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Disclaimer:

SuperLig® 639 Resin Performance using 8 Molar LAW Feed

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Savannah River National Laboratory™

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

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EXECUTIVE SUMMARY

The primary chemical form of ^{99}Tc found in Hanford Low Activity Waste (LAW) is as pertechnetate anion (TcO_4^-). Pertechnetate is highly soluble in water, and is mobile if released to the environment. Pertechnetate will not be removed from the aqueous waste in the Hanford waste treatment plant, and will primarily end up immobilized in the LAW glass waste form, which will be disposed in the Integrated Disposal Facility (IDF).

Washington River Protection Solutions (WRPS) is developing some conceptual flow sheets for LAW treatment and disposal that could benefit from technetium removal. One of these flow-sheets will specifically examine removing 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. One of the technologies, SuperLig® 639[1], is an elutable Molecular Recognition Technology (MRT) resin available from a vendor. In practice, the resin performs like an ion exchange resin, but it elutes with water instead of caustic or acid. This resin has been shown very effective in removing pertechnetate from LAW.

All prior testing with SuperLig® 639 has been done with the aqueous concentration of LAW at ~5 M [Na^+], where the resin sinks, and can be used in a conventional down-flow column orientation. However, the aqueous LAW stream from the Waste Treatment Plant is expected to be ~8 M [Na^+]. The resin would float in this higher density liquid, potentially disrupting the ability to achieve a good decontamination due to poor packing of the resin that leads to channeling. Testing was completed with a higher salt concentration in the feed simulant (7.8 M [Na^+]) in an engineering-scale apparatus with two columns, each containing ~0.9 L of resin. Testing of this system used a simulant of the LAW solution, and substituted ReO_4^- as a surrogate for TcO_4^-. Results were then compared using computer modeling. Bench-scale testing was also performed, and examined an unconstrained resin bed, while engineering-scale tests used both constrained and unconstrained beds in a two-column, lead and lag sequential arrangement.

The resin loading cycle was performed at 25 °C (±3 °C), with a flow rate of 3.2-3.4 BV/hour, and eluted with water at 50-55 °C at 1 BV/hour. Three engineering-scale tests were performed with (1) up-flow with free-floating beds; (2) up-flow with restrained beds; and (3) down-flow with restrained beds. The key objective was to determine if the high density LAW solution can be treated to remove Tc without dilution by operating in up-flow mode and allowing the bed to float or by restraining the bed using a plunger to prevent bed movement. To do this, the tests measured the breakthrough profile of Re to determine if it is comparable to prior testing with lower density fluid in down-flow mode, indicating whether or not the floated bed packing is adequate to maintain a good decontamination factor. Samples were collected periodically and analyzed with ICP-ES or ICP-MS to determine the breakthrough loading profile. Results will be used to guide a decision on whether the LAW would need to be diluted to ~5 M [Na^+], which is known to be successful.

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

In the first (bench scale) test, with the unconstrained bed, the resin bed was observed to move as a single unit, i.e., the resin beads did not fluidize and the entire bed slid upwards inside the column. Engineering scale beds behaved similarly. Loading and elution performance was largely unaffected by bed configuration or operation for the tested conditions. However, the loading profile of the resin exhibited a much earlier breakthrough than predicted by computer modeling by ~40%. The exact cause of this has not been determined, but speculated reasons include precipitation of solids in the resin, inaccurate projections due to ionic strength effects, resin degradation, bubbles causing uneven flow patterns, or flow channeling in the beds. At this time, it is recommended that any plans for using this process assume that the feed must be diluted to ~5 M [Na^+], where the process has been demonstrated to be successful many times. Further testing would be needed to determine the exact cause of the early breakthrough, and until the cause can be determined and mitigated, planning should assume dilution of the feed.

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LIST OF ABBREVIATIONS

AD	Analytical Development, Savannah River National Laboratory
BV	resin bed volume
eHAP	electronic Hazards Assessment Package
g	grams (mass)
HLW	High Level Waste
ICP-ES	inductively coupled plasma –emission spectroscopy
ICP-MS	inductively coupled plasma – mass spectroscopy
IDF	Integrated Disposal Facility
IX	ion exchange
L	liter
LAW	Low Activity Waste
MRT	Molecular Recognition Technology
PA	Performance Assessment
QA	Quality Assurance
RPP	River Protection Project
SRNL	Savannah River National Laboratory
TTQAP	technical task and quality assurance plan
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 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 is the principal 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 (211,100 years)[2] and is highly mobile [Icenhower, 2008, 2010], it has potential to be a major dose contributor to the Performance Assessment (PA) of the Integrated Disposal Facility (IDF) [Mann, 2003], although the glass wasteform matrix is effective at retaining it. Due to the aqueous solubility 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 to immobilize the LAW portion of the tank waste are being explored. Removal of ^{99}Tc, followed by off-site disposal of technetium from the supplemental LAW flow sheet, would eliminate a key risk contributor for the IDF PA for supplemental waste forms, and has potential to reduce treatment and disposal costs and accelerate mission completion. 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. One of the technologies, SuperLig® 639[3], is an elutable MRT resin available from a vendor. This resin has been shown very effective in removing pertechnetate from LAW.

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, if present, can be removed by filtration.

This report contains results of experimental column testing using the resin SuperLig® 639 to selectively remove perrhenate from simulated supplemental LAW and comparisons to computer modeling prediction of the column performance. All prior testing with SuperLig® 639 has been done with the aqueous concentration of LAW at ~5 M [Na^+], where the resin sinks, and can be used in a conventional down-flow column orientation. However, the WTP baseline flow-sheet condition for LAW feed that exits the pretreatment facility is at 7.8 M [Na^+] and is at 45°C. At this density, the resin floats, and this condition has potential to cause poor decontamination due to disrupted packing and channeling in the bed. The engineering-scale rig was designed such that the liquid flow can be up-flow or down-flow through the resin bed, and with a movable screen at the top of the bed that can act to constrain the beads from floating. Testing is intended

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[2] Live Chart of Nuclides – IAEA, Vienna, Austria

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

to show if the high density liquid can be processed by either allowing the bed to float, or by constraining it from floating, while still achieving a good decontamination factor. The resin bead density (i.e., the liquid density that causes resin beads to float) of this batch of resin is 1.258 g/mL. In the normal configuration of an unconstrained bed with liquid flowing in a downward direction, it would be necessary to dilute the liquid beneath this density so that the beads do not float, causing a fluidized bed subject to channeling and poor decontamination.

Removal of pertechnetate from tank waste samples using SuperLig®639 has been demonstrated many times [Hamm, 2013], but the current tests examine removal from a more concentrated tank waste composition that represents the entire tank waste inventory. The current 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 mathematical averaging. 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, 2013]. Chromate was left out of the formulation because it is a minor component that is not needed for effective prediction of performance, and would have made the simulant characteristically hazardous for chromium. 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 for this MRT process, once adjusted for the measured bias in performance [Hamm, 2013]. Actual analytical measurements of the simulant components indicated good agreement with the target composition, and are shown in Attachment A.

Table 1-1. HTWOS Average 7.8 M Simulant Target Molar Composition

Ion	Molarity (M)
NO_3^-	2.53
OH^-	2.43
SO_4^{-2}	0.13
$Al(OH)_4^-$	0.48
NO_2^-	0.88
CO_3^{-2}	0.43
K^+	0.051
Acetate	0.060
F^-	0.049
PO_4^{-3}	0.076
Cl^-	0.066
ReO_4^-	5.23E-05
Total [Na+]	7.8

2.0 Experimental

2.1 Resin Preconditioning

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

The resin was weighed into glass beakers. Resin for the engineering scale lead column was 422.999 grams of resin while the engineering scale lag column was 423.007 grams (resin weight as received and before pretreatment). The pretreatment procedure for the as-received resin involved two stages: First, the resin was measured into individual beakers filled with 60-65 °C deionized water, and placed in an Isotemp oven at 65 ±5 °C for 3 hours. The soaking resin beads were left in the oven overnight as it cooled to room temperature. The resins were then transferred to their respective columns with water. The water in the two columns was then displaced with 6 L of 0.25 M NaOH solution at 25 °C at a flow rate of 1 Bed Volume (BV)/hour.

2.2 Simulant Preparation and Use

A 210 L batch of the simulant was prepared by a vendor, analyzed, and shipped to SRNL. The instructions for preparation of the simulant are shown in Appendix A. The Certificate of Analysis is shown in Appendix B. No Re was initially in the simulant. The sodium perrhenate was added after the simulant was analyzed and added to the feed tank. Although the as-received simulant did not initially contain any Re, the simulant batch was re-used for the second and third tests, so it contained a small amount of Re from the preceding test. Analytical results were used then to add the correct amount of sodium perrhenate to achieve the desired initial feed concentration of 5.23E-5 M for tests 2 and 3. The density of the simulant was measured prior to each run to confirm it had not been inadvertently diluted and was acceptable for re-use. Measurement of the initial density for test 1 and after test 3 was 1.34 gm/ml.

For each run, the resin was first flushed with “blank simulant”, i.e., 7.8 M simulant that did not contain any Re. This serves to pack the bed prior to beginning the loading cycle. Care was exercised in ensuring that the simulant did not inadvertently become diluted during the tests so that it could be re-used. This was controlled by discarding the six Bed Volumes of blank simulant because it mixes with the dilute caustic used for resin conditioning.

2.3 Engineering Scale Rig

The engineering scale rig was constructed by SRNL to perform this test program. The principal components were:

Poly Feed tank (~300 L) with mixer and a stainless steel coil for water bath recirculation
Recirculating water bath
Feed filter (poly)
Feed pump (variable speed)
Feed flow meter
Water-jacketed clear PVC columns (2) equipped with stainless mesh plungers
Density meter
Lag column output filter
Automatic samplers (2)
Product receipt tank

The columns were constructed of clear PVC with an internal diameter of 7.4 cm and total height between the screens of 40 cm with plungers fully withdrawn. The columns were designed to operate half full, i.e., with ~1 L of resin and have ~1 L of freeboard. Each plunger was equipped with a stainless steel mesh screen that prevented the resin from exiting the column. Plungers could be manually moved using a shaft that extended above the top of the column.

The valves and pump were controlled with a computer operating LabView® software. The rig was designed for unattended operation. A photograph of the rig is shown in Figure 1 (adjusted to obscure background). The Piping and Instrumentation Diagram (P&ID) is attached as Appendix C. The equipment list is shown in Appendix D. The rig was designed based on the following criteria:

1. Columns will be set up in a lead-lag configuration with equipment to support ~200 bed volume (BV) processing cycles (i.e., ~200 L of simulant for 1 L resin)
2. The resin bed Length/Diameter ratio will be ~3 with 2-4 inch diameter columns. The columns will be designed to be ~ 50% full of resin.
3. The rig will be designed to perform the resin loading cycle with simulant containing perrhenate (ReO_4^- as a substitute for pertechnetate, TcO_4^-) at 25 °C (±3 °C) at 3.2-3.4 BV/hour in (1) up-flow with free-floating beds; (2) up-flow with restrained beds; and (3) down-flow with restrained beds.
4. The rig will be designed to perform the elution at 60-65 °C* at 1 BV/hour in down-flow with up to 20 BV volume of water (i.e., 20 L water for 1 L of resin). (Both columns will be eluted together in lead-lag series and will not swap lead-lag positions)
5. The rig will be designed to perform displacement, rinse, and preconditioning at 3 BV/hour in down-flow.
6. The rig will be designed to perform the resin bed pre-conditioning in up-flow with a dense salt solution simulant that does not contain perrhenate.
7. The rig will be capable of periodic sample collection (5-10 mL) from both columns for off-line analysis to determine the Re breakthrough loading profile. Sample analysis (by ICP-MS for Re) will be used to examine the loading and elution profile.
8. The rig will contain filters to enable measuring mass of resin carry-over/particle degradation, if observed.
9. The rig will be designed to measure eluate volume, and operating cycle parameters (displacement liquid volume, preconditioning fluid density and volume, column pressure).
10. The rig will continuously measure temperature of the fluid entering the lead column.
11. The rig will periodically measure fluid density exiting the lead column either on-line or with off-line samples.

