mL/min from 11 sample measurements and 0.57 mL/min for the campaign average. Data were processed using recorded time and a flow rate of 0.56 mL/min. Loading took place at an average flow rate of 3.19 BV/hr. The loading phase lasted 33.6 hours and sampling of the three columns was done with three hours spacing, or just under every 10 BV. During this sampling evolution, samples were collected for 10 minutes per column. Collection began with a sample from column 3 and continued upstream as before so that sampling did not affect the function of columns not yet sampled. During each sampling set, column parameters were also collected, including temperature, bed heights, and liquid levels.

During loading of the columns, 106 BV were processed (input to column 1). Column 1 reached 73% breakthrough by the end of loading (Figure 3-2). ICP-MS analysis for rhenium was used as before to augment ICP-ES analysis because of its lower detection limits. Note that fewer than 106 BV were processed through columns 2 and 3 because of the “loss” of effluent from upstream columns during their sampling. This loss is accounted for in the data plotted below. Detailed experimental results can be found in Appendix B. C/C_0 for rhenium was limited at the low end by the detection limits from ICP-MS.

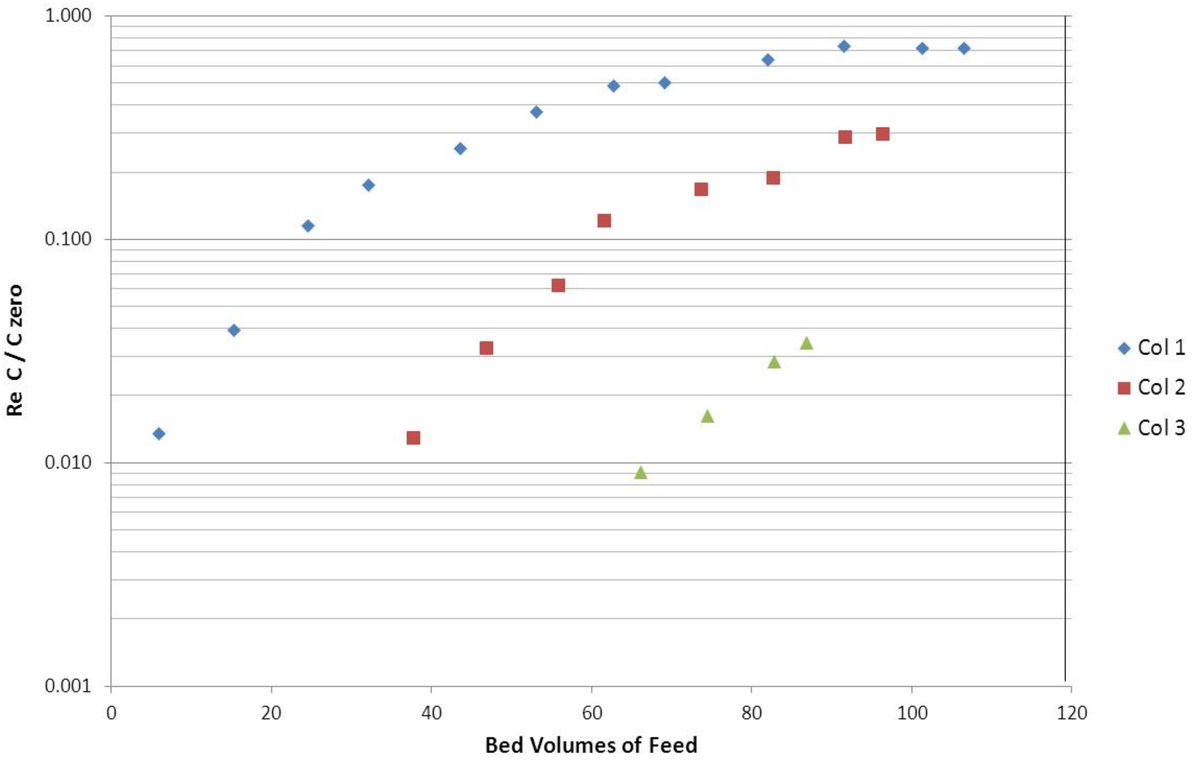

Figure 3-2. Rhenium Breakthrough Curves at 45 °C

3.3.2 *Displacement*

Table 3-6 shows the conditions for the displacement step for each of the columns. Displacement temperature was nominally 25 °C. In each case about three BV of 0.1 M NaOH was pumped through each column individually in one hour.

Table 3-6. Displacement Data for the 45 °C Campaign

Column	Mass Fed, g	Mass Collected, g	Average bed Volume, mL*	BV/hr for the one hour	Rhenium Concentration, mg/L
Column 1	34.57	38.23	10.5	3.29	3.06
Column 2	34.58	35.75	10.5	3.29	1.18
Column 3	34.52	38.24	10.3	3.35	<1

*from bed level measurement

It is to be noted that the pump metered a consistent quantity of liquid into each column during each 1-hour displacement. However, masses collected in each case were higher because simulant of higher density (>1.23 g/ml) was being displaced and mixed with the 0.1 M NaOH. At room temperature 0.1 M NaOH has a density of 1.003 g/mL.

3.3.3 *Elution*

Columns were eluted separately with 65 ±3°C DI water for 20 hours at 0.96 BV/hr. Elution effluents for columns 2 and 3 were collected in a single container and those were analyzed for sodium, potassium, and rhenium. However, column 1 effluent was routed to a fractional sampler set to collect samples in 40 minute increments. All elutions were started in the afternoon and set to run overnight. Column 1 sampling results are shown in Figures 3-3 and 3-4 below.

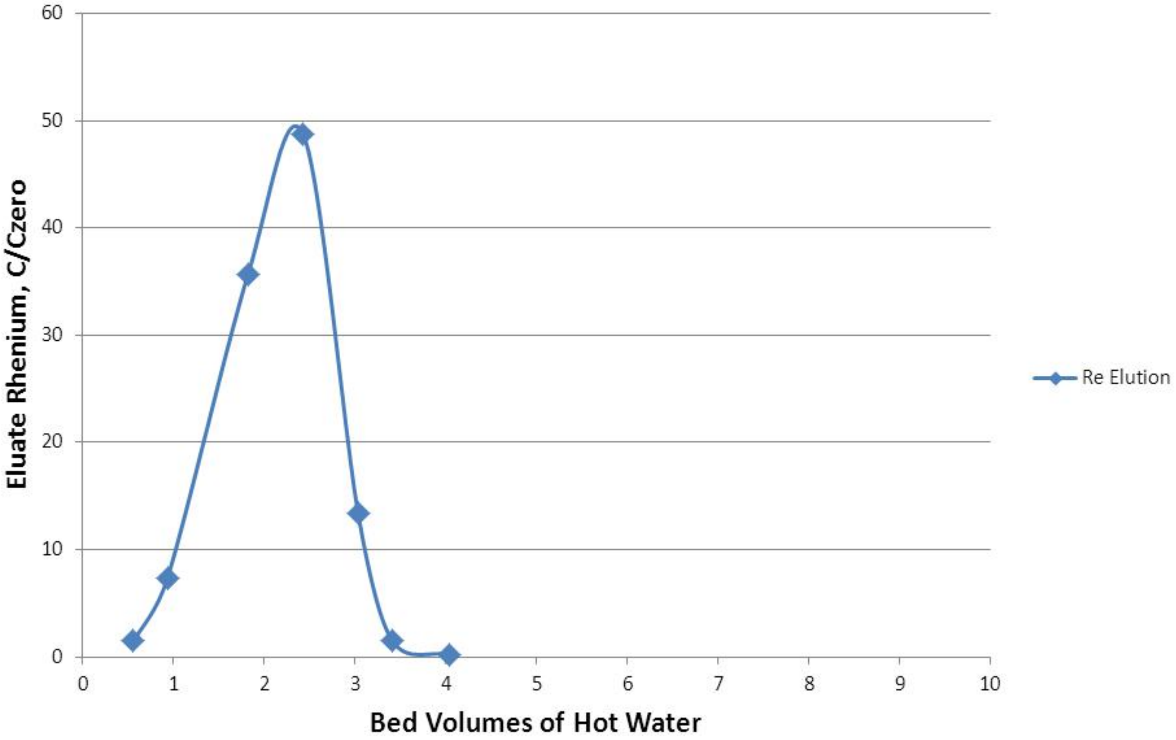

Figure 3-3. Elution of Rhenium in the Second Campaign

Figure 3-3 shows that C/C_0 was almost 50 times the feed rhenium concentration, and that elution was essentially complete in only 4 bed volumes of hot water. To obtain an elution curve on a log scale of several decades would require the much better detection limits of a radioactive experiment. The duration of effective elution was also found to be about 4 BV for six experiments in [King, 2003a]. See Figures 4-7 and 4-14 in that report. The peak C/C_0 values in that work ranged from 35 to 170. The tall narrow elution peaks that are characteristic of this resin would add variability to the measured maximum peak height. Detailed experimental results can be found in Appendix B.

Figure 3-4 shows the elution behavior of sodium (log scale, better detection limits), and also the ratio of potassium to sodium mass coming off of the eluting resin. This mass ratio is shown here because it is much higher than it was in the simulant (0.011). The more than 10X concentration factor found here demonstrates the special affinity that

SuperLig® 639 has for potassium over sodium. This is true even when the resin is near the end of elution where it is in the presence of essentially pure water.

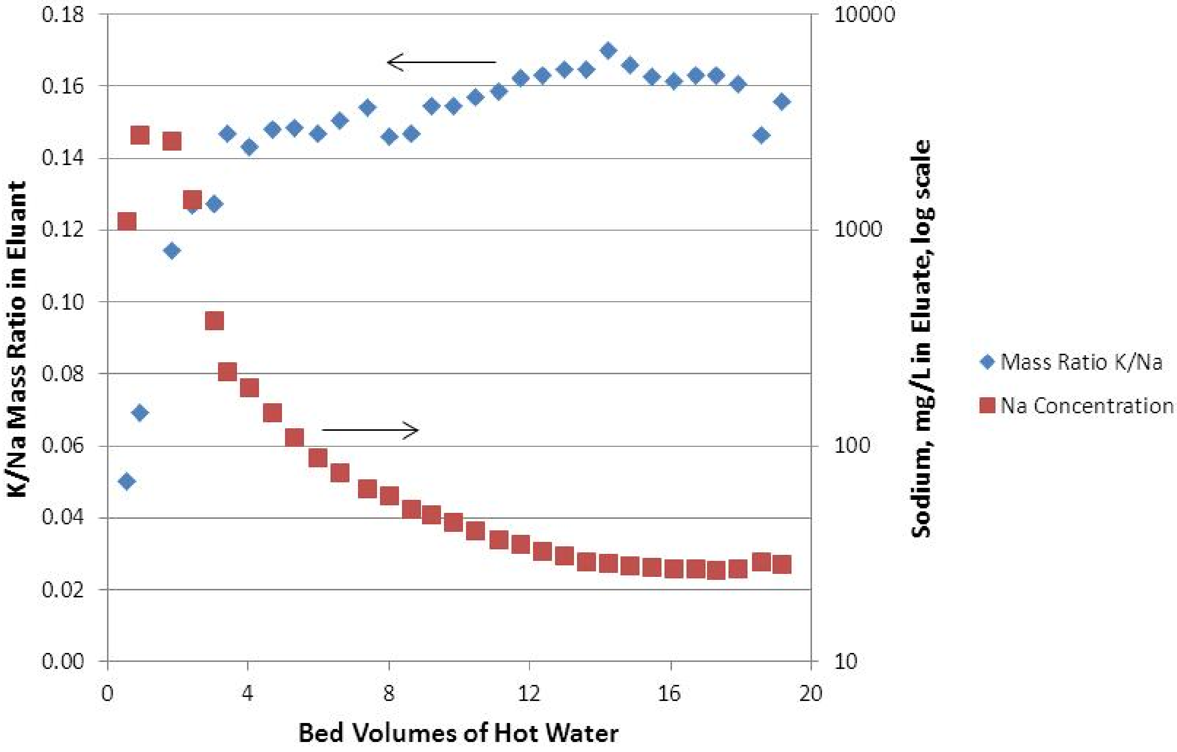

Figure 3-4. Elution of Sodium and Potassium in the Second Campaign

4.0 Conclusions

The new batch of SuperLig® 639 exhibited good distribution coefficients and successfully removed the perrhenate from the simulant in column testing at 25˚ and 45˚C. Three columns were necessary to achieve 99% removal, which is more than was typically observed with prior testing. This is due to the high nitrate and low potassium concentration in this simulant compared to that used in most prior testing. This simulant is representative of an average of all 177 waste tanks at Hanford, which includes dissolved saltcake that is high in nitrate and low in potassium. Prior testing utilized samples or simulants of specific Double Shell Tanks, which are much higher in hydroxide and lower in nitrate. It is expected that better performance would also be observed when using pertechnetate because of the ~2 times higher distribution coefficient for pertechnetate versus perrhenate. The breakthrough is a relatively flat curve, which is caused by the high nitrate and low potassium content, and indicates that attempting to operate at higher flow rates would probably cause earlier breakthrough. Overall, the resin performed well, with no incidence of resin floating.

The results indicate that the computer modeling is a reasonably good, conservative prediction of performance. Those results [Hamm, 2013] indicated that a lead-lag pair of 1 m^3 columns at 25˚C could process 102 bed volumes of waste prior to 1% cumulative breakthrough. To demonstrate the 1% breakthrough in the experiments reported here, a third column was added to account for the difference in performance between pertechnetate and perrhenate. If a third column is included in a full-scale system, it would also improve the performance, allowing the lead column to become more saturated with Tc, reducing the frequency and volume of elution cycles. The results indicate that a full-scale system is viable with the HTWOS Average 5 M [Na^+] composition. Since the elution and regeneration cycle time is shorter than the loading cycle time, a continuous process can be implemented using a carousel-type operation with one column taken offline for elution while another rotates in for loading. The volume of eluate generated in this test was approximately 12% of the LAW feed volume, which could be further reduced by optimization of re-use of eluate, on-line monitoring of Tc to minimize over-elution, and by evaporation of the eluate. Removal of 99% of the pertechnetate from the LAW could be achieved with this process (non-pertechnetate forms of Tc in Hanford waste are not removed by this resin).

This testing confirms that the new batch of resin performs well, and, although challenged by the high nitrate concentration and higher temperature, the HTWOS Average 5 M [Na^+] composition can be decontaminated with this process. Performance and behavior of the resin and the process are consistent with prior work. The prior testing program, coupled with the new resin testing and computer modeling, can be used to establish process design criteria.

As shown in the appendix C, computer modeling was able to match the experimental data very well, with an average VERSE prediction within about 22% of the experimental results (based on a root mean square calculation). Both at 25˚ and 45˚C, the perrhenate breakthrough profiles fit the model calculations, once the capacity for this particular batch of resin was used.

Full-scale computer modeling using pertechnetate was also performed (Appendix D). The parameters used for column configuration matched that provided in the Engineering Study [Russell, 2013]. Column geometries used in the past are typically matched to the WTP throughput, with a Length:Diameter ratio of 3:1. The modeling results indicate that for a flow rate of ~3.3 BV/hr and 1.37 m^3 of resin at 25˚C, three columns in series will process 207 BV (~75,000 gallons) of LAW prior to an accumulated breakthrough of 1%. Using three columns in series instead of two results in ~19% higher throughput. (note that this is the “stabilized” condition of three columns being re-used repeatedly in a carousel-type sequence where the lead column is removed from service for elution, then replaced into the last position.) At 45˚C, the quantity of waste processed per cycle drops by ~50%. Operationally, this means that to achieve the same decontamination at 45˚C, the elution would occur twice as often, generating twice as much eluate that would need to be evaporated or disposed. Modeling results shown in appendix D are highly versatile, and allow comparison of benefits of equipment size, flow rate, and throughput.

Operating at 25˚C with three columns in series, with four total columns available, would be operationally viable. The three columns would be in the loading cycle for ~69 hours, and elution of the fourth could occur simultaneously, taking ~20 hours. Operating at 45˚C would also be viable. The loading cycle would be ~35 hours, which is enough time for elution. However, this would generate twice as much eluate as operation at 25˚C. Reducing to two columns at 45˚C would be more challenging, since the loading cycle would be only slightly longer than the elution cycle, minimizing time available for maintenance work or resin replacement. This would also generate more eluate solution. Ultimately, an engineering study would be needed to determine the optimum configuration and operating conditions.

5.0 Path Forward

If it is desired to operate at 45˚C, additional work is needed to examine the chemical stability of SuperLig® 639 resin at elevated temperature in LAW solution through many cycles. Testing with pertechnetate would be needed to verify the correlation with perrhenate at the elevated temperature in a column configuration.

Similarly, other potential process conditions and a broad range of feed compositions under consideration have not been demonstrated. If processing LAW under different conditions is needed to extend the envelope of conditions demonstrated, testing would be required to examine the impact of key constituents. Conditions such as using a higher density (higher [Na^+]) LAW feed, would require examination of the fluidization and movement of the resin due to floating in high density fluids. Up-flow tests would be needed at a larger scale to examine the effect of an unconstrained bed versus a constrained bed.

Testing of up-stream and down-stream impacts has not been demonstrated, but significant issues are not expected. The prior testing program in 1996-2003 examined treatment of LAW that had been demonstrated with a different cesium-removal resin, so integrated testing is needed. Similarly, the prior testing examined vitrification of the Tc-decontaminated LAW. If other waste forms are desired, integrated testing is needed.

An option for monitoring the elution performance should be investigated in future tests with pertechnetate. Since ^{99}Tc is difficult to measure, and many samples need to be analyzed during elution, alternate methods of monitoring it may be worth investigating. Toward the end of elution, the sodium concentration and the Re concentration are decreasing, perhaps conductivity of the eluate could be used as a very easy analysis method. Although probably not useful for monitoring the elution peak, conductivity may be an adequate indicator of the completion of elution. Further work would be needed to determine if this is plausible.

6.0 References

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Appendix A. Simulant Formulation

Table A-1. Simulant Formulation

	Target, M	As-Batched, M	Measured, M*
Sodium	5.00	4.97	4.84
Nitrate	1.60	1.597	1.60
Free OH	1.611	1.560**	NM
Sulfate	0.086	0.086	0.084
Aluminum	0.307	0.307	0.315
Nitrite	0.565	0.565	0.624
Carbonate	0.274	0.274	NM
Potassium	0.0328	0.0328	0.0342
Acetate	0.0385	0.0385	NM
Fluoride	0.0316		<0.0053
Mono-H Phosphate	0.049	0.049	<0.001
Chloride	0.042	0.0422	0.043
Perrhenate	4.5E-05	4.48E-05	4.3E-05

*ICPES and IC Anions, nominally 10% uncertainty
**Calculated considering aluminum conversion to aluminate
NM = Not Measured

Appendix B – Detailed Experimental Data

Pump Calibration Measurement Results

Table B-1. Pump 4 measured flow rates with deionized (ASTM D1193) water

Dial Setting	time (min)	mass of water(g)	volume (mL)	Flow rate (mL/min)
2.000	10.00	4.3181	4.32502	0.432502
2.250	10.00	4.7665	4.774139	0.477414
2.500	10.00	5.1787	5.186999	0.5187
2.750	10.00	5.6595	5.66857	0.566857
3.000	10.00	6.1382	6.148037	0.614804
3.250	10.00	6.6572	6.667869	0.666787
3.500	10.00	7.0886	7.09996	0.709996

temp=19C
density=0.9984 (g/mL) at 19°C

Table B-2. Pump 4 measured flow rates with 0.1M NaOH.

Dial Setting	time (min)	mass of NaOH(g)	volume (mL)	Flow rate (mL/min)
2.800	10.00	6.1171	6.1171	0.61171
2.610	11.00	6.3089	6.3089	0.573536
2.500	10.00	5.5439	5.5439	0.55439
2.500	10.00	5.5567	5.5567	0.55567
2.390	10.00	5.342	5.342	0.5342
2.430	10.00	5.5165	5.5165	0.55165

temp=19C
density=1.00 (g/mL) at 19°C

Table B-3. Pump 5 Measured Flow Rates.

Dial Setting	time (min)	mass of water(g)	volume (mL)	Flow rate (mL/min)
0.000	10.00	0.0000	0.0000	0.0000
1.000	5.00	0.6268	0.6278	0.1256
1.100	5.00	0.7728	0.7740	0.1548
1.200	5.00	0.3342	0.3347	0.0669
1.200	5.00	0.8206	0.8219	0.1644
1.250	8.00	1.3585	1.3607	0.1701
1.220	5.00	0.8183	0.8196	0.1639
1.226	5.00	0.8306	0.8319	0.1664
1.228	5.00	0.8331	0.8344	0.1669
1.227	5.00	0.8360	0.8373	0.1675

temp=19C
density=0.9984 (g/mL) at 19°C

Ion Exchange Column Loading Cycle Test Data

(Column headers are: Bed temperature, Resin Bed Height, Cumulative Bed Volume processed, Rhenium concentration in effluent samples, calculated fractional rhenium concentration breakthrough)

Table B-4. Loading Cycle Data, First Campaign (~25˚C), Column #1

Temperature, °C	Bed height., cm	Cumulative BV	[Re] mg/L	C/C_0
22.9	5.7	43.1	0.72	0.095
23.1	5.7	49.7	1.03	0.136
23.6	5.7	59.4	1.45	0.191
24.6	5.7	69.1	1.93	0.255
24.8	5.7	78.7	2.30	0.304
24.5	5.7	88.5	2.75	0.363
24.0	5.7	98.0	3.24	0.427
24.0	5.7	107.7	3.48	0.459
23.6	5.7	117.4	Not measured	
23.3	5.7	127.3	3.91	0.517
23.8	5.7	136.8	4.29	0.566
24.3	5.7	146.5	4.60	0.607
24.5	5.7	155.4	4.91	0.648

Table B-5. Loading Cycle Data, Second Campaign (45˚C), Column #3

Temperature, °C	Bed height., cm	Cumulative BV	[Re] mg/L	C/C_0
22.9	5.7		Below detection	
23.1	5.7		Below detection	
23.5	5.7	55.8	0.0507	0.0063
24.6	5.7	64.9	0.108	0.0119
24.7	5.7	73.9	0.135	0.0168
24.4	5.7	83.0	0.302	0.0334
23.8	5.7	92.0	0.368	0.0457
23.8	5.7		Not measured	
23.5	5.7	110.1	0.519	0.068
23.2	5.6	119.3	0.701	0.093
23.7	5.6	128.2	0.844	0.116
24.2	5.6	137.4	1.14	0.152
24.7	5.6	145.5	1.32	0.177

Table B-6. Loading Cycle Data, First Campaign (~25˚C), Column #3

Temperature, °C	Bed height., cm	Cumulative BV	[Re] mg/L	C/C_0
22.8	5.7	38.7	Below detection	
23.0	5.6	44.0	Below detection	
23.3	5.6	52.5	Below detection	
24.4	5.6	60.9	Below detection	
24.5	5.6	69.4	Below detection	
24.3	5.6	77.9	Below detection	
23.7	5.6	86.3	Below detection	
23.7	5.6	94.8	Below detection	
23.4	5.6	103.2	Below detection	
23.3	5.6	111.9	0.0512	0.0057
23.5	5.6	120.2	0.0729	0.0091
24.0	5.6	128.6	0.106	0.0117
24.8	5.6	136.3	0.125	0.0155

Table B-7. Loading Cycle Data, Second Campaign (45˚C), Column #1

Temperature, °C	Bed height., cm	Cumulative BV	[Re] mg/L	C/C_0
44.7	5.7	5.9	0.115	0.013
45.0	5.6	15.2	0.334	0.039
45.5	5.7	24.5	0.981	0.115
45.3	5.6	32.1	1.55	0.176
44.0	5.6	43.5	2.24	0.254
44.0	5.6	53.1	3.285	0.373
44.2	5.7	62.6	4.285	0.486
44.2	5.7	69.0	4.405	0.500
44.2	5.7	81.9	5.635	0.639
44.4	5.7	91.5	6.43	0.729
44.2	5.7	101.2	6.34	0.719
44.5	5.7	106.4	6.31	0.716

Table B-8. Loading Cycle Data, Second Campaign (45˚C), Column #2

Temperature, °C	Bed height., cm	Cumulative BV	[Re] mg/L	C/C_0
44.8	5.4	2.7	Below Detection	
45.6	5.4	11.5	Below Detection	
46.0	5.4	20.1	Below Detection	
45.4	5.4	27.1	Below Detection	
44.2	5.4	37.8	0.11	0.0129
44.3	5.4	46.8	0.278	0.0325
44.5	5.4	55.9	0.53	0.0620
44.5	5.4	61.6	1.07	0.121
44.7	5.4	73.8	1.485	0.168
44.7	5.4	82.7	1.66	0.188
44.8	5.4	91.7	2.535	0.288
44.6	5.4	96.4	2.615	0.297

Table B-9. Loading Cycle Data, Second Campaign (45˚C), Column #3

Temperature, °C	Bed height., cm	Cumulative BV	[Re] mg/L	C/C_0
45.7	5.4	0.3	Below Detection	
45.3	5.5	7.8	Below Detection	
45.6	5.5	16.1	Below Detection	
45.6	5.5	22.3	Below Detection	
44.3	5.4	32.6	Below Detection	
44.5	5.4	41.0	Below Detection	
44.6	5.5	49.3	Below Detection	
44.6	5.5	54.5	0.0776	0.00908
44.7	5.5	66.0	0.139	0.01626
44.8	5.5	74.3	0.243	0.02842
44.9	5.5	82.7	0.296	0.03462
44.7	5.5	86.8	6.31	0.716

Ion Exchange Column Elution Cycle Test Data

(Column headers are: Cumulative Bed Volume eluted, Potassium concentration in effluent samples Sodium concentration in effluent samples, Rhenium concentration in effluent samples, fractional calculated rhenium concentration eluted)

Table B-10. Elution Cycle Data, Second Campaign (45˚C loading), Column #1 (Elution at 65˚C)

Cumulative BV	Potassium Concentration, mg/L	Sodium Concentration, mg/L	Rhenium Concentration, mg/L	Rhenium C/C_0
0.93	190.8	2760.0	13.0	1.50
1.82	296.0	2589.8	63.6	7.31
2.43	174.2	1375.0	310.0	35.63
3.04	48.5	381.0	424.0	48.74
3.41	32.2	219.6	116.0	13.33
4.05	26.5	184.8	13.4	1.53
4.68	21.1	142.5	1.76	0.20
5.32	16.3	109.8	Below detection	
5.97	13.0	88.5	Below detection	
6.61	11.4	75.6	Below detection	
7.40	9.80	63.6	Below detection	
8.02	8.55	58.7	Below detection	
8.63	7.51	51.2	Below detection	
9.23	7.44	48.1	Below detection	
9.84	6.85	44.3	Below detection	
10.48	6.34	40.5	Below detection	
11.11	5.82	36.7	Below detection	
11.75	5.71	35.2	Below detection	
12.38	5.31	32.6	Below detection	
13.00	5.06	30.8	Below detection	
13.62	4.80	29.2	Below detection	
14.25	4.86	28.6	Below detection	
14.87	4.61	27.8	Below detection	
15.49	4.45	27.3	Below detection	
16.10	4.32	26.8	Below detection	
16.71	4.36	26.7	Below detection	
17.32	4.30	26.4	Below detection	
17.93	4.29	26.8	Below detection	
18.57	4.23	28.9	Below detection	
19.18	4.38	28.2	Below detection	

Appendix C – Resin Batch Assessment

The experimental batch contact and column testing provided in this report focused on the behavior of a more recent batch of resin provided by IBC (i.e., a May 2013 batch with lot # 130611552-56). Isotherm model development earlier in this calendar year included all prior resin batch data within its assessment. In this appendix, the isotherm model (i.e., CERMOD) is reexamined and updated to reflect this more recent database. In the most recent version of CERMOD (see Hamm et al., 2013) the temperature dependence for TcO_4^- absorption was not addressed and was limited to approximately 20° to 25°C operation. With this newer database CERMOD now has included temperature dependence over the range of interest (i.e., 25° to 45°C).