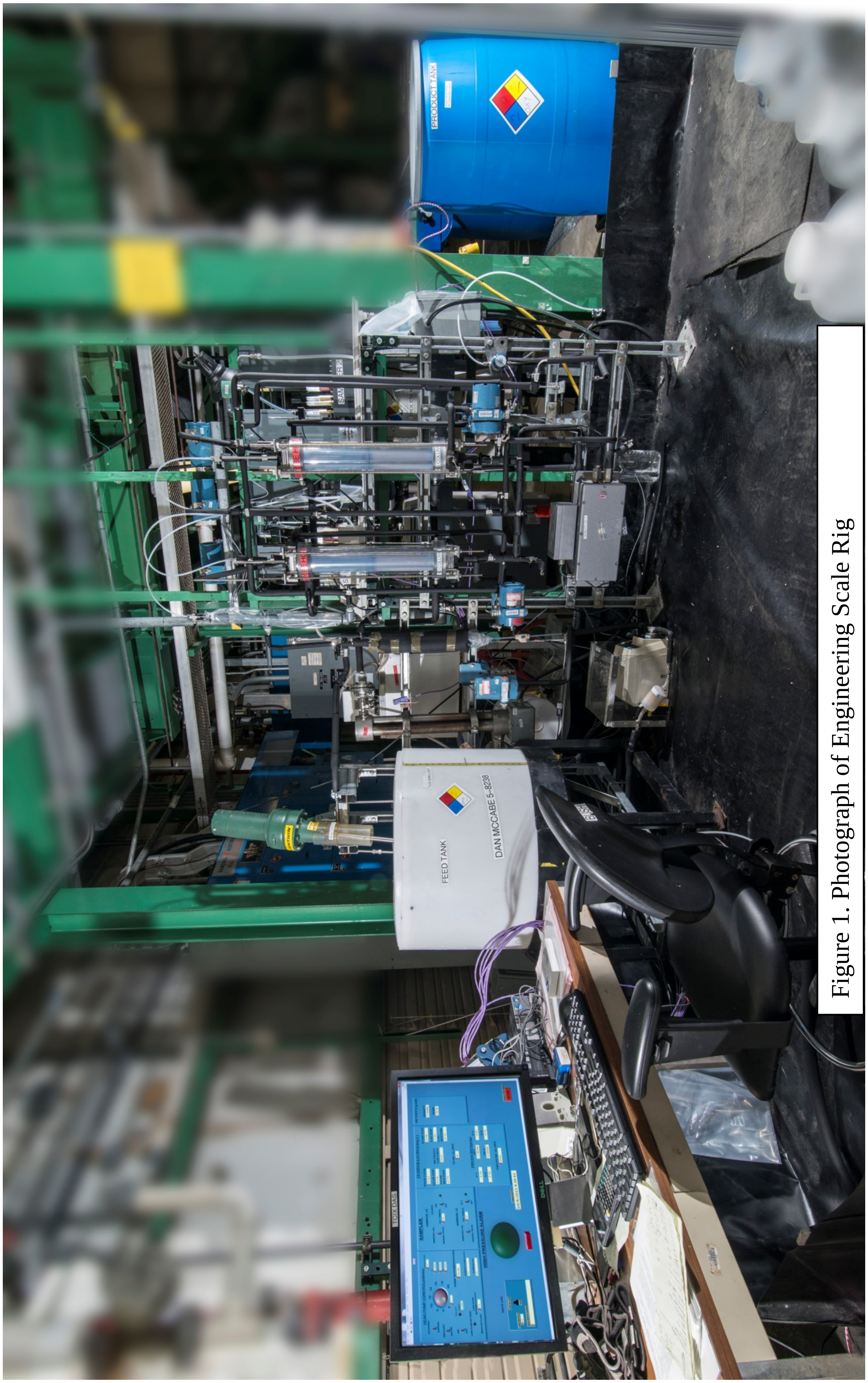

Figure 1. Photograph of Engineering Scale Rig

12. The columns will be manufactured of a clear material to permit visual observation of the resin bed. The set-up will permit photography &/or videography of resin bed packing/settling at selected periods of operation.
13. The set-up will provide for spill protection.
14. The rig will be set up to capture and re-use simulant after re-spiking with Re.

*Due to pressure protection issues with the materials of construction of the columns, the rig was not certified to operate above 55 °C. Since the objective of the test was unrelated to the elution temperature, this was considered acceptable. Note that during elution, the resin sinks, and the bed packing is not an issue. This is identical to the condition used for elution when testing other simulant formulations.

Displacement and elution steps were performed with both columns in series and in the same sequence of lead to lag fluid flow. All elutions were performed in down-flow mode (since the resin sinks). Both columns were completely eluted at the completion of each loading cycle.

2.4 Quality Assurance

This work was performed according to requirements in the Task Technical and Quality Assurance Plan for Technetium Ion Exchange Resin Manufacturing Maturation, SRNL-RP-2012-00708, Revision 4. This task is described in Task 7.1 Technetium Removal from High Sodium Molarity LAW Feed.

This document completes the requirements for Washington River Protection Solutions for Task 3.9 in WFO-15-005, PTS-15-005-55220-4, (updated 2/17/15).

Detailed results for the bench-scale rig can be found in Laboratory Notebook WSRC-NB-2001-00063. Detailed results for the engineering-scale rig can be found in Laboratory Notebooks ELN T9204-00155-01 and SRNL-NB-2015-00008.

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.

2.5 ES&H

This work was performed according to requirements in the electronic Hazards Assessment Package (SRNL-L3100-2015-00013) that was prepared for this program.

2.6 Bench Scale Column

Testing with a small bench scale single column was performed in November, 2014, to scope out the behavior of floating resin beds for one operational cycle. The jacketed glass column was 1.56 cm in ID, and there was about 10 cm between the upper and lower stainless steel screens (200 mesh). Figure 2-1 shows the arrangement. Note that the lower screen is at the 1 cm mark. Table 2-1 has the volumes of components that were used to consider delay times for sample data.

Table 2-1. Rig Volumes for the Bench Scale Column

System Part	Tubing Length, cm	Volume, mL	Sum of Volumes, mL
pump inlet tubing	49	0.970	
pump outlet to funnel	38	0.752	
funnel to column	78.3	1.550	
below screen		7	
screen to bed	2.2 cm x area	4.205	
top screen to tube inlet	2 cm x area		3.823
small vertical tube	3.5	8.89	0.594
output to drip		30	0.594
sampler line	37	93.98	1.861

A mass of 4.8045 grams of Lot# 130611SS2-56 of SuperLig® 639 resin was submerged in DI water in a poly bottle and placed in a stirred water bath for 3 hours at 65 +/- 3 °C. The water was changed out with 0.25 M NaOH and the resin was slurried into the column with the caustic water. The top screen and other hardware were inserted in the column to prepare it for flow.

Pretreatment was completed by pumping 0.25 M NaOH solution at room temperature, in upflow, at 1 BV/hr, for 6 hours. One important goal was to displace air from the system and settle the resin bed.

The first step with the pretreated resin in the column after resin pretreatment was to float the bed using dense simulant that did not contain any perrhenate. This was to prepare the bed for loading. The column and settled bed initially contained 0.25 M NaOH so that introduction of simulant would not cause any major pH change or precipitation of aluminum hydroxide.

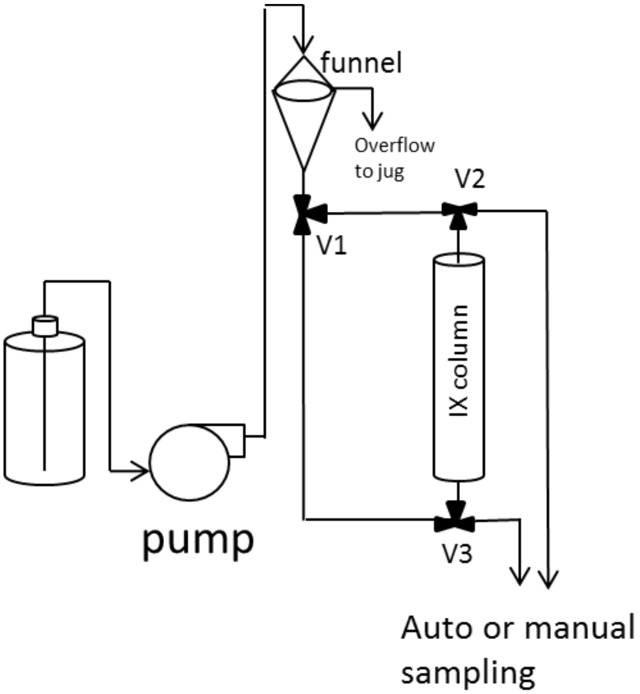

Figure 2-1. Diagram of the Bench Scale Column System

3.0 Results and Discussion

3.1 Simulant Formulation

For the Engineering Scale rig, two samples were pulled from each drum of simulant, and results of the analysis by SRNL of the simulant are shown in Table 3-1. Major components are in good agreement with the target composition. Three minor components are somewhat off, with potassium and phosphate about 32% and 100% low, respectively, and chloride about 100% higher than the target. A small amount of solids was present in the drums, which was removed by filtration. This was likely the phosphate, which is marginally soluble in this solution. No adjustments were made to the solution because of the good match of the results in the vendor's certificate of analysis. Also, it was not practical to remove the excess chloride, which was probably present as impurities in the other chemicals used in the preparation. Although the potassium was slightly low, it was not adjusted because adding more of any salt could cause more precipitation of other species, and a low potassium concentration would be expected to give a conservative result to the resin performance, since potassium has a positive correlation with rhenium/technetium distribution coefficients.

Table 3-1. SRNL Analysis of Simulant Solution

Component	Target	Sample A-1	Sample A-2	Sample B-1	Sample B-2	Sample Average
Al (mg/L)	12951	12300	12300	12300	12400	12325
K (mg/L)	1993	1320	1380	1360	1360	1355
Na (mg/L)	179322	179000	182000	184000	190000	183750
P (mg/L)	2354	1130	1140	1140	1140	1138
Re (mg/L)	0	<0.100	<0.100	<0.100	<0.100	<0.100
S (mg/L)	4168	4630	4680	4880	4840	4758
F (mg/L)	931	863	889	NA	NA	889
Cl (mg/L)	2340	4560	4690	NA	NA	4625
NO_2 (mg/L)	40480	47600	47000	NA	NA	47300
NO_3 (mg/L)	156860	156000	156000	NA	NA	156000
SO_4 (mg/L)	12480	12300	13000	NA	NA	12650
density (g/L)	1.34	1.3446	1.3445	1.3437	1.3437	1.3441
Total solids	38.7	38.2%	NA	38.3%	NA	38.3%
soluble solids	38.7	38.2%	NA	38.3%	NA	38.3%
insoluble solids	0	<0.100%	NA	<0.100%	NA	<0.100

3.2 Bench Scale Single Column

This section provides the results from operating a single small column for one cycle using dense simulant as the feed.