Analytic Isotherm Model

Two aspects of the isotherm model were addressed: (1) providing temperature dependence over the range of interest and (2) establishing a total capacity value for the newer resin batch provided by IBC within the range of waste compositions of interest. The capacity is defined as the total quantity of the perrhenate/pertechnetate that the resin will sorb, typically described in units of millimole of perrhenate per gram of resin. (Note that this is composition-dependent, and is not intended to be compared with the vendor-generated acceptance criteria test results.)

For absorption processes generally the total capacity (perhaps better referred to as an "apparent" capacity) is dependent upon the liquid-phase ionic strength as well as the constituents that make up the competing neutral species. The current resin procurement acceptance criterion for total capacity is based on a simple 3M NaOH solution whose measured capacity may not reflect the absorption environment of interest for modeling. As demonstrated below the expected operating range of the resin is well below its total (or apparent) capacity. Differing capacity and selectivity values can yield nearly identical isotherms in the range of interest (i.e., only a consistent set of parameter values is required).

From the previous modeling report [Hamm et al., 2013] the analytic isotherm becomes (see Eq. (2-17) of that report):

$$Q_x = \frac{Q_T c_x}{c_x + \beta} , \qquad \text{(C-1)}$$

where

Q_T - Total available solid-phase loading sites on resin (mmole of sites per gram resin)

Q_x - Solid-phase loading of species x onto resin

c_x - Liquid-phase concentration of species x in solution

β - Beta factor representing the composite impact associated with enhancers and competitors

x - Shorthand notation for species of interest (i.e., ReO_4^- or TcO_4^-)

and where the estimated beta parameter is expressed as (see Eq. (2-19) of that report):

$$\beta = \frac{1 + (K_{no}c_n + K_{ko}c_k)c_o + (K_{np}c_n + K_{kp}c_k)c_p}{\eta\left[K_{nx}c_n + K_{kx}c_k\right]} \ . \qquad \text{(C-2)}$$

Note that η represents the Re versus Tc "surrogate" factor:

$$\eta = \begin{bmatrix} 1.000 & \text{for} & \text{Tc} \\ 0.505 & \text{for} & \text{Re} \end{bmatrix} .$$

where

η - A "surrogate" factor representing the chemical differences between Re versus Tc

n, k, o, p - Shorthand notation for Na^+, K^+, NO_3^-, and NO_2^-

K_{ij} - Thermodynamic equilibrium coefficient in mass action equation for species i and j

The simplest van't Hoff expression is provided by:

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^o}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] , \qquad \text{(C-3a)}$$

which can be rearranged to:

$$K(T) = K_1 \exp\left\{E\left[\frac{1}{T} - \frac{1}{T_1}\right]\right\} , \qquad \text{(C-3b)}$$

where

K_i - Thermodynamic equilibrium coefficient for a specific species at temperature i

T_i - Absolute temperature at state i

ΔH^o - Heat of absorption for a particular mass action equation at a specific reference state

R - Universal gas constant

E - A fitting parameter that represents the activation energy for the mass action

Taking the parameter values that were determined during the CERMOD optimization process and assuming liquid-phase nonidealities cancel out, Eq. (C-1) above can be compared analytically with data.

Experimental data from Rapko was [Rapko et al., 2003] collected for resin batch 3 and AN-105 simulant is available at both 25° and 65°C [see Hamm et al., 2013]. This is our most consistent set of data to extract out a value of coefficient E defined in Eq. (C-3b) above. A value of -4400.0 provides a reasonable set of predictions to the available data where only the temperature dependence for Na^+ and K^+ was considered (i.e., assumed the same while omitting the temperature dependence for the competitors NO_3^- and NO_2^-). The predicted isotherms from the analytic model are compared to the Rapko data in Figure C-1 below.

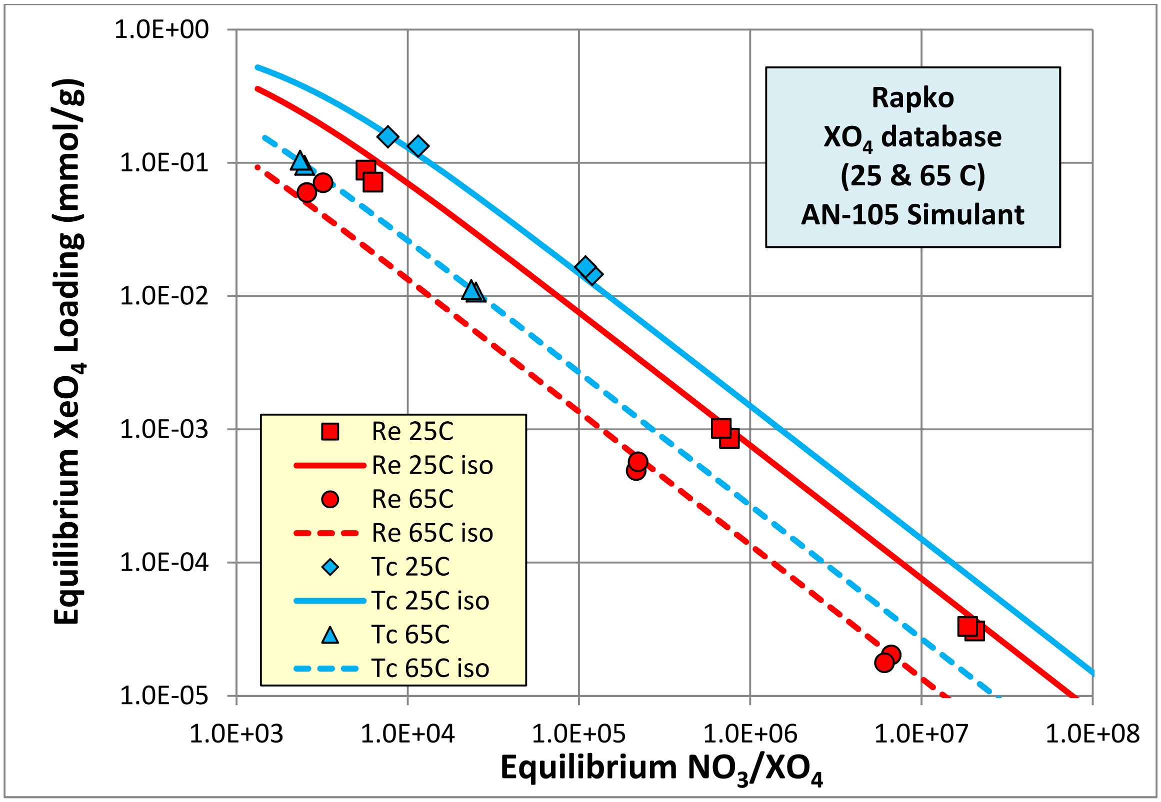

Figure C-1. Comparison of analytic isotherm model to selected Rapko data at 25˚ and 65˚C for both Re and Tc

These quick analytic results shown in Figure C-1 indicated that a van’t Hoff formulation should provide acceptable results when used in CERMOD.

CERMOD Databank Upgrade

CERMOD has a temperature dependent K_{eq} whose parameter values are contained within the “Databank” directory. A general expression is provided based on a general heat of reaction equation and its integration within the van’t Hoff identity:

$$\left[\frac{\partial K_{eq}}{\partial\left(\frac{1}{T}\right)}\right]_p = -\frac{\Delta H^o(T)}{R} , \qquad \text{(C-4)}$$

where

K_{eq} - Thermodynamic “equilibrium” coefficient that is temperature dependent

The resulting K_{eq} expression provided in CERMOD is:

$$\ln(K_{eq}) = \frac{E}{T} + B\ln(T) + CT + D , \qquad \text{(C-5)}$$

where

B, C, D, E - Fitting coefficients for expressing the heat of absorption temperature dependence

The D coefficient given in Eq. (C-5) can be obtained using Eq. (C-3a) as:

$$D = \ln(K_1) - \frac{E}{T_1} , \qquad \text{(C-6)}$$

Temperature dependence extracted from only the Rapko database relies on one specific resin batch and one specific feed solution. Impacts associated with varying batches and feed solutions are anticipated to result in shifts in the predicted isotherms taken from CERMOD. As discussed below comparison to column predictions can be employed in adjusting the expected temperature dependence for specific batch and feed composition pairs.

CERMOD Isotherm Predictions

For the SRNL simulant and the IBC May batch of SuperLig® 639 resin, CERMOD predicted isotherms for ReO_4^- at the temperatures of 25˚, 45˚, and 65˚C were computed and are shown in Figure C-2. These isotherms reflect an ~20% adjustment (i.e., reduction in) made to K(T) dependence based on comparisons with column performance data (to be shown below).

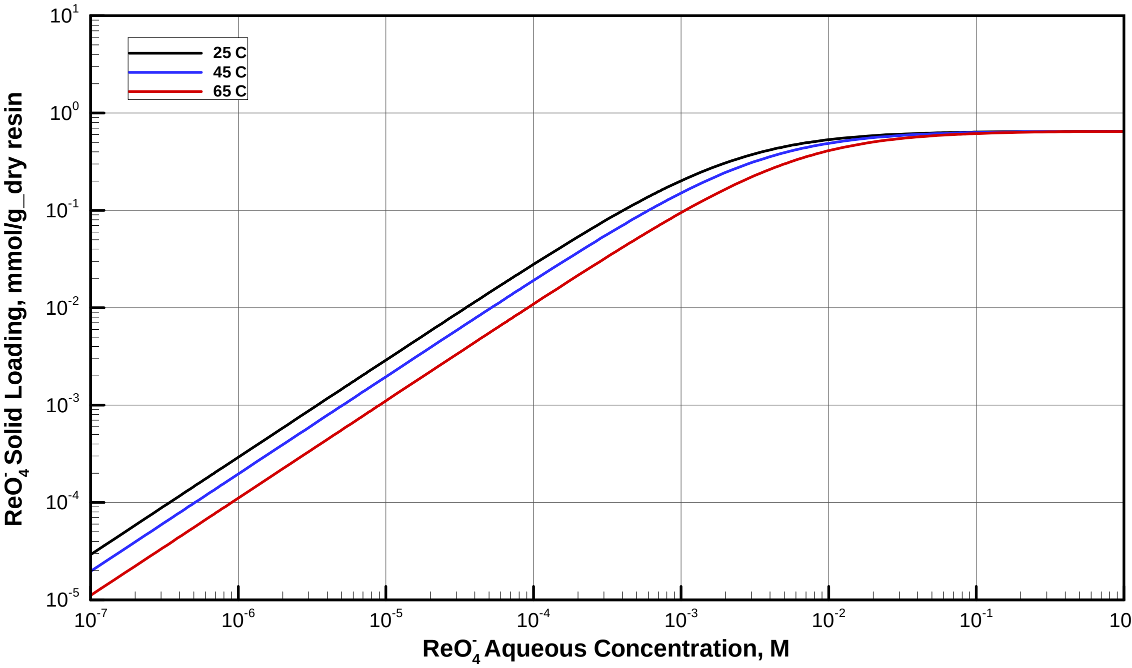

Figure C-2. Comparison of CERMOD predicted ReO_4 isotherms at 25˚, 45˚, and 65˚C for the IBC May batch of SuperLig® 639 resin.

For each temperature above, the corresponding TcO_4^- isotherm was predicted using CERMOD. Figure C-3 provides a direct comparison of each Re and Tc isotherm at all three temperatures.

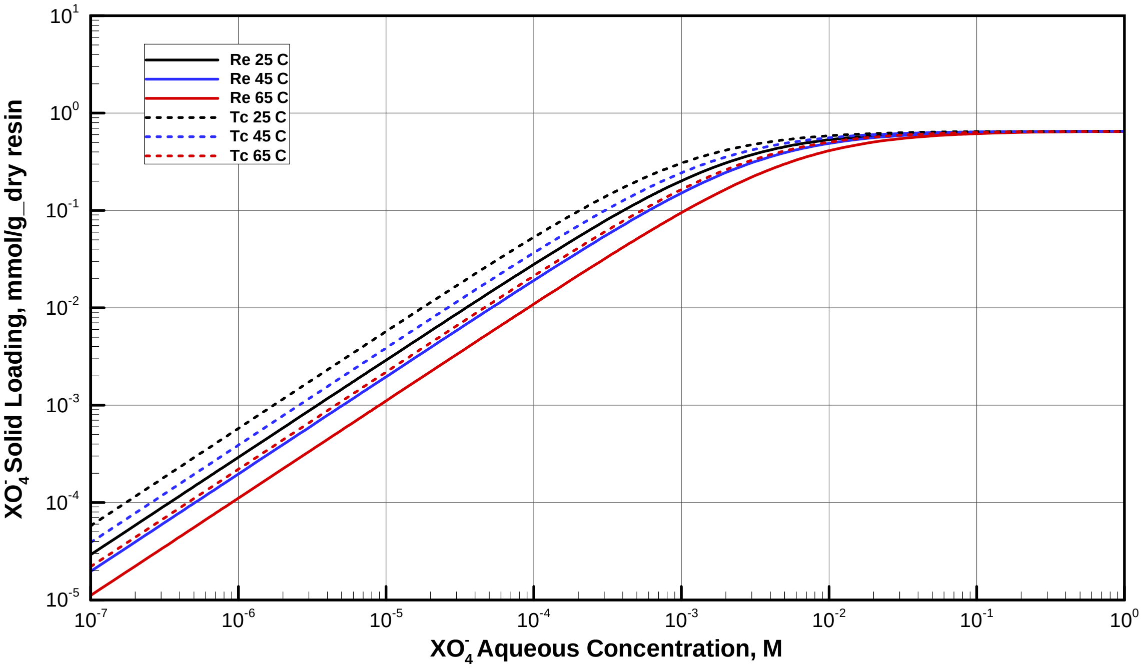

Figure C-3 Comparison of CERMOD predicted ReO_4 and TcO_4 isotherms at 25˚, 45˚, and 65˚C for the IBC May batch of SuperLig® 639 resin

The various isotherms presented above were generated employing CERMOD. At the end of each series of numerical batch contact simulations by CERMOD, a least-squared fitting of the numerical isotherm generated data was performed. The data was fitted to an "effective" binary Langmuir isotherm model:

$$Q_{XO4} = \frac{Q_T c_{XO4}}{c_{XO4} + \beta} \ . \tag{C-7}$$

For use in VERSE-LC the total capacity is placed on a per bed volume, rather than on a per resin mass, basis where the VERSE-LC inputted isotherm becomes:

$$Q_{XO4} = \frac{\rho_{bed} Q_T c_{XO4}}{c_{XO4} + \beta} = \frac{a \cdot c_{XO4}}{c_{XO4} + \beta} \ , \tag{C-8}$$

where

$$a = \rho_{bed} Q_T \ . \tag{C-9}$$

and where

ρ_{bed} - Bed density defined as the total resin mass in bed per total volume of bed

a - VERSE parameter representing the total available sites in bed per total volume of bed

The various binary isotherms generated are provided in Table C-1. Note that Q_{tot} and ρ_{bed} employed within CERMOD for this particular resin batch (IBC Lot #130611552-56) have the numerical values of:

$$Q_T = 0.6518 \ \ (\text{mmole}/g_{resin}) \ , \tag{C-10a}$$

and $$\rho_{bed} = 0.4498 \ \ (g_{resin}/ml_{bed}) \ . \qquad (C\text{-}10b)$$

In the fitting process both the capacity (Q) and beta (β) values are considered as parameters that are fitted to the series of numerical batch contact data available. As Table C-1 indicates, the fitted estimate for capacity is very close to the expected value provided in Eq. (C-10a). This capacity could have been imposed as fixed to the value 0.6518 instead of allowing it to vary; however, allowing it to vary also gives more confidence that the overall process is working as expected and produces a slightly better fit to the CERMOD data, which is not constrained to be Langmuir-like.. The bed density value is based on the measured values within the lab-scale testing and is assumed to be valid for the full-scale applications.

Table C-1. "Effective" binary isotherms employed in current study

XO4	T (˚C)	Qtot (fit)	a = $\rho_{bed}Q_{tot}$ (fit)	Beta (fit)	Application
ReO4	25	0.6518	0.29318	2.23285E-03	SRNL Lab-Scale
	45	0.6519	0.29323	4.15318E-03	SRNL Lab-Scale
	65	0.6523	0.29341	1.06619E-02	-
TcO4	25	0.6517	0.29314	1.12755E-03	Full-Scale
	45	0.6518	0.29318	2.09704E-03	Full-Scale
	65	0.6520	0.29327	5.38178E-03	-

VERSE SRNL Column Predictions

For the SRNL simulant and the IBC May batch of SuperLig® 639 resin, VERSE column predictions were made for the three column experiments run at SRNL. The same three column carousel configuration was tested at 25˚C and at 45˚C. The results of the two column predictions, along with the 25˚C column data, are shown in Figure C-4. The solid lines represent the 25˚C breakthrough curves. 25˚C batch contact data was employed in estimating the total capacity of this particular batch of resin. The dashed lines represent the 45˚C breakthrough curves. Here, one set of Rapko batch contact data was employed to estimate the temperature dependence of key K_{eq} values.

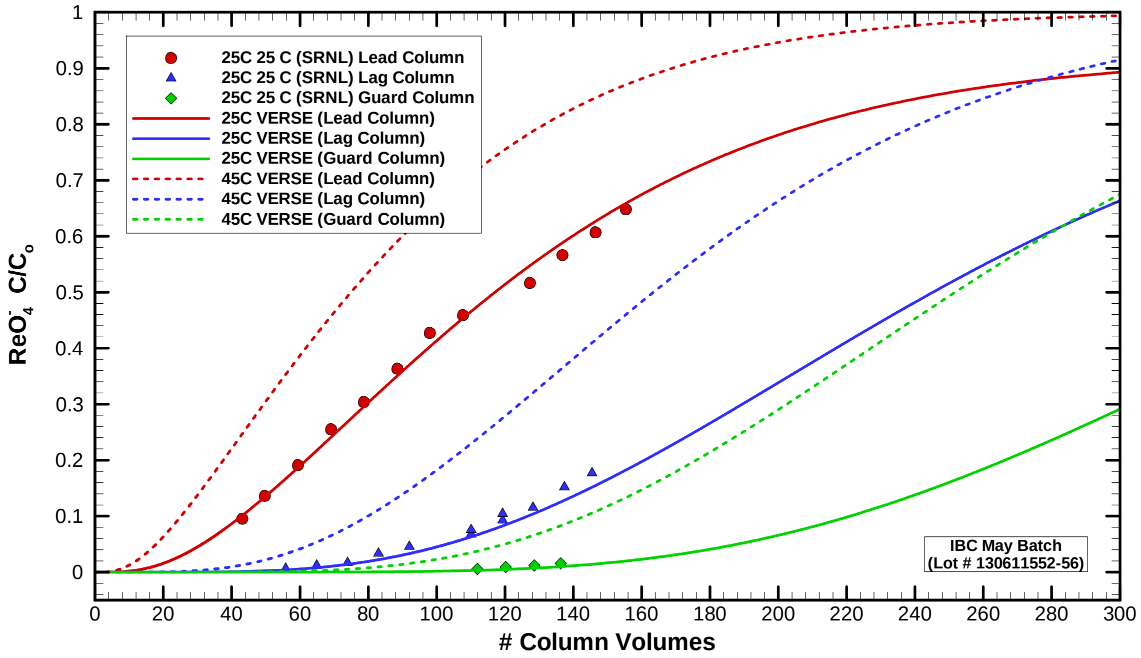

Figure C-4. Comparison of VERSE predicted ReO$_4$ column performance at 25˚ and 45˚C for the IBC May batch of SuperLig$^{®}$ 639 resin.

From these initial column breakthrough predictions, refinements were made to update fluid properties to be consistent with the average HTWOS feed composition (i.e., adjustment caused slight rightward shifting in the VERSE curves). As stated above, the resin total capacity was established by adjusting VERSE predictions for only the 25˚C data. The estimated total capacity for this new IBC resin (Lot # 130611552-56) becomes:

$$Q_T = 0.6517 \text{ (mmole/g)} \quad , \tag{C-11}$$

This value is very consistent with the overall average value of 0.6472 mmole/g observed in prior estimated batch capacities (i.e., within 1% of this value).

The comparison of VERSE predicted breakthrough curves with the available 45˚C column data indicated that the estimated 45˚C ReO$_4^-$ isotherm from CERMOD was approximately 20% higher than the data would support. This discrepancy could be the result of two possibilities:

1. The use of only Rapko data in determining K(T) dependence batch and feed composition effects were not being handled adequately in CERMOD; and/or
2. The use of a temperature independent capacity.

The shifting of VERSE breakthrough predictions to be consistent with the 45˚C column data can be made by either adjusting K(T) dependence or by adjusting total capacity (or any combination of these two). Both methods were examined.

An 80% factor (i.e., 20% reduction) on total capacity was required to get 45˚C column data to match the experimental results. Essentially identical results were achieved by adjusting Keq values (a larger temperature effect due to column benchmarking versus IBC data and column data for same batch) while leaving total capacity at this original value. The resulting 25˚ and 45˚C predicted ReO$_4^-$ and TcO$_4^-$ isotherms are shown in Figures C-5 and C-6.

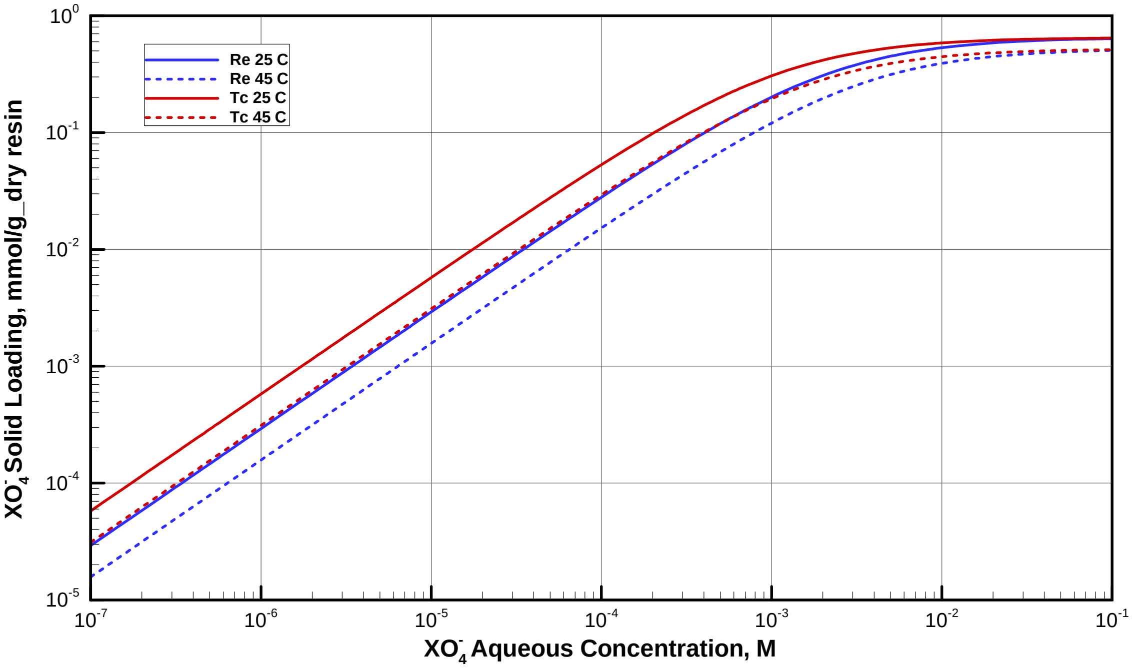

Figure C-5. Comparison of CERMOD predicted ReO_4^- and TcO_4^- isotherms at 25˚ and 45˚C for the IBC May batch of SuperLig® 639 resin (temperature dependent total capacity).

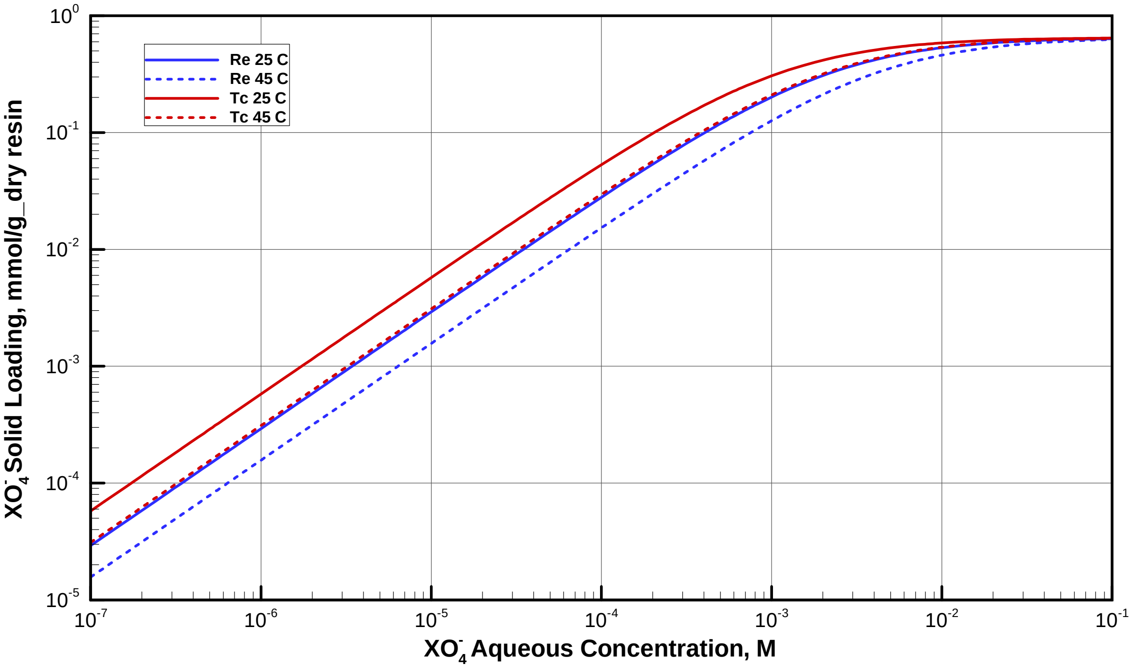

Figure C-6. Comparison of CERMOD predicted ReO_4^- and TcO_4^- isotherms at 25˚ and 45˚˚C for the IBC May batch of SuperLig® 639 resin (temperature depend K_{eq}).