3.2.1 Bed Behavior with Dense Simulant Introduction

An initial 3 BV of the unspiked simulant (i.e., simulant without ReO_4^-) was used to float the bed, with an upflow introduction at 3.47 BV/hr. The bed floated as one unit as shown in Figures 3-1 and 3-2. A total of 37.57 grams or 28.20 mL was used in this bed floating operation.

It was clear that the resin bed only moved as a unit and did not exhibit individual buoyant beads. Apparently the introduction of dense simulant from the bottom would increase bed buoyancy, the lower beads pushing up on the upper part of the bed, until the bed began to move. The figures were taken during the 3 BV of unspiked simulant introduction less than 60 minutes after starting the pump. The bed moved smoothly and cleanly with only a few beads left clinging at the bottom. This behavior is key to operating a floating bed and was thus expected for larger bed operation.

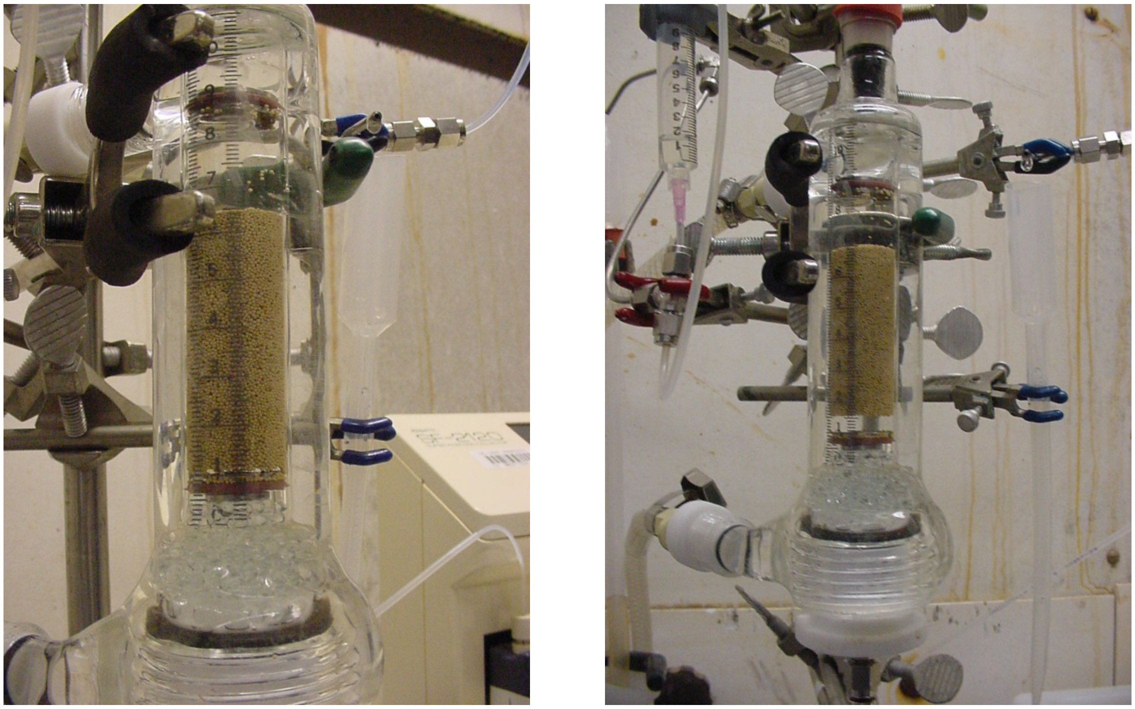

Figure 3-1. Beginning of Bed Floating with Dense Simulant Introduction

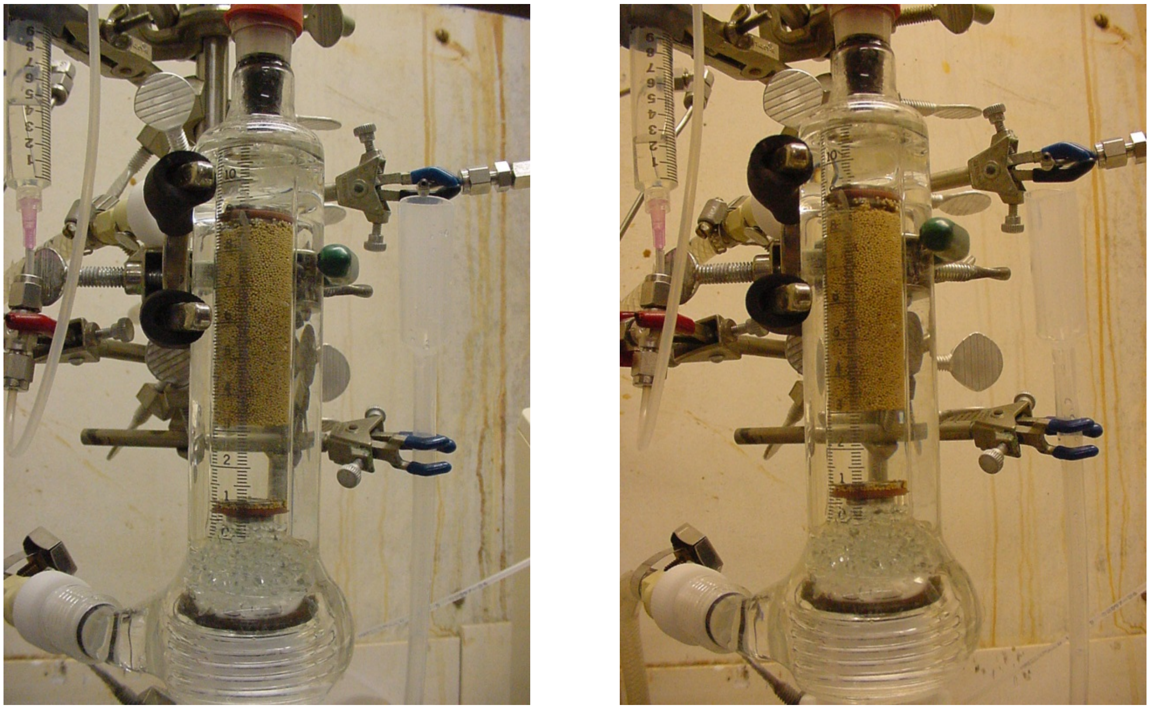

Figure 3-2. Completion of Bed Floating with Dense Simulant

3.2.2 Bench Scale Loading

Figure 3-3 below shows the loading curve using ICP-MS data for rhenium measurement. The curve accounts for the 21.4 mL dead volume between the spike feed simulant bottle and the bottom of the floating bed. It also uses the average value of 3.47 BV/hr. The test lasted for 36 hours of continuous operation. The total mass of feed processed was 1807.5 g or 1357 mL. This measurement is 1.4% more than the 1338 mL obtained as the product of 36 hours and average flowrate. This is excellent agreement, and the data were processed using masses of simulant pumped.

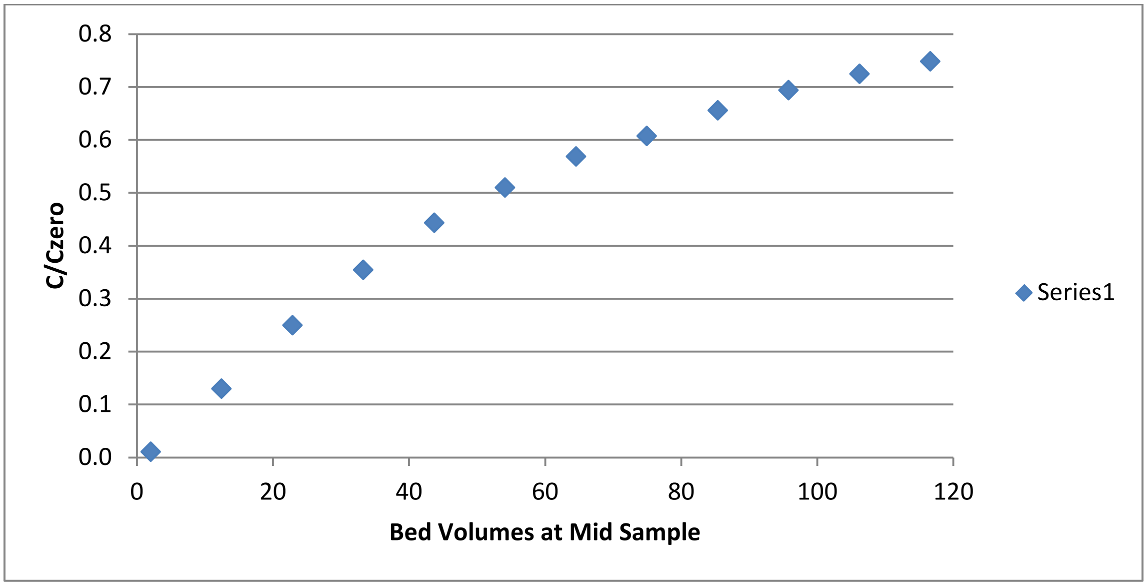

Figure 3-3. Rhenium Breakthrough seen with the Bench Scale Column

3.2.3 Displacement

The displacement step is meant to remove the high density simulant from the column so that the bed is prepared for elution with hot deionized water. This step thus necessarily causes the bed to sink, and it did so as one unit. See the photographs in Figures 3-4 through 3-6. It appeared to be a reverse event of the dense simulant introduction that floated the bed before loading. This again is a key result showing how the bed behaves as a unit when the bed moves from buoyancy effects.