The two sets of isotherms are essentially identical in the operating ranges of interest. They only begin to vary when concentration exceeds ~1x10^{-4} M (i.e, the non-linear region). Using either of these isotherms, the column benchmark runs resulted in excellent comparisons, as shown in Figure C-7.

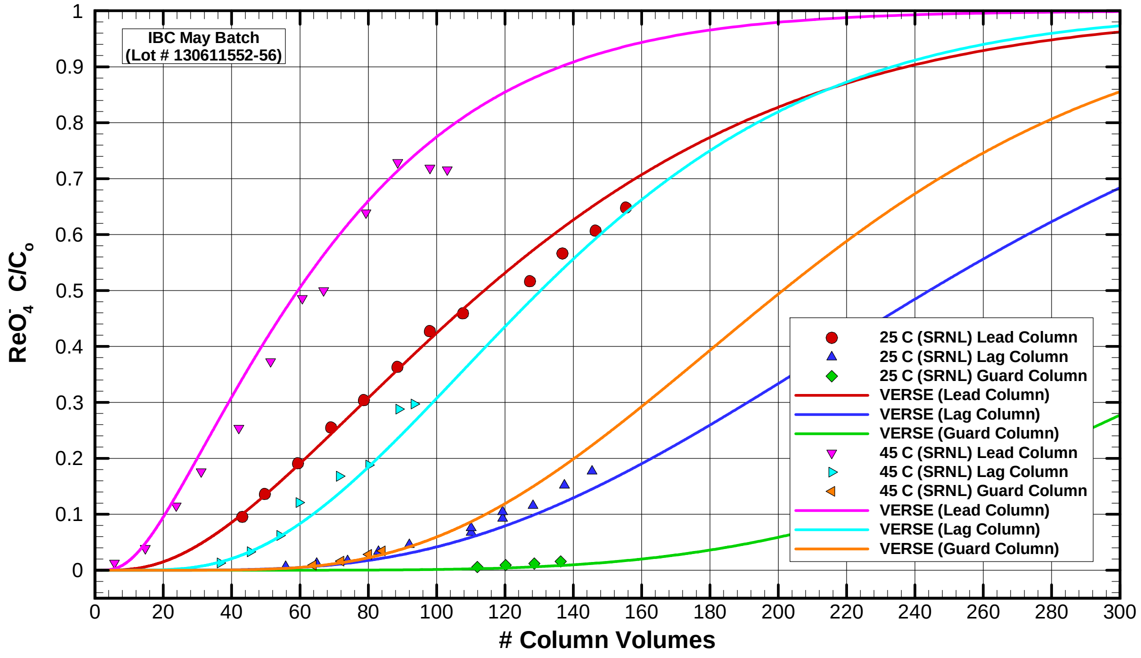

Figure C-7. Comparison of VERSE predicted ReO$_4$ column performance at 25˚ and 45˚C for the IBC May batch of SuperLig® 639 resin.

The actual S-shape of the VERSE breakthrough curves depends upon the particle kinetics through the particle pore diffusivity value. Historical values for both ReO_4^- and TcO_4^- have been set to 50% of their free stream (i.e., molecular) values. This 50% value has been shown repeatedly to be acceptable in prior studies where operating temperatures varied from ~18˚C to 27˚C. However, at 45˚C the experimental S-shape observed indicated that a lower value was more appropriate. In Figure C-7 a value of 15.4% of the free stream value was employed. At higher temperatures net ionic and neutral species migration appears to be hindered.

For scale-up perspectives, based on the isotherm and column assessments presented above, the SuperLig® 639 methodology was updated to reflect:

- New total capacity for the IBC resin identified as Lot # 130611552-56 (here total capacity is assumed to be temperature independent);
- New temperature dependent K_{eq} values for Na^+ and K^+ based on Rapko batch contact data and the new batch contact and column measurements present in this report; and
- New temperature dependence placed to the particle pore diffusivity values.

The remaining methodology is unchanged from prior modeling efforts. As the older methodology indicates, physical properties such as resin density and porosities are assumed to be temperature independent.

As Figure C-7 indicates, the updated methodology can provide a reasonably high degree of confidence in predicting ReO_4^- breakthrough behavior. The essential physics required is readily scalable up to full-scale without concerns due to facility sizing. The largest uncertainties still remain to be (1) the ReO_4^- versus TcO_4^- chemistry effects and (2) resin batch variability.

To provide some indication as to the level of accuracy to be expected in predicting breakthrough curves, the root-mean-square (rms) values for each data point in the 25˚C and 45˚C column tests were computed. Residuals at each data point (r_i) were computed using:

$$r_i = \frac{\left(\frac{c}{c_o}\right)_i^{VERSE} - \left(\frac{c}{c_o}\right)_i^{Exp}}{\left(\frac{c}{c_o}\right)_i^{Exp}} , \qquad \text{(C-12)}$$

where

c - ReO_4^- concentration at each column exit [M]

c_o - ReO_4^- inlet feed concentration to column carousel [M]

i - Data point i (for either lead, lag, guard column and either 25˚C or 45˚C temperature)

Exp - Experimental value

VERSE - Computed VERSE value

The rms values were computed using (percentage values presented):

$$rms = 100 \times \sqrt{\left[\frac{\sum_{i=1}^{N_{set}} (r_i)^2}{N_{set}}\right]} , \qquad \text{(C-13)}$$

where

N_{set} - Number of data points being considered (e.g., 12 points for lead column at 25˚C)

Here the predicted VERSE results versus the experimental concentrations at the same bed volume value were computed. Table C-2 provides a summary of these calculations where the data within each column are combined into a rms value (i.e., a percentage value). Also provided in Table C-2 is the overall rms value for the carousel at each temperature (i.e., here the rms value is weighted by the number of data points contained within each column). On average the VERSE predictions are typically within about 22%. Data from Figure C-7 is replotted in semi-log scale in Figure C-8 to more clearly visualize the results of the second and third columns.

Table C-2. Root-Mean-Square (rms) values for VERSE predictions when compared to SRNL column breakthrough data

	number data pts	25 C rms (%)	number data pts	45 C rms (%)
Lead	12	5.3	12	27.4
Lag	12	28.2	8	15.5
Guard	4	51.7	4	20.4
wt. avg	28	21.7	24	21.3

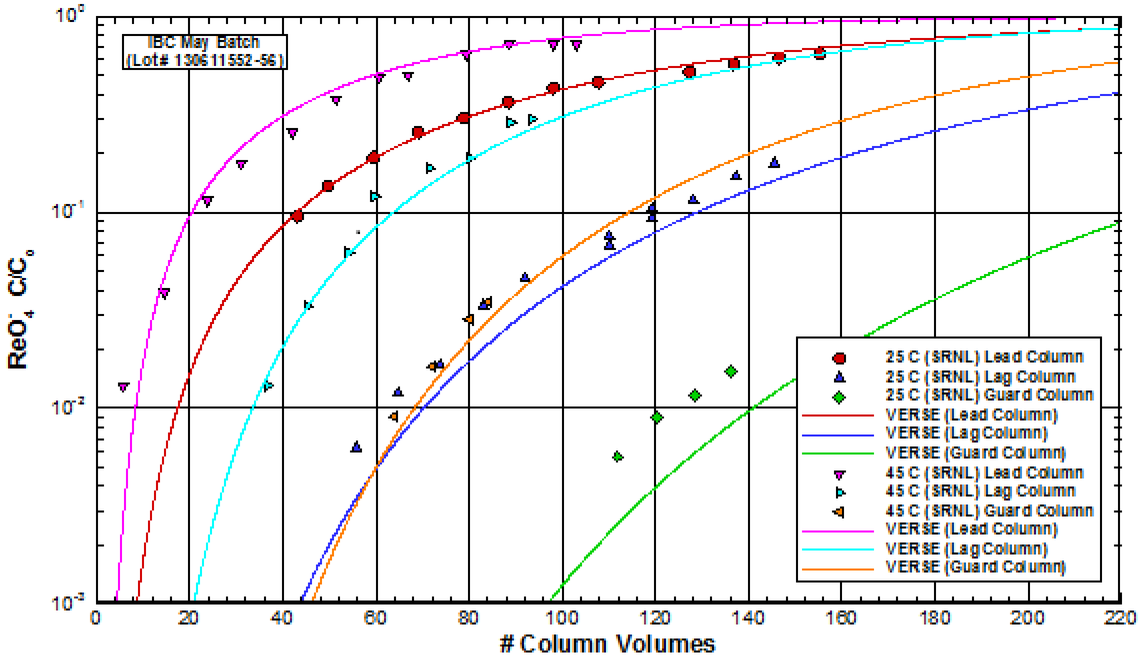

Figure C-8. Semi-log scale comparison of VERSE predicted ReO_4 column performance at 25˚ and 45˚C for the IBC May batch of SuperLig® 639 resin.

Listings of the computed residuals are provided in Tables C-3 and C-4 for the 25˚C and 45˚C tests, respectively. As Figure C-8 indicates predicted breakthrough typically occurs after the experimentally measured values. To estimate this "bias" in the model predictions, an average bias factor was computed using:

$$\langle \delta \rangle = 100 \times \left[\frac{\sum_{i=1}^{N_{set}} [r_i]}{N_{set}} \right] , \qquad \text{(C-14)}$$

where

$\langle \delta \rangle$ - Average bias factor in predicted versus experimental breakthrough

The computed rms and bias values (on a percentage basis) are also provided in Table C-3 and C-4. At both operating temperatures the same trend in bias factors are observed: (1) slightly better breakthrough performance is predicted than observed for the lead column and (2) progressively poorer performance for the lag and guard columns. These systematic bias trends suggest that improved predictive capability could be achieved; however, no attempts were made in this assessment effort to reduce overall bias factors. A more thoroughly complete error analysis should also include measurement bias and uncertainties.

Table C-3. Computed (c/c_o) residual values for the 25˚C breakthrough data

	Lead Column				Lag Column				Guard Column			
i	**BV**	**Exp**	**VERSE**	**resid**	**BV**	**Exp**	**VERSE**	**resid**	**BV**	**Exp**	**VERSE**	**resid**
1	43.1	0.0953	0.1002	0.0512	55.8	0.0063	0.0035	-0.4487	111.9	0.0057	0.0026	-0.5463
2	49.7	0.1361	0.1339	-0.0165	64.9	0.0119	0.0070	-0.4105	120.2	0.0091	0.0040	-0.5594
3	59.4	0.1909	0.1873	-0.0187	73.9	0.0168	0.0125	-0.2557	128.6	0.0117	0.0060	-0.4915
4	69.1	0.255	0.2436	-0.0447	83	0.0334	0.0202	-0.3941	136.3	0.0155	0.0083	-0.4632
5	78.7	0.3038	0.3003	-0.0115	92	0.0457	0.0304	-0.3349			%rms	51.7
6	88.5	0.3633	0.3580	-0.0146	110.1	0.0676	0.0589	-0.1285			%bias	-51.5
7	98	0.4273	0.4127	-0.0342	119.3	0.0926	0.0775	-0.1626				
8	107.7	0.459	0.4667	0.0167	128.2	0.1155	0.0982	-0.1500				
9	127.3	0.5165	0.5676	0.0990	137.4	0.1519	0.1221	-0.1965				
10	136.8	0.5661	0.6120	0.0812	145.5	0.1770	0.1451	-0.1804				
11	146.5	0.607	0.6541	0.0776	110.1	0.0757	0.0589	-0.2216				
12	155.4	0.648	0.6898	0.0644	119.3	0.1043	0.0775	-0.2568				
			%rms	5.3			%rms	28.2				
			%bias	+2.1			%bias	-26.2				

Table C-4. Computed (c/c_o) residual values for the 45˚C breakthrough data

	Lead Column				Lag Column				Guard Column			
i	**BV**	**Exp**	**VERSE**	**resid**	**BV**	**Exp**	**VERSE**	**resid**	**BV**	**Exp**	**VERSE**	**resid**
1	5.7	0.013	0.0027	-0.7951	36.6	0.0130	0.0145	0.1164	63.9	0.0091	0.0071	-0.2228
2	14.7	0.039	0.0478	0.2264	45.4	0.0330	0.0331	0.0040	72	0.0163	0.0132	-0.1867
3	23.8	0.115	0.1338	0.1635	54.1	0.0620	0.0603	-0.0278	80.1	0.0284	0.0223	-0.2150
4	31.1	0.176	0.2127	0.2087	59.7	0.1210	0.0821	-0.3216	84.1	0.0346	0.0280	-0.1909
5	42.1	0.254	0.3316	0.3054	71.5	0.1680	0.1377	-0.1802			%rms	20.4
6	51.4	0.373	0.4256	0.1411	80.1	0.1880	0.1849	-0.0164			%bias	-20.4
7	60.7	0.486	0.5114	0.0523	88.9	0.2880	0.2374	-0.1758				
8	66.9	0.5	0.5636	0.1272	93.4	0.2970	0.2654	-0.1065				
9	79.3	0.639	0.6556	0.0260			%rms	15.5				
10	88.6	0.729	0.7142	-0.0203			%bias	-8.8				
11	98	0.719	0.7649	0.0639								
12	103.1	0.716	0.7891	0.1021								
			%rms	27.4								
			%bias	+5.0								

Appendix D – Full-Scale Column Performance Assessment

Full-scale multi-column run calculations were performed where 1% cumulative breakthrough of TcO_4^- concentration was used as the exit criterion. The "cumulative" average concentration (i.e., cumulative breakthrough sum) was computed and once this 1% value was reached in the liquid exiting the last column, the first column in the configuration was removed and replaced with a clean column at the end. This model step mathematically represents removing the lead column out of the system for elution. In the 2-column system, the new last column would be the "lag" or second column, and would be the "polish" or third column in the 3-column system. Conceptually, the process operates as a carousel, with the lead column valved out of series when it is saturated, and replaced by a new column in the last position.