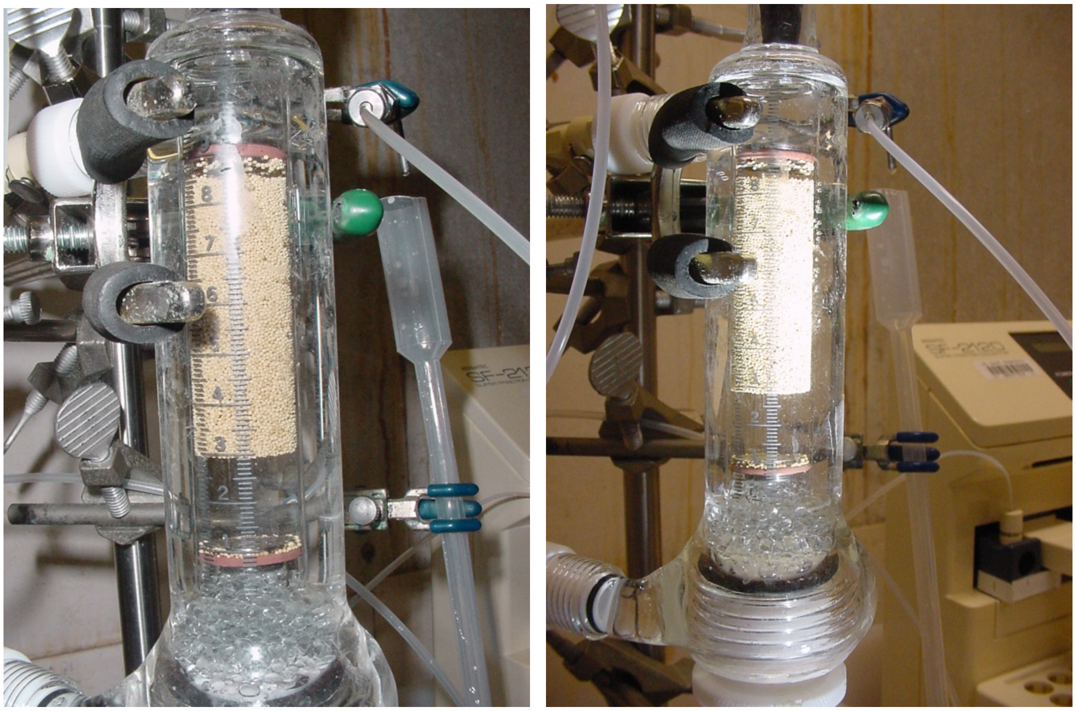

Figure 3-4. Resin Bed Sinking during Displacement

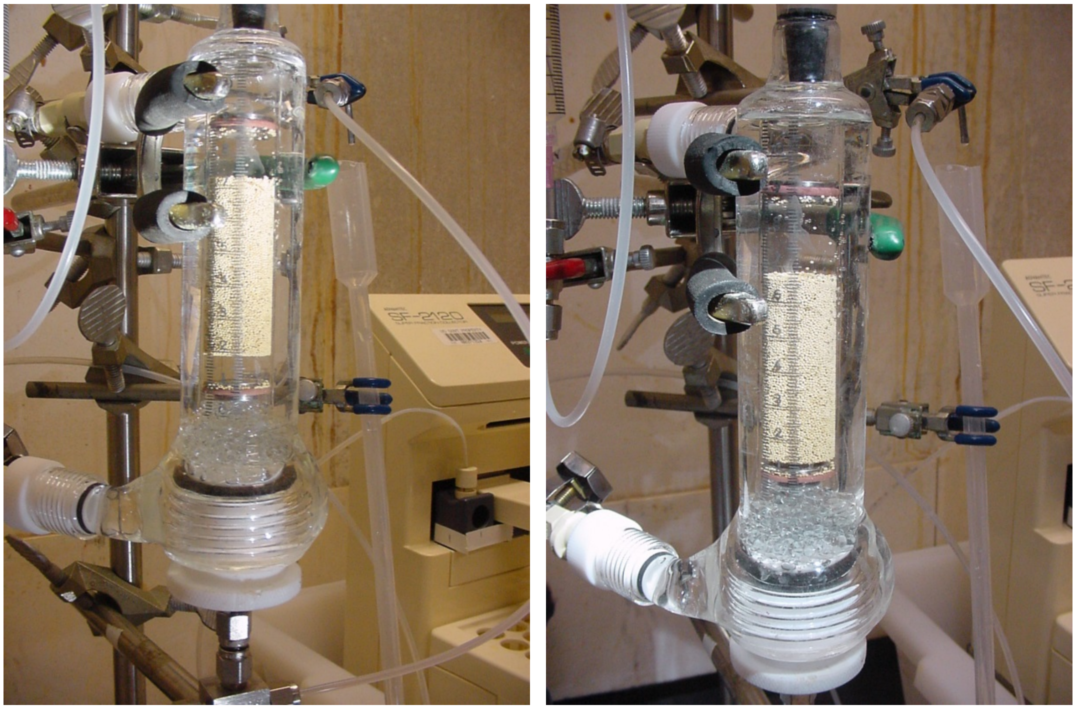

Figure 3-5. Continuation of Resin Bed Sinking during Displacement

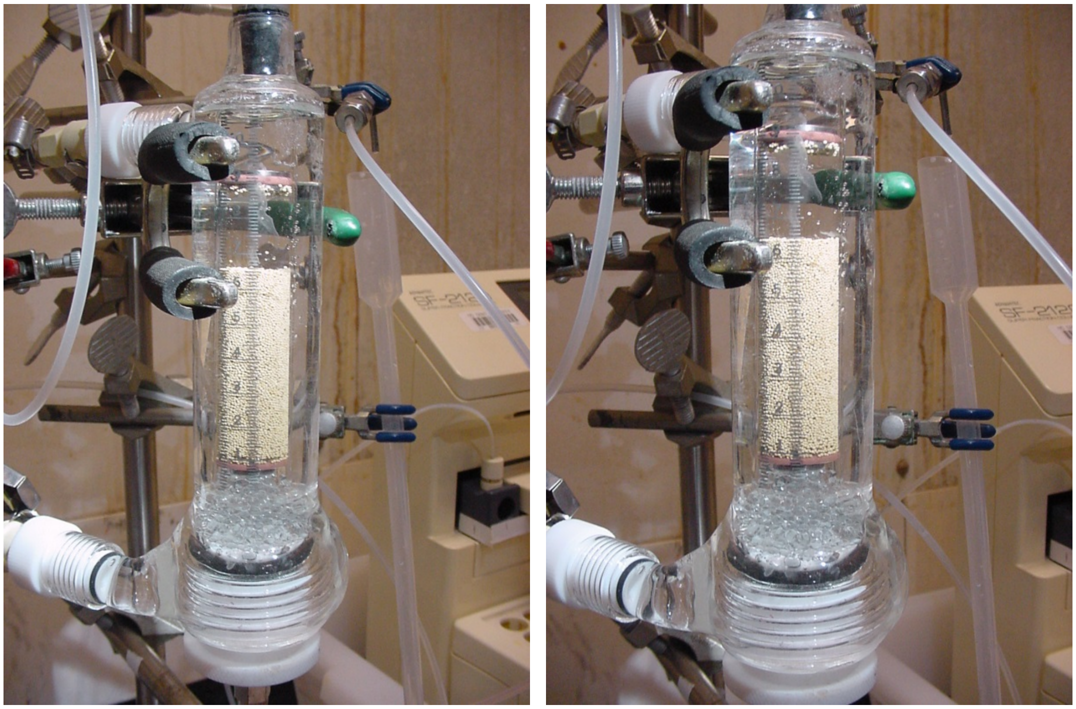

Figure 3-6. Completion of Resin Bed Sinking during Displacement

3.2.4 Elution

Elution was performed with 0.182 mL/min DI water, or 1.06 BV/hr, for a total of 218.6 mL. The jacket temperature of 65 +/- 3 °C was maintained for the 20 hour elution. Figure 3-7 shows that elution started early (probably also during displacement) and that the peak concentration of eluted rhenium was in the first 1-2 BV of heated eluate. It is thus likely that reduced ionic strength is the strongest effect of elution, with higher temperature assisting the kinetics.

Figure 3-8 shows the elution of Na, K, Re, and Al in terms of absolute concentration. Data were limited at the higher bed volumes for some analyzed elements because of detection limitations. Elements outside of rhenium declined about two orders of magnitude while the more strongly adsorbed rhenium declined over 4 orders of magnitude during elution. Most of the elution process was completed in about 7 bed volumes of hot water.

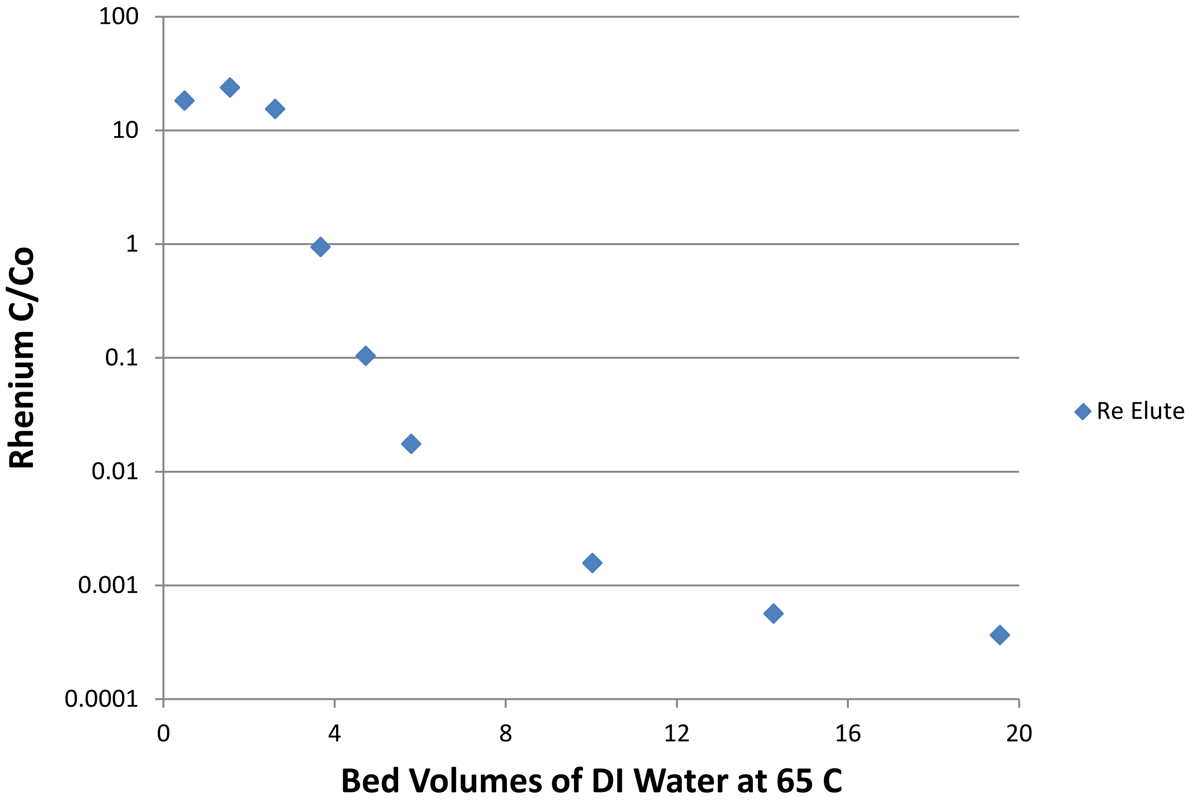

Figure 3-7. Elution of Rhenium from the Bench Scale Column

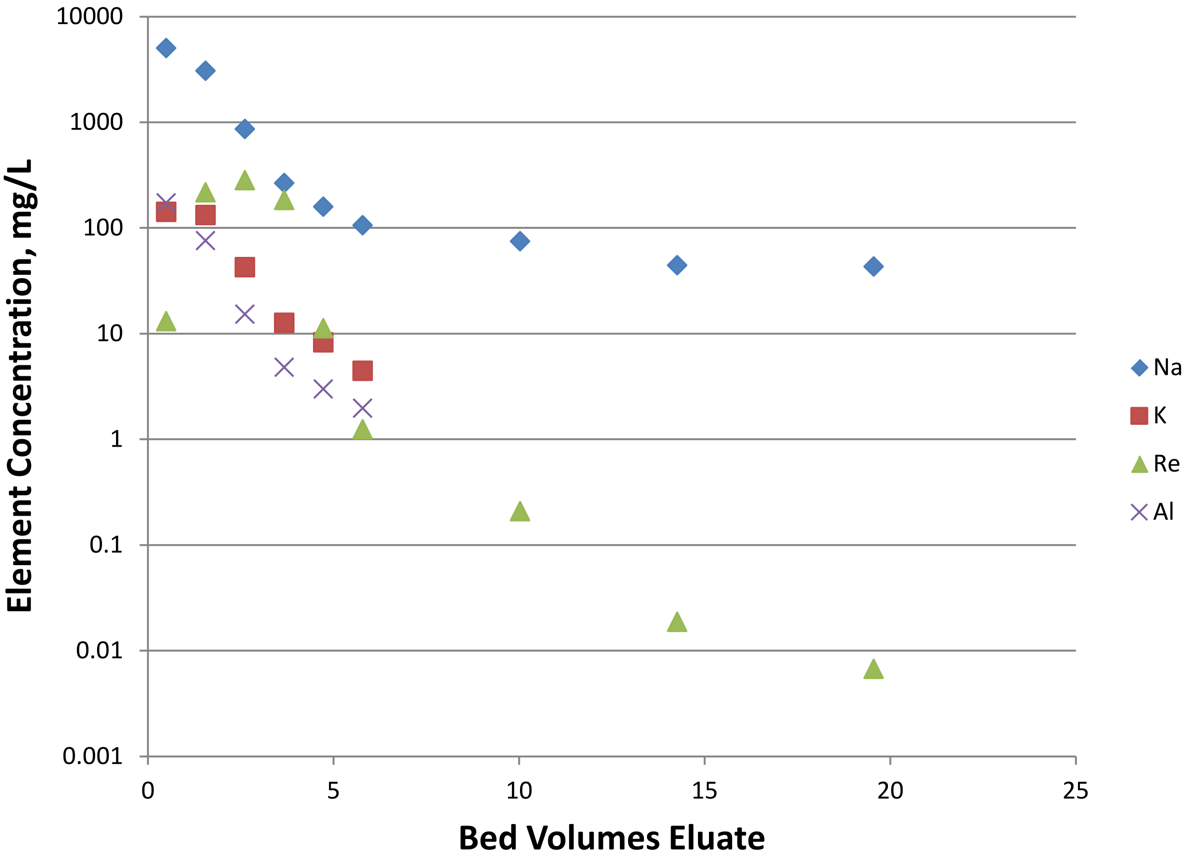

Figure 3-8. Elution of Elements from the Bench Scale Column

3.3 Engineering scale

3.3.1 Bed Floating

Figures 3-9 to 3-11 show how the lead resin bed, on the left of the photos, progressively lifted as a unit during the upflow introduction of unspiked simulant (i.e., simulant without ReO_4^-). Initially, the lag column, always on the right in the photos, was receiving the dilute caustic from the freeboard in the first column in upflow direction and the bed was not buoyant yet in the first photo. Figure 3-11 shows that once dense liquid reached the lag, that bed also rose as a unit. The lead bed was completely pressed against its upper screen by that point. Bubbles were observed in the rig at several points during the floating transition. Some bubbles worked their way through the resin bed, but it was not possible to determine if any bubbles remained within the bed or just under the top screen.

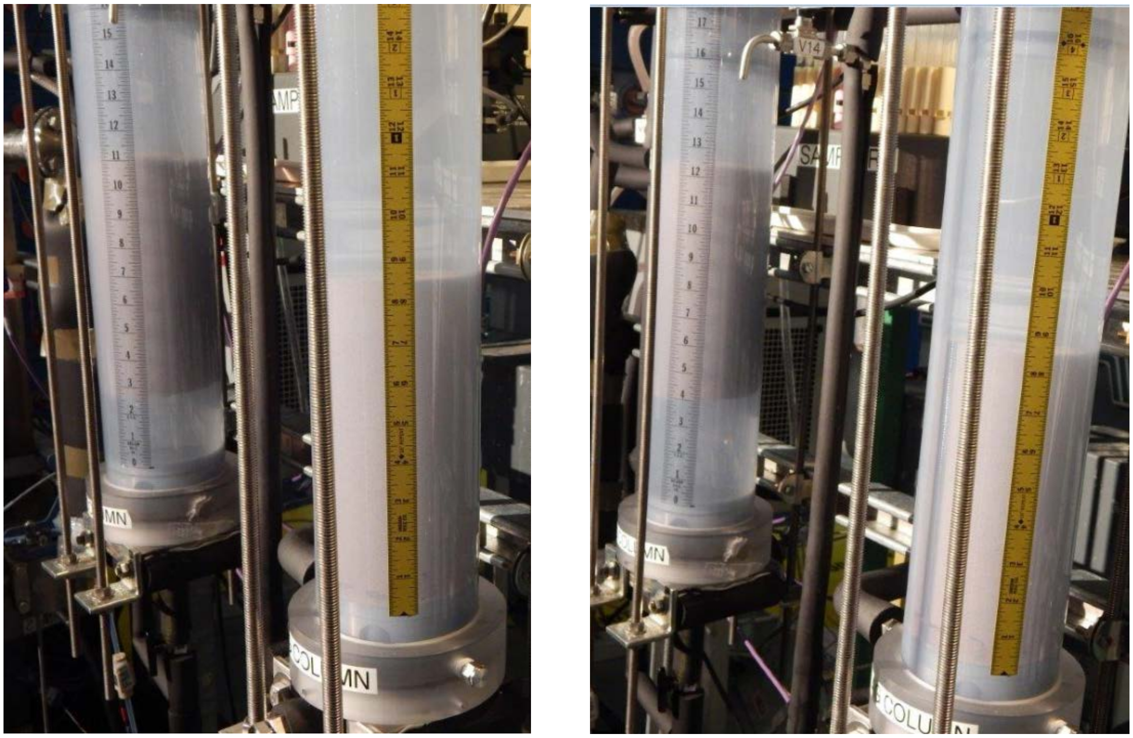

Figure 3-9. Resin Bed Floating in the Engineering Scale Test

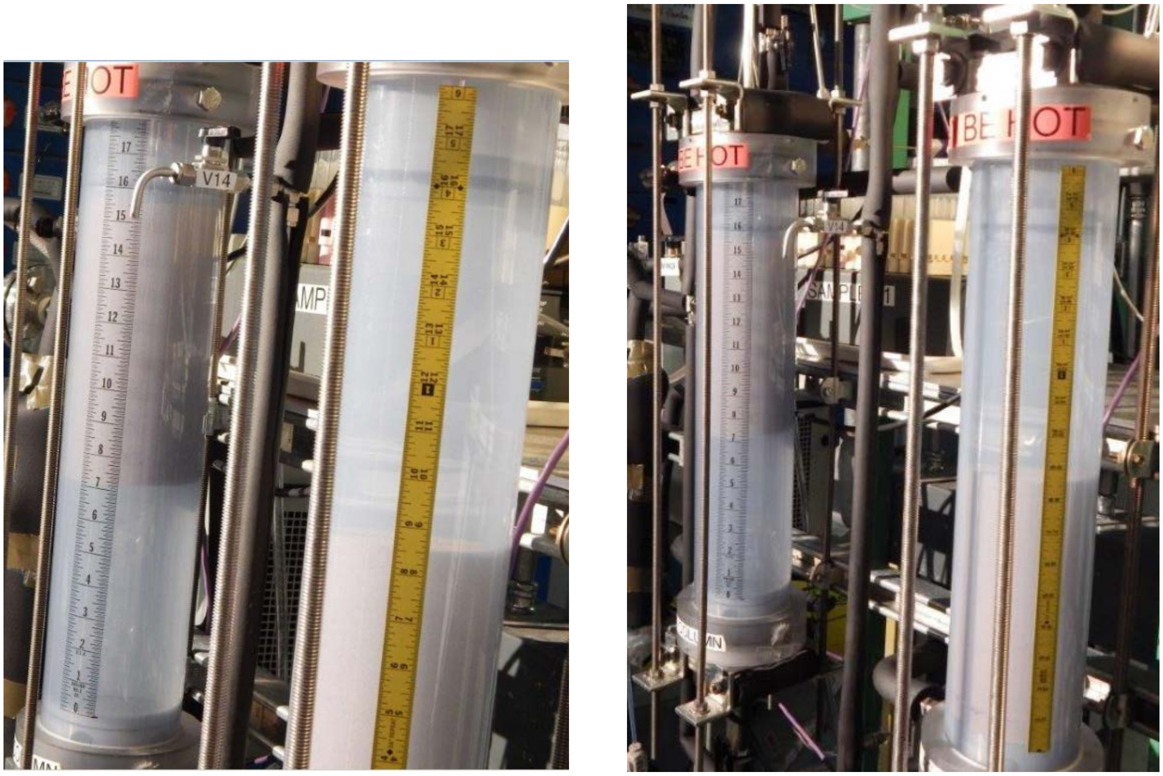

Figure 3-10. Completion of Resin Bed Floating in the First Engineering Column

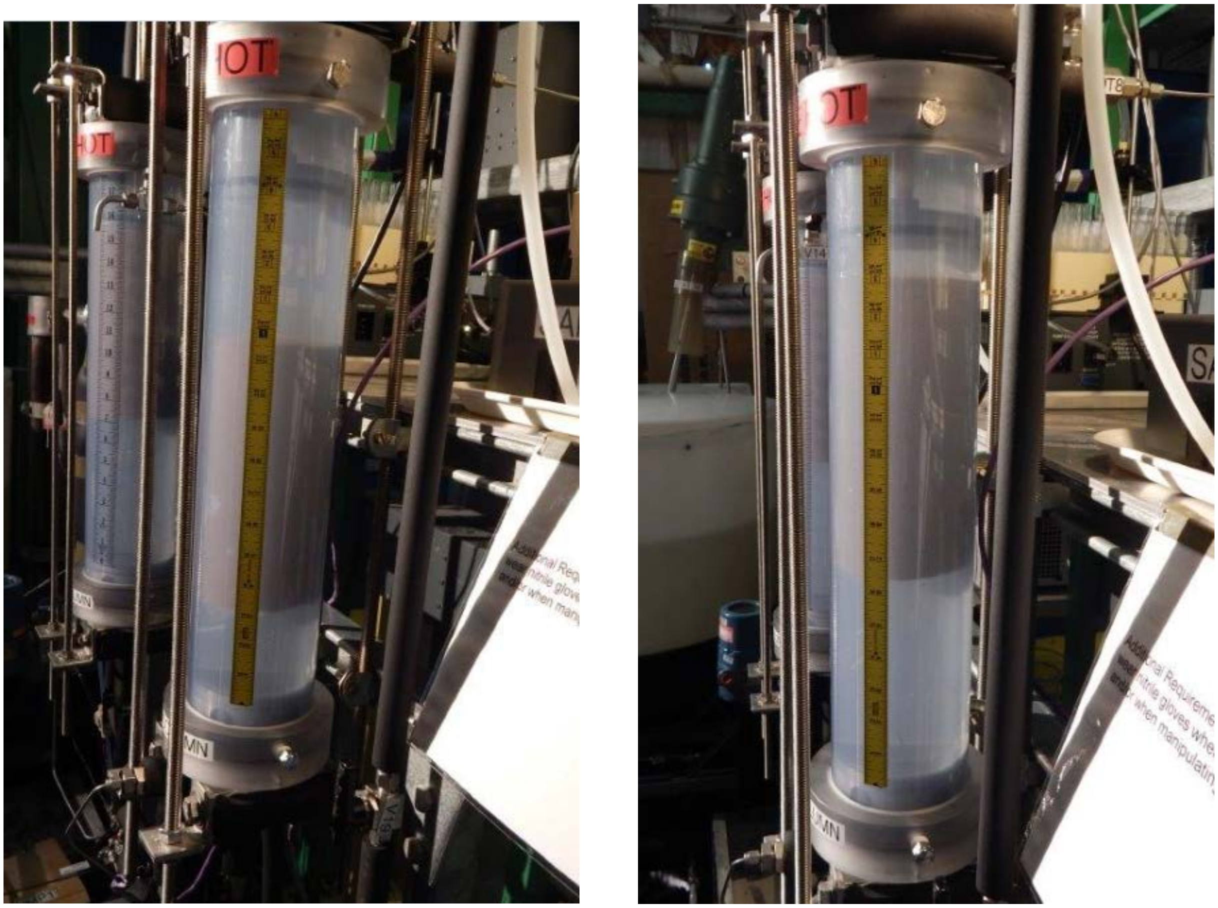

Figure 3-11. Floating of the Second Engineering Column Bed

(Lead column is always to the left of the lag column in all photographs)