A matrix of VERSE simulations was performed. All simulations assumed the same SuperLig® 639 resin batch as employed in the SRNL testing (i.e., the May batch from IBC with Lot #130611552-56). To provide future design guidance a range of design parameters were considered. The following items were employed to setting the simulation matrix:

- Both a 2-column and a 3-column carousel configuration were calculated.
- The standard L/D bed volume geometry of 3.0 was fixed.
- A range of flowrates spanning from 2.75 to 3.25 BV/hr was selected to accommodate the various flowrates considered in prior efforts.
- Both 25˚C and 45˚C were considered.
- Based on prior full-scale performance results and the current estimates employing the recent IBC resin batch, a lower range of active bed volumes ranging from 100 to 400 gallons was selected.
- Inlet TcO_4^- concentration of 1.98×10^{-5} [M] was selected.
- A cumulative average exit TcO_4^- concentration of 1% of the inlet value (i.e., 1.98×10^{-5} M) was selected (i.e., DF = 100).

Once a choice of active bed volume (gallons) and flowrate (BV/hr) has been selected all of the other geometrical parameters are fixed. For example, the length and diameter of a column is determined by:

$$D = \left(\frac{4V_{BV}}{3\pi} \right)^{1/3} , \qquad \text{(D-1)}$$

using

$$L = 3D \ . \qquad \text{(D-2)}$$

where

V_{BV} - Active bed volume of each column in the carousel configuration
D - Diameter of each active bed (assumed to be equal for all columns in operation)
L - Length of each active bed (assumed to be equal for all columns in operation)

At each temperature a total of 12 VERSE simulations were run for each carousel configuration. These 24 cases are listed in Table D-1 where only the total column length differed between the 2-Column versus the 3-Column configurations.

Table D-1. Simulation matrix considered for developing a design guidance correlation.

Case ID	Flowrate (BV/hr)	Volume (gal)	Diameter (cm)	2-Column Length (cm)	3-Column Length (cm)	Flowrate (ml/min)	CSTR-Volume (ml)
A	2.75	100.00	54.36	326.18	489.26	17349.81	378541.2
B		200.00	68.49	410.96	616.43	34699.61	757082.4
C		300.00	78.40	470.43	705.64	52049.42	1135623.6
D		400.00	86.30	517.77	776.66	69399.22	1514164.8
E	3.00	100.00	54.36	326.18	489.26	18927.06	378541.2
F		200.00	68.49	410.96	616.43	37854.12	757082.4
G		300.00	78.40	470.43	705.64	56781.18	1135623.6
H		400.00	86.30	517.77	776.66	75708.24	1514164.8
I	3.250	100.00	54.36	326.18	489.26	20504.32	378541.2
J		200.00	68.49	410.96	616.43	41008.63	757082.4
K		300.00	78.40	470.43	705.64	61512.95	1135623.6
L		400.00	86.30	517.77	776.66	82017.26	1514164.8

For each temperature and case defined above in Table D-1, VERSE simulations were performed to determine the steady-state number of bed volumes required to reach the cumulative average exit criterion. The results are tabulated in Tables D-2 through D-5 for each temperature and column configuration of interest. Only the key results of each VERSE simulation are tabulated in Tables D-2 through D-5. The entire 48 cases considered were run using DOS scripts connected to a Microsoft Excel® spreadsheet and the VERSE executable. About 12 hours of Central Processing Unit time (i.e., a single overnight run) was required to complete the entire 48 cases.

Table D-2. Number of bed volumes processed per cycle at 25˚C and for a 2-Column configuration.

Case ID	Batch Volume (1000 gal)	Active Bed Volume	Flowrate (BV/hr)	Number of BVs Processed	Process Time (hr)
A	19.0	100	2.75	190.0	69.1
B	38.0	200	2.75	190.0	69.1
C	57.0	300	2.75	190.0	69.1
D	76.1	400	2.75	190.3	69.2
E	18.4	100	3.00	184.0	61.3
F	36.9	200	3.00	184.5	61.5
G	55.4	300	3.00	184.7	61.6
H	73.9	400	3.00	184.8	61.6
I	17.9	100	3.25	179.0	55.1
J	35.8	200	3.25	179.0	55.1
K	53.8	300	3.25	179.3	55.2
L	71.7	400	3.25	179.3	55.2

Table D-3. Number of bed volumes processed per cycle at 25˚C and for a 3-Column configuration..

Case ID	Batch Volume (1000 gal)	Active Bed Volume	Flowrate (BV/hr)	Number of BVs Processed	Process Time (hr)
A	21.4	100	2.75	214.0	77.8
B	42.8	200	2.75	214.0	77.8
C	64.3	300	2.75	214.3	77.9
D	85.8	400	2.75	214.5	78.0
E	21.1	100	3.00	211.0	70.3
F	42.3	200	3.00	211.5	70.5
G	63.4	300	3.00	211.3	70.4
H	84.6	400	3.00	211.5	70.5
I	20.8	100	3.25	208.0	64.0
J	41.7	200	3.25	208.5	64.2
K	62.5	300	3.25	208.3	64.1
L	83.4	400	3.25	208.5	64.2

Table D-4. Number of bed volumes processed per cycle at 45˚C and for a 2-Column configuration.

Case ID	Batch Volume (1000 gal)	Active Bed Volume	Flowrate (BV/hr)	Number of BVs Processed	Process Time (hr)
A	9.0	100	2.75	90.0	32.7
B	18.0	200	2.75	90.0	32.7
C	27.1	300	2.75	90.3	32.8
D	36.1	400	2.75	90.3	32.8
E	8.6	100	3.00	86.0	28.7
F	17.3	200	3.00	86.5	28.8
G	26.0	300	3.00	86.7	28.9
H	34.7	400	3.00	86.8	28.9
I	8.3	100	3.25	83.0	25.5
J	16.6	200	3.25	83.0	25.5
K	25.0	300	3.25	83.3	25.6
L	33.3	400	3.25	83.3	25.6

Table D-5. Number of bed volumes processed per cycle at 45˚C and for a 3-Column configuration.

Case ID	Batch Volume (1000 gal)	Active Bed Volume	Flowrate (BV/hr)	Number of BVs Processed	Process Time (hr)
A	10.9	100	2.75	109.0	39.6
B	21.7	200	2.75	108.5	39.5
C	32.6	300	2.75	108.7	39.5
D	43.4	400	2.75	108.5	39.5
E	10.6	100	3.00	106.0	35.3
F	21.3	200	3.00	106.5	35.5
G	31.9	300	3.00	106.3	35.4
H	42.6	400	3.00	106.5	35.5
I	10.4	100	3.25	104.0	32.0
J	20.8	200	3.25	104.0	32.0
K	31.2	300	3.25	104.0	32.0
L	41.6	400	3.25	104.0	32.0

The number of bed volumes required to reach the desired cumulative average exit concentration was correlated for each column configuration to the simple bilinear formula:

$$n_{BV} = a + b[F - 3.0] + c[T - 25.0] + d[F - 3.0][T - 25.0] \quad , \qquad \text{(D-3)}$$

where

n_{BV} - Number of active bed volumes processed per repeatable cycle
T - Average operating temperature of entire carousel columns
F - Inlet volumetric flowrate expressed in terms of active BV/hr
a, b, c, d - Correlation coefficients dependent on number of columns in carousel

Initial startup of either carousel configuration will experience varying bed volume performance initially, but quickly a repeating pattern is established (i.e., about 3 cycles for the 2-column system and 4 cycles for the 3-column system). This is because the first cycle begins with all columns completely unused, whereas the columns are partially saturated in subsequent cycles, and it takes a few cycles to establish a consistent pattern. Every column within the carousel operates within the approximately linear region of the isotherm, thus making the overall transport equations linear.

A simple least squares fitting to the matrix results was performed for each column configuration. The results of the two fitting procedures yielded:

2-Column System:

$$n_{BV} = 184.563 - 21.833[F - 3] - 4.899[T - 25] + 0.392[F - 3][T - 25] \quad , \qquad \text{(D-4a)}$$

3-Column System:

$$n_{BV} = 211.292 - 11.750[F - 3] - 5.248[T - 25] + 0.121[F - 3][T - 25] \quad . \qquad \text{(D-4b)}$$

Graphically the predictions from the above two fits are compared in Figure D-1 with the VERSE results taken from Tables D-2 through D-5.

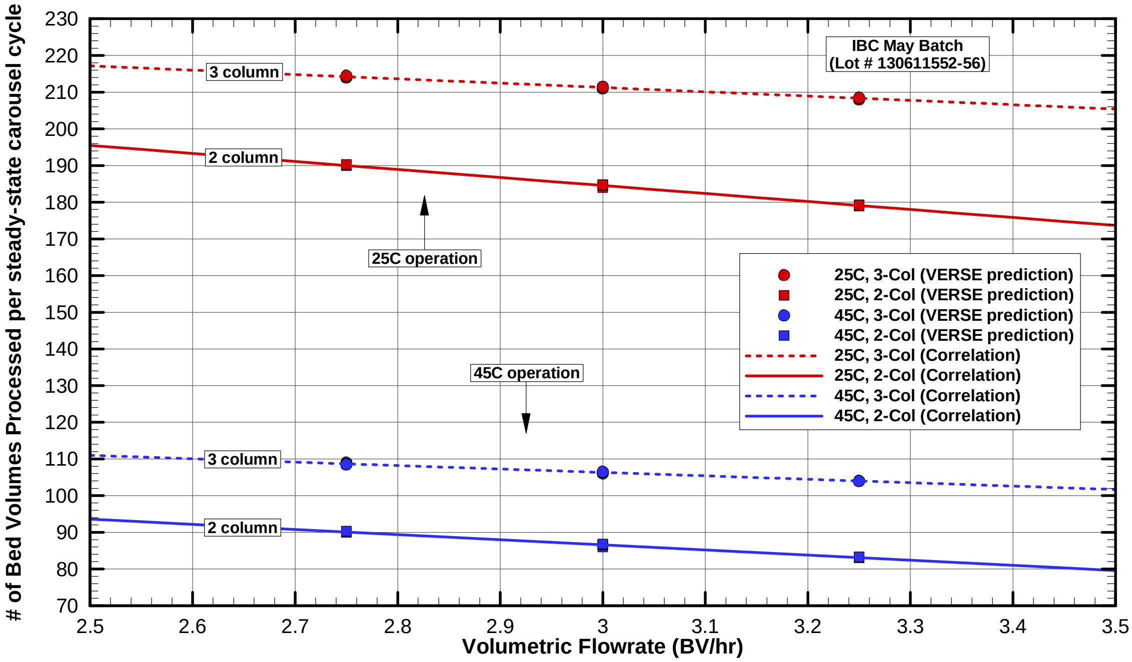

Figure D-1. Correlations for Bed Volumes Processes versus Flowrate

These correlations provide for quick design guidance and can be assumed to be acceptable over:

- The temperature range of 25˚ to 45˚C;
- The flowrate range of 2.5 to 3.5 BV/hr;
- Active bed volumes of 100 to 400 gallons;
- Either a 2 or 3 column carousel configuration;
- The estimated average HTWOS feed composition at 5M Na^+; and
- Inlet TcO_4^- concentrations up to approximately $1x10^{-4}$ M.

The key assumption here is that an essentially clean column is placed at the rear-column position at the start of each carousel cycle. Since the exit criterion (here a cumulative average value, but an instantaneous value could have been selected instead) is expressed as a percentage of the inlet concentration, the above column performance values are not dependent upon the actually chosen inlet concentration value. This remains true as long as the inlet concentration is in the linear region of the isotherm (i.e., linear transport equations apply) and for the selected feed composition indicates a value up to $1x10^{-4}$ M is acceptable.

As can be seen in Tables D-2 through D-5, as well as Figure D-1, the active bed volume plays a minor role in the number of such bed volumes that can be processed per cycle. However, the total volume of feed that can be processed is directly related to the active bed volume as shown in Figure D-2. As expected doubling the size of an active bed volume approximately doubles the amount of feed processed during a carousel cycle.

Also, going from 25˚C up to 45˚C reduces the processed volume by approximately 51.4% (i.e., 53.1% for 2-Column operations and 49.7% for 3-Column operations). Going from a 2-Column to a 3-Column configuration the processed volume is increased by approximately 18.7% (i.e., 14.5% for 25˚C operations and 22.9% for 45˚C operations).