3.3.2 Bed Compaction

Quantitative measurements of bed dimensions during loading showed that the engineering scale beds were compacted about the same as the bed of the small lab scale unit. Effective bed densities based on resin mass and overall bed volume are consistent across the work. Buoyancy and resin mass forces are responsible for compacting the beds. Table 3-2 shows the results. Table 3-3 shows similar data for elutions.

Table 3-2. Effective Resin Bed Densities for all Test Series, Loading

Column	Bed management	Resin Mass, g	Bed Volume, mL	Effective Resin Bed Density, g/mL
Lead	Upflow Unrestrained	422.999	940	0.450
Lag	Upflow Unrestrained	423.007	947	0.447
Small Lab Scale	Upflow Unrestrained	4.8045	10.7	0.449
Lead	Upflow Restrained	422.999	890	0.475
Lag	Upflow Restrained	423.007	900	0.470
Lead	Downflow Restrained	422.999	870	0.486
Lag	Downflow Restrained	423.007	880	0.481

Table 3-3. Effective Resin Bed Densities for all Test Series, Elution

Column	Bed management	Resin Mass, g	Bed Volume, mL	Effective Resin Bed Density, g/mL
Lead	Upflow Unrestrained	422.999	880	0.481
Lag	Upflow Unrestrained	423.007	890	0.475
Small Lab Scale	Upflow Unrestrained	4.8045	10.3	0.466
Lead	Upflow Restrained	422.999	870	0.486
Lag	Upflow Restrained	423.007	890	0.475
Lead	Downflow Restrained	422.999	870	0.486
Lag	Downflow Restrained	423.007	880	0.481

3.3.3 Breakthrough Curves

Lead and Lag breakthrough curves for the three engineering scale campaigns were visibly close in behavior despite the different methods of bed management (Figure 3-12). The small (bench) column data are included because that single column is comparable to lead columns of the engineering testing. Engineering Campaign 1 was an unrestrained bed in upflow, Campaign 2 was a restrained bed in upflow, and Campaign 3 was a restrained bed in downflow. The unrestrained bed of Campaign 1 shows a slightly faster breakthrough than the other tests, but the difference is small. The small lab scale column bed showed the slowest breakthrough. It is not clear why the bench column operated slightly better than the engineering test lead columns. The data of the previous section shows that the bed compaction was comparable for all tests.

Data processing for loading and elution accounted for the delay caused by displacing the liquid in the rig volume between the feed tank and sample point 1 (after the first column) and then on to sample point 2 (after the second column). The first volume summed to about 2.2 liters and the rig volume from sample point 1 to sample point 2 was about 1.7 liters. The logic was that rhenium-containing simulant started at the (mixed) feed tank exit at time zero, but the front of this spiked simulant took significant time to reach the sample points. Bed volumes were subtracted so that all load and elution figures account for this delay. This is the reason that elution plots in future sections and Appendix E have a few points at negative feed bed volume (liquid still containing displacement liquid). While processing of the bench scale column data also accounted for delay volumes, such volumes were generally less than 1 bed volume.

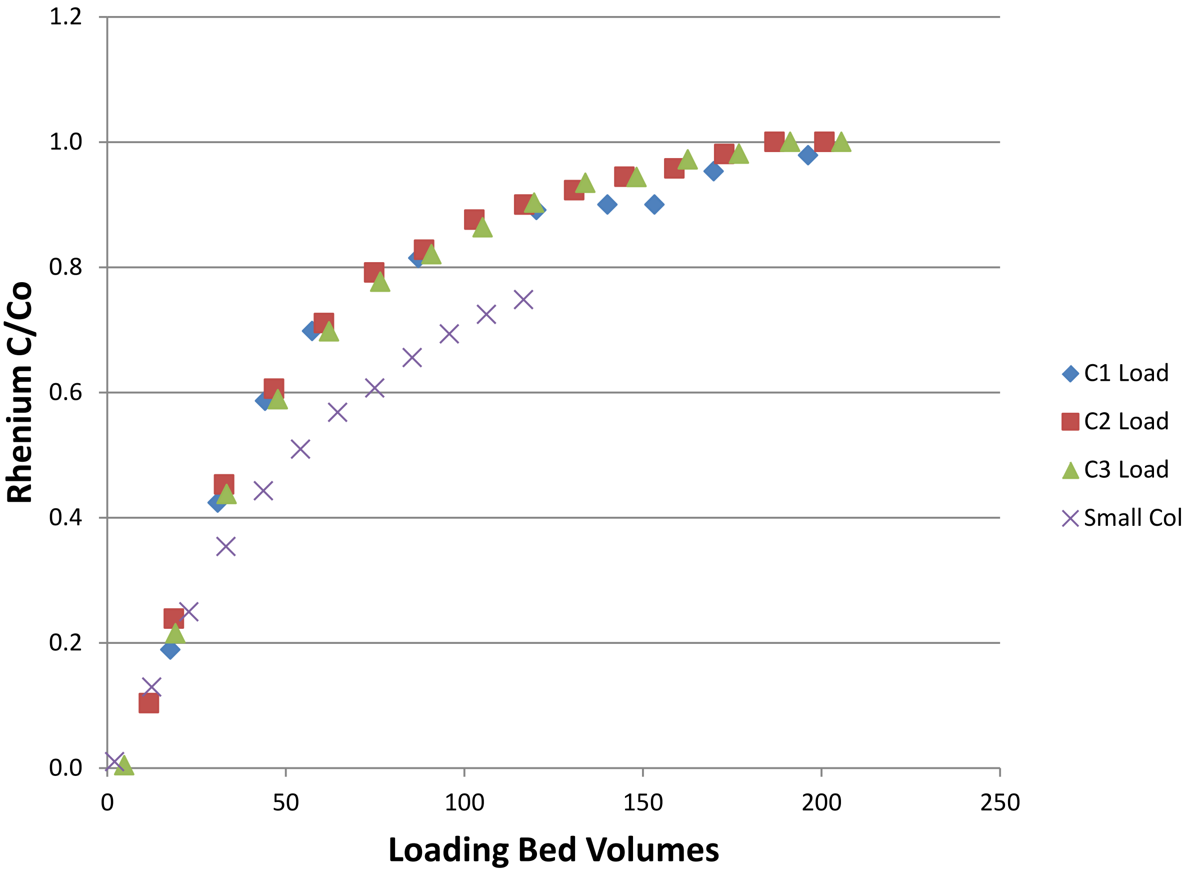

Figure 3-12. Lead Column Breakthrough Curves for Rhenium

Figure 3-13 shows rhenium breakthrough out of the lag column for the 3 engineering scale campaigns. Engineering scale lag column breakthrough shows the beginning of an S-shaped character in the first 50 BV or so. The data represent in effect a longer column bed, though there would be dead liquid volume and opportunities for mixing in the region between the two beds. The reproducibility of the 2-column breakthrough curves in Figure 3-13 is evident, despite the differing bed constraints and flow directions.

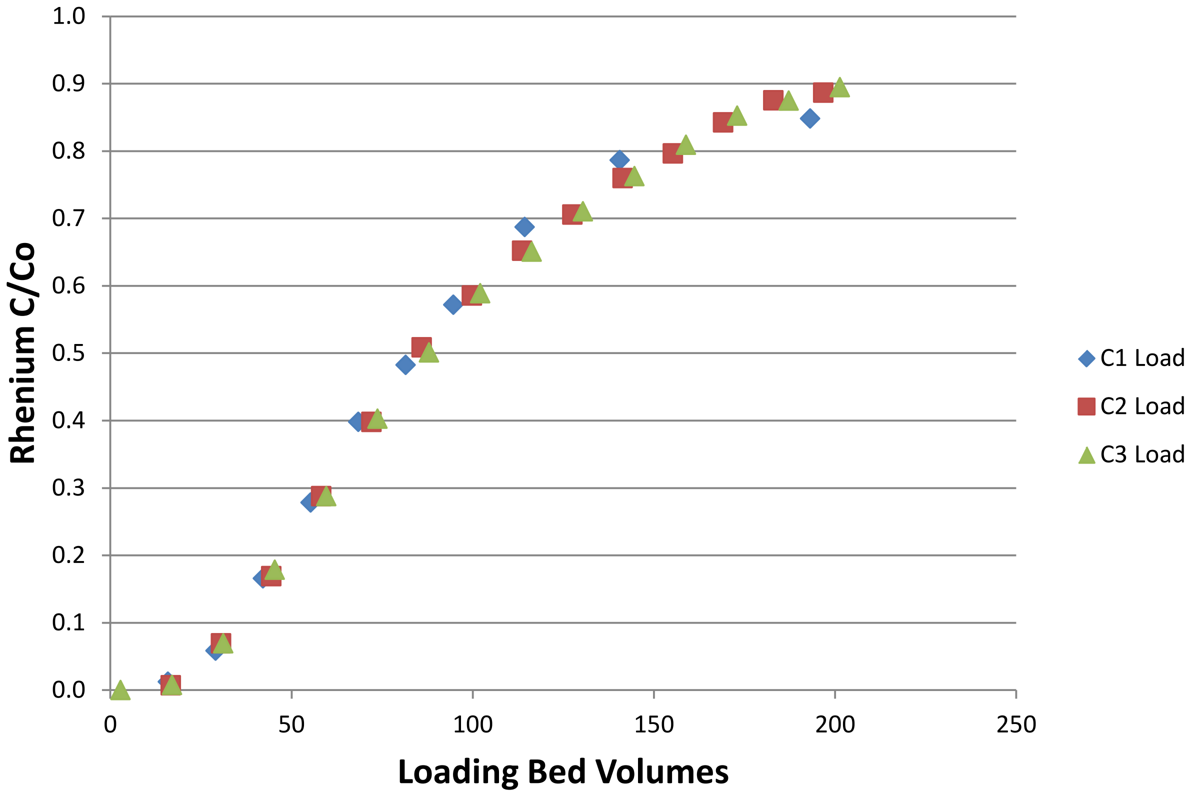

Figure 3-13. Lag (Engineering Scale) Rhenium Breakthrough Data

3.3.4 System Flow Rates and Pressures

The following text and figures describe the pressure data for the 3 campaigns. The pressure of the system increased over the first ~26 hours of operation during Test 1 (Figure 3-14). At 1.6 hours of operation, a slight leak in filter 2 was observed and a catch basin was placed below it. At 16.42 hours of operation, the pump was stopped and the filter 2 was replaced, but no change in the pressure or the increasing trend was observed upon pump restart. At 19.4 hours, filter 1 was observed looking dirty leading to a conclusion that solids were forming and accumulating throughout the system, restricting flow and increasing pressure. At 21.6 and 24.4 hours of operation during Test 1, the system experienced high pressure alarms which caused the pump to stop and the program had to be restarted with higher alarm setpoints. The system pressure increase was also observed during subsequent tests but at about half the magnitude of increase, as shown in Figure 3-15 for Test 2. The pump started at 64 ml/min flow for Test 2 and the pressures took a while to return to normal as there was additional system volume with the addition of the degasser unit after the flow was reduced to 52 ml/min. After 1 hour of operation, the pump was stopped to move the effluent line to the Product Tank After 19 hours of operation, liquid was observed under the pump and fittings were tightened to reduce leakage. At 21, 43 and 55.4 hours of operation, the Degasser was vented to lower pressure and reduce SV2 leakage. For Test 3 shown in Figure 3-16, DP 1 and 2 were added as well as additional valves for Restrained bed downflow operation. At 0.2 hours of operation, the DP1 and DP2 lines had to be vented causing spikes in the pressure indicated. Similarly, SV1 and SV2 adjustments were needed the first few hours to ensure sufficient sample produced for analysis. At 16 and 26 hours of operation, the columns were vented to remove air. At 42.5 hours of operation the DP1 and DP2 gauges had to be reflooded to produce a more stable operation. A plot of the DP data lead to the observation that air was getting into the high side lag line and several flooding attempts were made to stabilize operation.