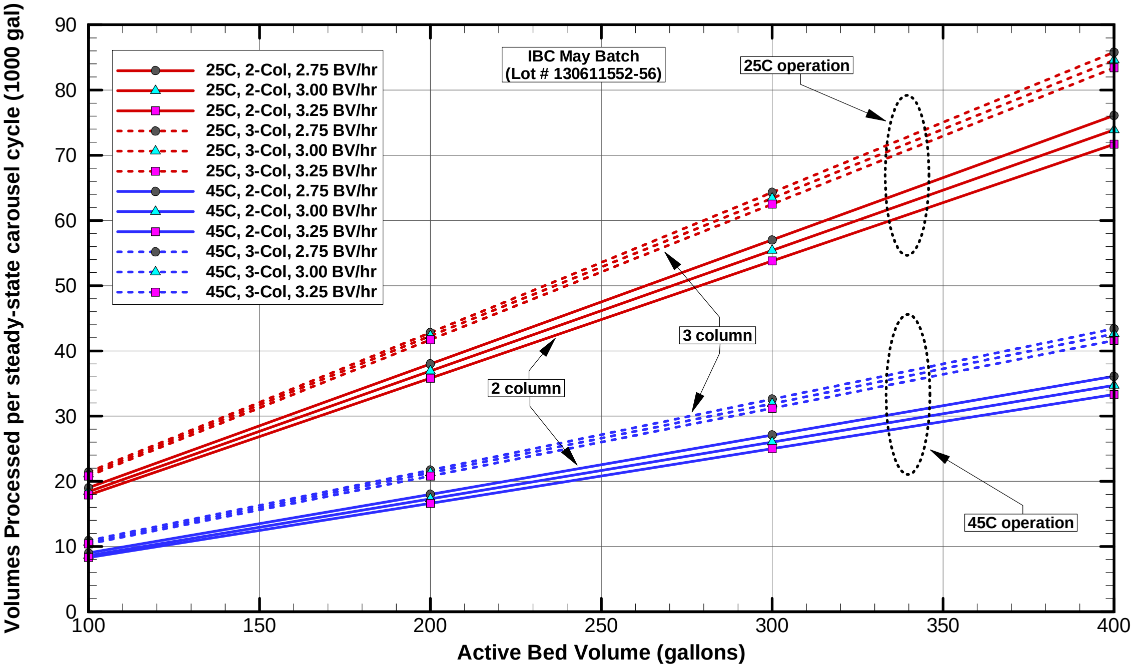

Figure D-2. Comparison predicted TcO_4 column performance at 25˚ and 45˚C for the IBC May batch of SuperLig® 639 resin.

To illustrate the use of Equations D-4a and D-4b, the following example is provided:

Parameter values chosen were taken from the recently issued engineering study performed by WRPS [Russell, 2013; see Section 2.3]:

- A 3-Column configuration (i.e., lead, lag, and polish columns);
- 25˚C operating temperature;
- 362 gallon active bed volume for each column; and
- 20 gpm feed stream flowrate (i.e., corresponds to a 3.315 BV/hr).

The other key assumptions being made are:

- Average HTWOS feed composition at 5M [Na^+];
- L/D ratio assumed to be fixed at 3.0; and
- Resin batch assumed to be consistent behavior with IBC Lot # 130611552-56.

Thus, at T = 25˚C and F = 3.315 BV/hr, using a 3-Column configuration Eq. (D-4b) applies. The computed “number” of bed volumes processed becomes:

$$n_{BV} = 207.59 \tag{D-5}$$

and for the given active bed volume size of 362 gallons the total volume of feed processed per cycle (i.e., after the first 4 startup cycles) becomes:

$$V_{processed} = 75{,}150 \quad \text{(gallons)} \tag{D-6}$$

where

$V_{processed}$ - Total volume of feed solution processed per repeatable cycle

Appendix E – Laboratory-Scale Column Input and Output Files

For reference the VERSE-LC input and output files for the laboratory-scale (SRNL) column benchmarking (i.e., 25˚C and 45˚C runs) are provided in this appendix. Both column tests were performed using perrhenate. The input and output files for each temperature run are listed below:

VERSE Input File for Lab-Scale 25C Perrhenate Column (SRNL) Test

```
Simulation at 25C of ReO4- removal on experimental SL639 3 column system
1 component (ReO4-) isotherm (HTWOS simulant)
1, 150, 4, 6                      ncomp, nelem, ncol-bed, ncol-part
FCWNA                             isotherm,axial-disp,film-coef,surf-diff,BC-col  FCUNA
NNNNN                             input-only,perfusable,feed-equil,datafile.yio
M                                 comp-conc units
17.1, 1.56, 0.585, 3.4            Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
387.0, 0.363, 0.437,  0.0         part-rad(um), bed-void, part-void, sorb-cap()
0.0                               initial concentrations (M)
S                                 COMMAND - conc step change
1, 0.0, 4.30d-5, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                 COMMAND - viscosity/density change
0.02314, 1.2230                   fluid viscosity(posie), density(g/cm^3)
m                                 COMMAND - subcolumns
50, 150, 0, 1, 0.1, 0, 10000     elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                 COMMAND - effluent history dump
2, 1.0, 1.0, 0.25, 0.1            unit op#, ptscale(1-4) filtering
h                                 COMMAND - effluent history dump
4, 1.0, 1.0, 0.25, 0.1            unit op#, ptscale(1-4) filtering
h                                 COMMAND - effluent history dump
6, 1.0, 1.0, 0.25, 0.1            unit op#, ptscale(1-4) filtering
D
-1, 3000.0, 1, 0.0
-                                end of commands
6000.0, 0.1                      end time(min), max dt in B. s
1.0d-7, 1.0d-4                   abs-tol, rel-tol
-                                non-negative conc constraint
1.0d0                            size exclusion factor
1.269d-4                         part-pore diffusivities(cm^2/min) 50% of free values
3.625d-4                         Brownian diffusivities(cm^2/min)
0.29318                          Freundlich/Langmuir Hybrid a    (moles/L B.V.)
1.0                              Freundlich/Langmuir Hybrid b    (1/M)
1.0                              Freundlich/Langmuir Hybrid Ma   (-)
1.0                              Freundlich/Langmuir Hybrid Mb   (-)
2.23285E-03                      Freundlich/Langmuir Hybrid beta (-)
```

VERSE Output File for Lab-Scale 25˚C Perrhenate Column (SRNL) Test

```
===============================================================================
 VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
 ===============================================================================
 Input file: case
 Simulation of ReO4- removal on experimental SL639 3 column system
 1 component (ReO4-) isotherm (HTWOS simulant)
 Begin Run:  18:14:47 on 11-07-2013   running under Windows 95/8
 Finite elements    - axial:150  particle: 1
 Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
 Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
 Use Profile File? N   Generate Profile File? N
 Axial dispersion correlation:   Chung & Wen (1968)
 Film mass transfer correlation: Wilson & Geankoplis (1966)
 Sub-Column Boundary Conditions: Axial Dispersion and CSTR
 ===============================================================================
```

```
SYSTEM PARAMETERS (at initial conditions):

t(stop)        =   6000.00000 min         dtheta max     =       .10000 BV
abs. tol.      =       .10000E-06         rel. tol.      =       .10000E-03
Total Length   =     17.10000 cm          D              =      1.56000 cm
Tot. Capacity  =       .00000 eq/L solid  Col. Vol.      =     32.68400 mL
F              =       .58500 mL/min      Uo (linear)    =       .84316 cm/min
R              =    387.00000 microns     L/R            =    441.86047
Bed Void frac. =       .36300             Pcl. Porosity  =       .43700
Spec. Area     =     49.37984 1/cm        Time/BV        =      6.76028 min
Vol CSTRs      =      3.40000 mL

Component no.  =      1
Ke  [-]        =  .10000E+01
Eb  [cm2/min]  =  .11744E+00
Dp  [cm2/min]  =  .12690E-03
Doo [cm2/min]  =  .36250E-03
kf  [cm/min]   =  .56646E-01
Ds  [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re             =  .20867E-01
Sc(i)          =  .31317E+04
Peb(i)         =  .40923E+02
Bi(i)          =  .39531E+02
Nf(i)          =  .52093E+02
Np(i)          =  .25031E+00
Pep(i)         =  .58841E+03

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .29318E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .22329E-02
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units          M
===============================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .4300E-04 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2314E-01 poise and density to 1.223     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+05 min.
     When comp.  1 reaches .1000     M     at end of node 150,
     shift  50 axial elements out the feed end
  4: 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
  5: Monitor conc. history at stream  4.  Filename = case.h02
     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
  6: Monitor conc. history at stream  6.  Filename = case.h03
     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
  7: Dump full profile file at  3000.     min
     Execute   1 times, every .0000     mins.
===============================================================================
VERSE-LC finished in  8905 steps.  Average step size .6738     minutes
End run:  18:16:30 on 11-07-2013
Integrated Areas in History Files:
case.h01                   .155271
case.h02                   .682112E-01
case.h03                   .194819E-01
```

VERSE Input File for Lab-Scale 45˚C Perrhenate Column (SRNL) Test

```
Simulation at 45C of ReO4- removal on experimental SL639 3 column system
1 component (ReO4-) isotherm (HTWOS simulant)
1, 150, 4, 6                      ncomp, nelem, ncol-bed, ncol-part
FCWNA                             isotherm,axial-disp,film-coef,surf-diff,BC-col  FCUNA
NNNNN                             input-only,perfusable,feed-equil,datafile.yio
M                                 comp-conc units
17.1, 1.56, 0.560, 3.4            Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
387.0, 0.363, 0.437,  0.0         part-rad(um), bed-void, part-void, sorb-cap()
0.0                               initial concentrations (M)
S                                 COMMAND - conc step change
1, 0.0, 4.67d-5, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                 COMMAND - viscosity/density change
0.01530, 1.2050                   fluid viscosity(posie), density(g/cm^3)
m                                 COMMAND - subcolumns
50, 150, 0, 1, 0.1, 0.0, 10000   elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                 COMMAND - effluent history dump
2, 1.0, 1.0, 0.25, 0.1            unit op#, ptscale(1-4) filtering
h                                 COMMAND - effluent history dump
4, 1.0, 1.0, 0.25, 0.1            unit op#, ptscale(1-4) filtering
h                                 COMMAND - effluent history dump
6, 1.0, 1.0, 0.25, 0.1            unit op#, ptscale(1-4) filtering
D
-1, 3000.0, 1, 0.0
-                                end of commands
6000.0, 0.1                      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
0.900d-4                         part-pore diffusivities(cm^2/min) 50% of free values
5.850d-4                         Brownian diffusivities(cm^2/min)
0.29323                          Freundlich/Langmuir Hybrid a    (moles/L B.V.)
1.0                              Freundlich/Langmuir Hybrid b    (1/M)
1.0                              Freundlich/Langmuir Hybrid Ma   (-)
1.0                              Freundlich/Langmuir Hybrid Mb   (-)
4.15318E-03                      Freundlich/Langmuir Hybrid beta (-)
```

VERSE Output File for Lab-Scale 45˚C Perrhenate Column (SRNL) Test

```
===============================================================================
 VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
 ===============================================================================
 Input file: case
 Simulation of ReO4- removal on experimental SL639 3 column system
 1 component (ReO4-) isotherm (HTWOS simulant)
 Begin Run:  18:47:57 on 11-07-2013   running under Windows 95/8
 Finite elements    - axial:150  particle: 1
 Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
 Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
 Use Profile File? N   Generate Profile File? N
 Axial dispersion correlation:   Chung & Wen (1968)
 Film mass transfer correlation: Wilson & Geankoplis (1966)
 Sub-Column Boundary Conditions: Axial Dispersion and CSTR
 ===============================================================================
 SYSTEM PARAMETERS (at initial conditions):

 t(stop)        =   6000.00000 min         dtheta max     =       .10000 BV
 abs. tol.      =       .10000E-06         rel. tol.      =       .10000E-03
 Total Length   =     17.10000 cm          D              =      1.56000 cm
 Tot. Capacity  =       .00000 eq/L solid  Col. Vol.      =     32.68400 mL
 F              =       .56000 mL/min      Uo (linear)    =       .80713 cm/min
 R              =    387.00000 microns     L/R            =    441.86047
 Bed Void frac. =       .36300             Pcl. Porosity  =       .43700
 Spec. Area     =     49.37984 1/cm        Time/BV        =      7.06208 min
 Vol CSTRs      =      3.40000 mL
```

```
Component no.  =      1
Ke  [-]        =  .10000E+01
Eb  [cm2/min]  =  .11224E+00
Dp  [cm2/min]  =  .90000E-04
Doo [cm2/min]  =  .58500E-03
kf  [cm/min]   =  .76809E-01
Ds  [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re             =  .29767E-01
Sc(i)          =  .13023E+04
Peb(i)         =  .40988E+02
Bi(i)          =  .75579E+02
Nf(i)          =  .73788E+02
Np(i)          =  .18545E+00
Pep(i)         =  .79420E+03

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .23454E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .33164E-02
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units          M
===============================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .4670E-04 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .1530E-01 poise and density to 1.205     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+05 min.
     When comp.  1 reaches .1000     M     at end of node 150,
     shift  50 axial elements out the feed end
  4: 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
  5: Monitor conc. history at stream  4.  Filename = case.h02
     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
  6: Monitor conc. history at stream  6.  Filename = case.h03
     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
  7: Dump full profile file at  3000.     min
     Execute   1 times, every .0000     mins.
===============================================================================
VERSE-LC finished in  8518 steps.  Average step size .7044     minutes
End run:  18:49:35 on 11-07-2013
Integrated Areas in History Files:
case.h01                 .216005
case.h02                 .152644
case.h03                 .942321E-01
```

Appendix F– Full-Scale Column Input Files

For reference VERSE-LC input files for full-scale column simulations are provided in this appendix. Output files are not included here since cumulative average calculations were performed. To perform a cumulative average calculation requires multiple VERSE-LC runs where the timing of carousel operations are iteratively determined. Thus, no single VERSE-LC output file exists. The cases presented here correspond to an "effective" single component isotherm modeling approach where the pertechnetate ion is modeled assuming the nitrate concentration remains essentially constant throughout the columns. Note that the maximum number of internal collocation points within the pores allowed by VERSE-LC was used. Early numerical testing to establish the minimum usable number of finite elements and collocation points that maintains acceptable accuracy indicated that radial concentration gradients within the particle pores were large and sharp.

As mentioned in Appendix D, twelve 2-Column and twelve 3-Column simulation runs were performed for each temperature resulting in a total of 48 cumulative average simulations. These 48 runs were performed during an overnight batch DOS scripting process. Only the Case F set of VERSE-LC input files will be provided, as an example. The remaining files can easily be determined by replacing the appropriate parameter values as listed in Table D-1.

Table F-1. Key parameter settings[a] for VERSE-LC simulation for the full-scale 2-Column configuration at 25˚C (here Case F from Table D-1).

Parameter	Parameter settings
Number of finite elements within bed	50 for each bed
Number of internal collocation points per finite element within bed	4 for each bed
Number of internal collocation points within pores	6 for each bed
Components explicitly modeled:	pertechnetate
Axial dispersion, E_b (cm^2/min)	Chung and Wen (1968) correlation
Film coefficient, k_f (cm/min)	Wilson and Geankoplis (1966) correlation
Active column lengths, L	205.48 cm for each bed
Column diameters, D	68.49 cm for each bed
Headspace volumes	757.08 L for each bed
Particle radius (μm)	387
Bed porosities, ε_b (-)	0.363 for each bed
Particle porosities, ε_p (-)	0.437 for each bed
Fluid dynamic viscosity, μ_w	0.02314 poise
Fluid density, ρ_w	1.223 g/ml
Lag column switching exit technetium concentration criterion (none for lead)	1.0% of feed concentration as cumulative average
Native (initial) concentration	0.0 M
Feed (loading) concentration	1.98×10^{-5} M
Molecular diffusion coefficient	3.625×10^{-4} cm^2/min
Particle pore diffusion coefficient	1.269×10^{-4} cm^2/min
Freundlich-Langmuir Hybrid **a** coefficient	2.9314×10^{-1} gmoles/L_{BV}
Freundlich-Langmuir Hybrid **b** coefficient	1.0 M^{-1}
Freundlich-Langmuir Hybrid $\mathbf{M_a}$ coefficient	1.0 (-)
Freundlich-Langmuir Hybrid $\mathbf{M_b}$ coefficient	1.0 (-)
Freundlich-Langmuir Hybrid **β** "effective" coefficient for pertechnetate	1.12755×10^{-3} (-)

[a] Isotherm model parameters are based on a bed density of 0.4498 g_{resin}/ml and a total ionic exchange capacity of 0.6517 mmole/g_{resin} consistent with IBC batch ID (Lot # 130611552-56).

Below the four VERSE-LC input files for Case F are provided (i.e., the 25˚C and 45˚C conditions for both the 2-Column and 3-Column configurations).

VERSE Input File for Full-Scale 25˚C Pertechnetate 2-Column System (Case F)

```
Simulation of TcO4- removal on full-scale SL639 2 column system [May IBC Batch Lot
#130611552-56]
1 component (TcO4-) isotherm (HTWOS simulant) at 25 C [Case_F]
1, 100, 4, 6                      ncomp, nelem, ncol-bed, ncol-part
FCWNA                             isotherm,axial-disp,film-coef,surf-diff,BC-col  FCUNA
NNNYY                             input-only,perfusable,feed-equil,datafile.yio
M                                 comp-conc units
410.96, 68.49, 37854.12, 757082.4 Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
387.0, 0.363, 0.437,  0.0         part-rad(um), bed-void, part-void, sorb-cap()
0.0                               initial concentrations (M)
S                                 COMMAND - conc step change
1, 0.0, 1.98d-5, 1, 0.0            spec id, time(min), conc(M), freq, dt(min)
V                                 COMMAND - viscosity/density change
0.02314, 1.223                    fluid viscosity(posie), density(g/cm3)
m                                 COMMAND - subcolumns
50, 100, 0, 1, 1.98d+7,0,10000  elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                 COMMAND - effluent history dump
1, 1.0, 1.0, 0.25, 0.1            unit op#, ptscale(1-4) filtering
h                                 COMMAND - effluent history dump
2, 1.0, 1.0, 0.25, 0.1            unit op#, ptscale(1-4) filtering
h                                 COMMAND - effluent history dump
3, 1.0, 1.0, 0.25, 0.1            unit op#, ptscale(1-4) filtering
h                                 COMMAND - effluent history dump
4, 1.0, 1.0, 0.25, 0.1            unit op#, ptscale(1-4) filtering
D
-1, 6000.0, 1, 0.0
-                                end of commands
6000.0, 0.1                      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
1.269d-4                         part-pore diffusivities(cm2/min) 50 of free values
3.625d-4                         Brownian diffusivities(cm2/min)
0.29314                          Freundlich/Langmuir Hybrid a    (moles/L B.V.)
1.0                              Freundlich/Langmuir Hybrid b    (1/M)
1.0                              Freundlich/Langmuir Hybrid Ma   (-)
1.0                              Freundlich/Langmuir Hybrid Mb   (-)
1.12755E-03                      Freundlich/Langmuir Hybrid beta (-)
```

VERSE Input File for Full-Scale 25˚C Pertechnetate 3-Column System (Case F)

```
Simulation of TcO4- removal on full-scale SL639 3 column system [May IBC Batch Lot
#130611552-56]
1 component (TcO4-) isotherm (HTWOS simulant) at 25 C [Case_F]
1, 150, 4, 6                      ncomp, nelem, ncol-bed, ncol-part
FCWNA                             isotherm,axial-disp,film-coef,surf-diff,BC-col  FCUNA
NNNYY                             input-only,perfusable,feed-equil,datafile.yio
M                                 comp-conc units
616.43, 68.49, 37854.12, 757082.4 Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
387.0, 0.363, 0.437,  0.0         part-rad(um), bed-void, part-void, sorb-cap()
0.0                               initial concentrations (M)
S                                 COMMAND - conc step change
1, 0.0, 1.98d-5, 1, 0.0            spec id, time(min), conc(M), freq, dt(min)
V                                 COMMAND - viscosity/density change
0.02314, 1.223                    fluid viscosity(posie), density(g/cm3)
m                                 COMMAND - subcolumns
50, 150, 0, 1, 1.98d+7,0, 10000  elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                 COMMAND - effluent history dump
1, 1.0, 1.0, 0.25, 0.1            unit op#, ptscale(1-4) filtering
h                                 COMMAND - effluent history dump
```

```
2, 1.0, 1.0, 0.25, 0.1           unit op#, ptscale(1-4) filtering
h                                COMMAND - effluent history dump
3, 1.0, 1.0, 0.25, 0.1           unit op#, ptscale(1-4) filtering
h                                COMMAND - effluent history dump
4, 1.0, 1.0, 0.25, 0.1           unit op#, ptscale(1-4) filtering
h                                COMMAND - effluent history dump
5, 1.0, 1.0, 0.25, 0.1           unit op#, ptscale(1-4) filtering
h                                COMMAND - effluent history dump
6, 1.0, 1.0, 0.25, 0.1           unit op#, ptscale(1-4) filtering
D
-1, 6000.0, 1, 0.0
-                               end of commands
6000.0, 0.1                     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
1.269d-4                        part-pore diffusivities(cm2/min) 50 of free values
3.625d-4                        Brownian diffusivities(cm2/min)
0.29314                         Freundlich/Langmuir Hybrid a    (moles/L B.V.)
1.0                             Freundlich/Langmuir Hybrid b    (1/M)
1.0                             Freundlich/Langmuir Hybrid Ma   (-)
1.0                             Freundlich/Langmuir Hybrid Mb   (-)
1.12755E-03                     Freundlich/Langmuir Hybrid beta (-)
```

VERSE Input File for Full-Scale 45˚C Pertechnetate 2-Column System (Case F)

```
Simulation of TcO4- removal on full-scale SL639 2 column system [May IBC Batch Lot
#130611552-56]
1 component (TcO4-) isotherm (HTWOS simulant) at 45 C [Case_F]
1, 100, 4, 6                     ncomp, nelem, ncol-bed, ncol-part
FCWNA                            isotherm,axial-disp,film-coef,surf-diff,BC-col  FCUNA
NNNYY                            input-only,perfusable,feed-equil,datafile.yio
M                                comp-conc units
410.96, 68.49, 37854.12, 757082.4 Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
387.0, 0.363, 0.437,  0.0        part-rad(um), bed-void, part-void, sorb-cap()
0.0                              initial concentrations (M)
S                                COMMAND - conc step change
1, 0.0, 1.98d-5, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                COMMAND - viscosity/density change
0.01530, 1.2050                  fluid viscosity(posie), density(g/cm3)
m                                COMMAND - subcolumns
50, 100, 0, 1, 1.98d+7,0, 10000  elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                COMMAND - effluent history dump
1, 1.0, 1.0, 0.25, 0.1           unit op#, ptscale(1-4) filtering
h                                COMMAND - effluent history dump
2, 1.0, 1.0, 0.25, 0.1           unit op#, ptscale(1-4) filtering
h                                COMMAND - effluent history dump
3, 1.0, 1.0, 0.25, 0.1           unit op#, ptscale(1-4) filtering
h                                COMMAND - effluent history dump
4, 1.0, 1.0, 0.25, 0.1           unit op#, ptscale(1-4) filtering
D
-1, 6000.0, 1, 0.0
-                               end of commands
6000.0, 0.1                     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
0.900d-4                        part-pore diffusivities(cm2/min) 50 of free values
5.850d-4                        Brownian diffusivities(cm2/min)
0.29318                         Freundlich/Langmuir Hybrid a    (moles/L B.V.)
1.0                             Freundlich/Langmuir Hybrid b    (1/M)
1.0                             Freundlich/Langmuir Hybrid Ma   (-)
1.0                             Freundlich/Langmuir Hybrid Mb   (-)
2.09704E-03                     Freundlich/Langmuir Hybrid beta (-)
```

VERSE Input File for Full-Scale 45˚C Pertechnetate 3-Column System (Case F)

```
Simulation of TcO4- removal on full-scale SL639 3 column system [May IBC Batch Lot
#130611552-56]
1 component (TcO4-) isotherm (HTWOS simulant) at 45 C [Case_F]
1, 150, 4, 6                       ncomp, nelem, ncol-bed, ncol-part
FCWNA                              isotherm,axial-disp,film-coef,surf-diff,BC-col  FCUNA
NNNYY                              input-only,perfusable,feed-equil,datafile.yio
M                                  comp-conc units
616.43, 68.49, 37854.12, 757082.4 Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
387.0, 0.363, 0.437,  0.0          part-rad(um), bed-void, part-void, sorb-cap()
0.0                                initial concentrations (M)
S                                  COMMAND - conc step change
1, 0.0, 1.98d-5, 1, 0.0             spec id, time(min), conc(M), freq, dt(min)
V                                  COMMAND - viscosity/density change
0.01530, 1.2050                    fluid viscosity(posie), density(g/cm3)
m                                  COMMAND - subcolumns
50, 150, 0, 1, 1.98d+7,0, 10000   elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                  COMMAND - effluent history dump
1, 1.0, 1.0, 0.25, 0.1             unit op#, ptscale(1-4) filtering
h                                  COMMAND - effluent history dump
2, 1.0, 1.0, 0.25, 0.1             unit op#, ptscale(1-4) filtering
h                                  COMMAND - effluent history dump
3, 1.0, 1.0, 0.25, 0.1             unit op#, ptscale(1-4) filtering
h                                  COMMAND - effluent history dump
4, 1.0, 1.0, 0.25, 0.1             unit op#, ptscale(1-4) filtering
h                                  COMMAND - effluent history dump
5, 1.0, 1.0, 0.25, 0.1             unit op#, ptscale(1-4) filtering
h                                  COMMAND - effluent history dump
6, 1.0, 1.0, 0.25, 0.1             unit op#, ptscale(1-4) filtering
D
-1, 6000.0, 1, 0.0
-                                 end of commands
6000.0, 0.1                       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
0.900d-4                          part-pore diffusivities(cm2/min) 50 of free values
5.850d-4                          Brownian diffusivities(cm2/min)
0.29318                           Freundlich/Langmuir Hybrid a    (moles/L B.V.)
1.0                               Freundlich/Langmuir Hybrid b    (1/M)
1.0                               Freundlich/Langmuir Hybrid Ma   (-)
1.0                               Freundlich/Langmuir Hybrid Mb   (-)
2.09704E-03                       Freundlich/Langmuir Hybrid beta (-)
```

Distribution:

S. L. Marra, 773-A
F. M. Pennebaker, 773-42A
T. B. Brown, 773-A
D.H. McGuire, 999-W
S. D. Fink, 773-A
C. C. Herman, 773-A
E. N. Hoffman, 999-W
W. R. Wilmarth, 773-A
P.A. Cavanaugh, WRPS
D.J. Swanberg, WRPS
W.G. Ramsey, WRPS
A.D. Cozzi. 999-W
K.M. Fox, 999-W
Records Administration (EDWS)