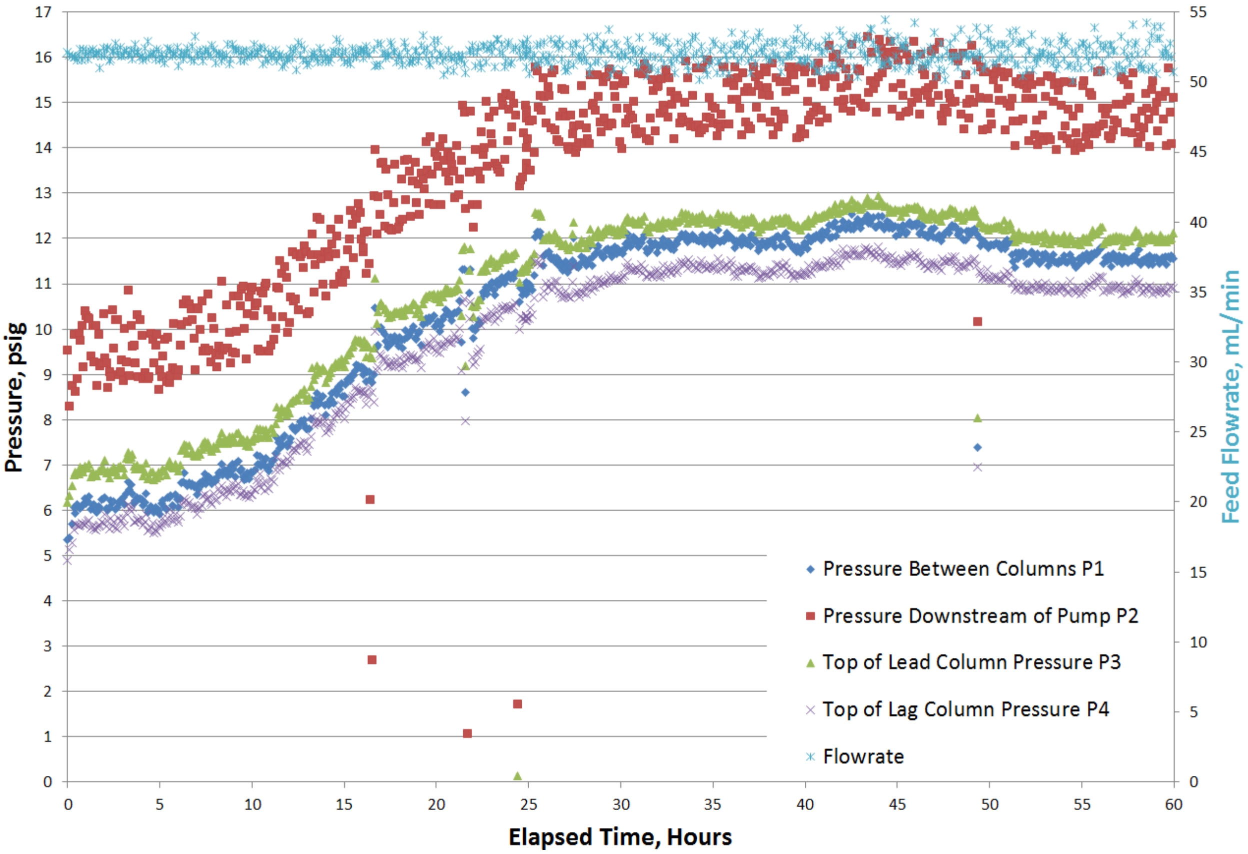

Figure 3-14. System Flowrate and Pressure during Test 1

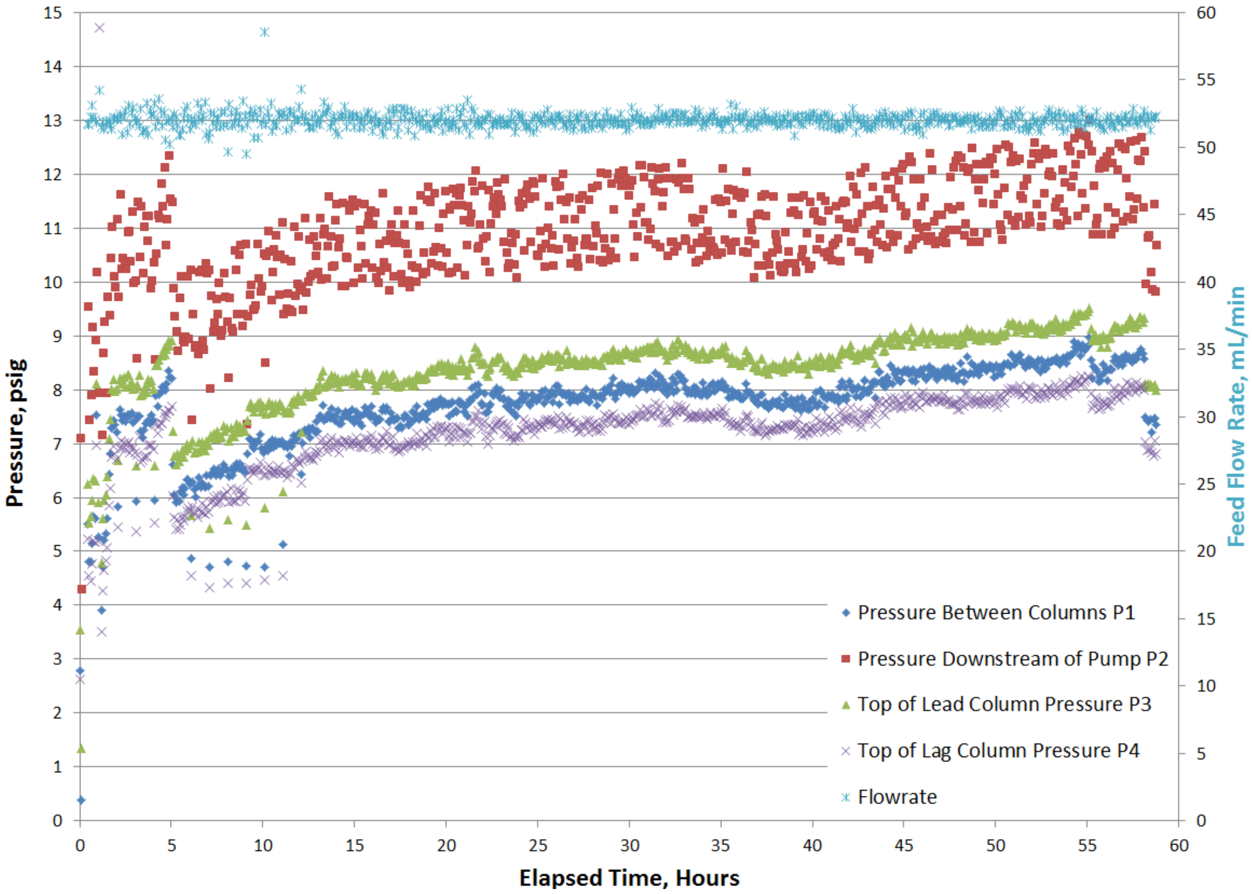

Figure 3-15. System Pressure and Flow Rate During Test 2

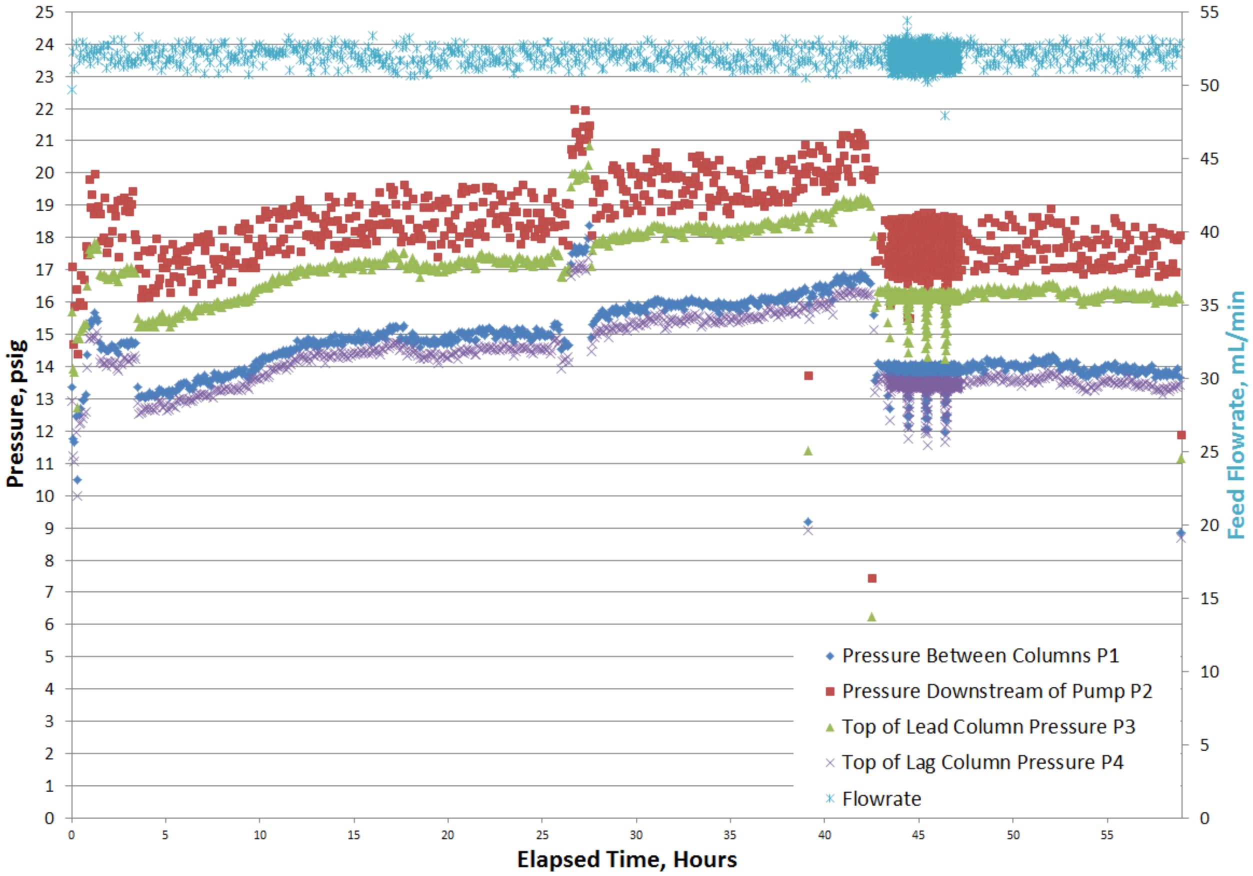

Figure 3-16. System Pressure and Flow Rate During Test 3

3.3.5 Ion Exchange Modeling

Computer modeling predictions of the column breakthrough behavior were previously provided [Nash et al., 2014]. Batch contact data at the targeted 7.8M Na level were determined for this batch of resin provided by IBC (i.e., a May 2013 batch with lot #130611552-56). To confirm that the predicted isotherm at 25 ºC to be employed in the column modeling effort is adequate a comparison of model to data is shown in Figure 3-17. The four different batch contact data sets and the location on the curve of the column inlet feed concentration are included.

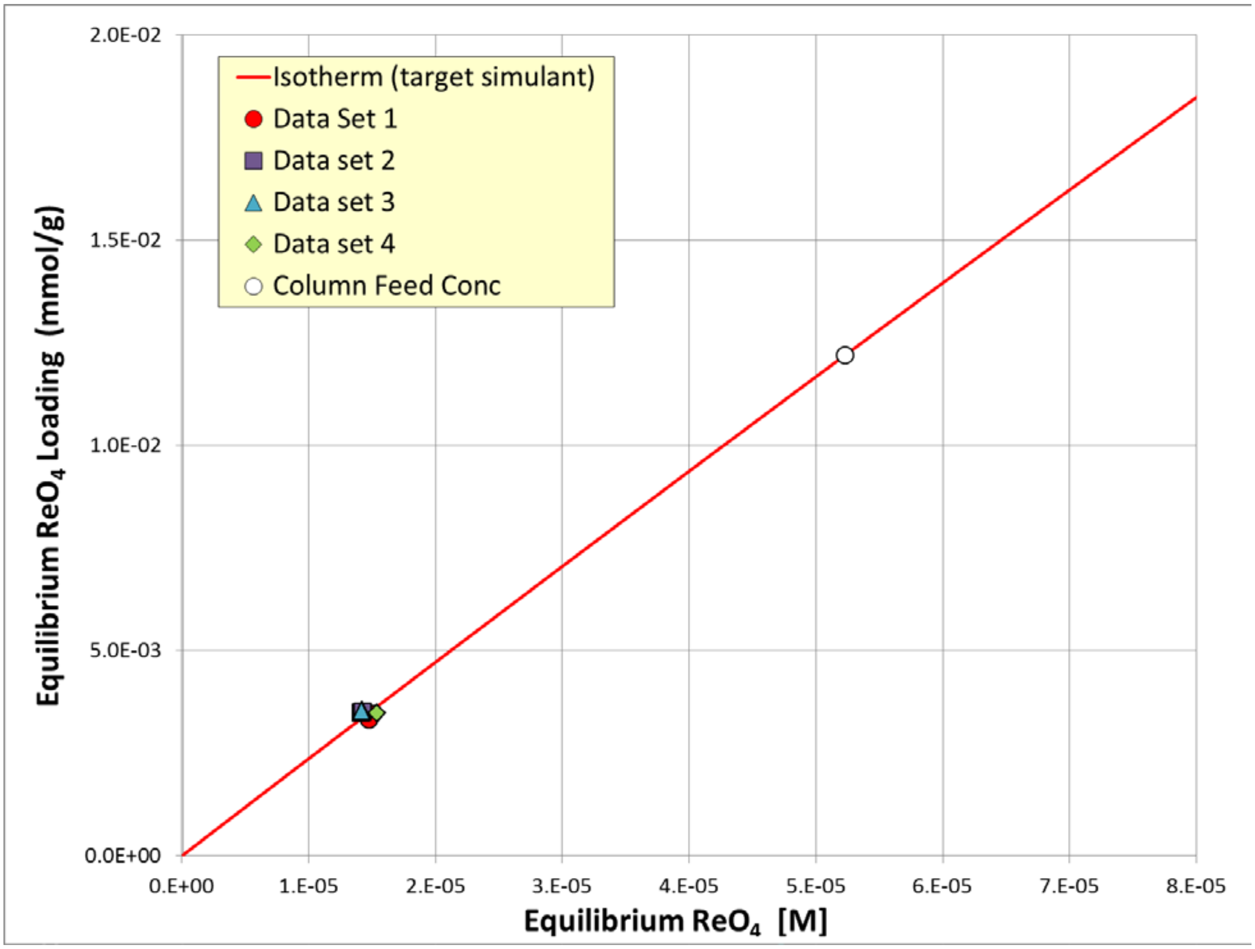

Figure 3-17. Comparison of analytic isotherm model to the Re batch contact data at 25 ˚C (see Nash et al., 2014).

The slight variation observed in the batch contact data is the result of varying K^+, NO_2^+, and NO_3^+ concentrations. The isotherm plotted represents the concentrations of these cations at the target concentrations. As Figure 3-17 indicates, the predicted isotherm model is a good representation of the earlier batch contact data.

Employing this isotherm model, VERSE runs were made for both the Small-Scale and Engineering-Scale lead and lag configurations. The same methodology previously [Nash et al., 2014] was employed (e.g., pore diffusion methods). A comparison of predicted versus measured ReO_4^- breakthrough profiles is provided in Figure 3-17.

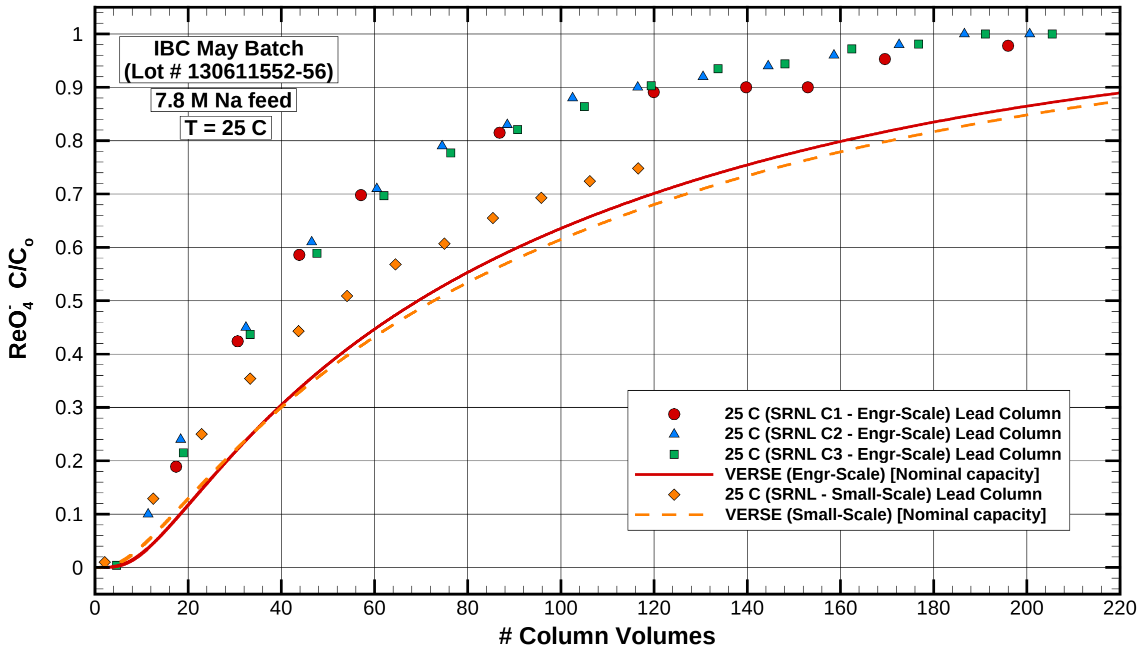

Figure 3-18. Comparison of VERSE predicted Small-scale and Engr-Scale ReO_4 column performance at 25 ˚C for the IBC May batch of SuperLig® 639 resin using the 7.8 M HTWOS Avg simulant.

For both sets of columns the VERSE predicted performance significantly exceeded measured values. In these dimensionless variables the breakthrough curves for the bench scale and the engineering scale should be very similar, as seen between the two VERSE predictions. however, a significant difference exists between the measured performances of the bench scale versus the engineering scale. Both column tests saw significant performance reductions when compared to expected performance. At this point in time we are unable to isolate the root causes for these differences. Typically, when the isotherm model is consistent with available batch contact data and the total mass of resin is known, VERSE column predictions are quite good. Especially when viewing the predicted 50% breakthrough point. Potential causes include precipitation of solids in the resin, inaccurate projections due to ionic strength effects, resin degradation, bubbles causing uneven flow patterns, or flow channeling in the beds.

3.3.6 Displacements

The displacement step was found to initiate elution of resin beds. In this step, done at 25 °C (±3 °C) in downflow with 0.1 M NaOH, samples collected from the column outputs exceeded a C/Co of unity, indicating the beginning of elution.

Table 3-4 shows the results of measurements. This result suggests that elution can be done at less than 65 °C if desired, since elution is not intended during displacement. Displacement is only meant to remove high-sodium feed from the bed while maintaining an alkaline condition, so that aluminum hydroxide solids do not precipitate. In this case, displacement also transitions the bed from a floating to a sunken state.

The average feed rhenium concentrations for calculating C/Co for Campaigns 1, 2, and 3, and small scale are 10.2, 10.4, 10.7, and 11.9 mg/L, respectively.

Table 3-4. Rhenium Concentrations Measured During Displacements

Column	Campaign	First Sample C/Co	Second Sample C/Co
Lead	1	1.01	3.62
Lag	1	0.98	3.19
Small Lab Scale	Small Scale	0.87	N/A

3.3.7 Elution

Lead column elution curves showed maximums for rhenium, while the other elements measured (Na, K, Al) tended to show declining washout.

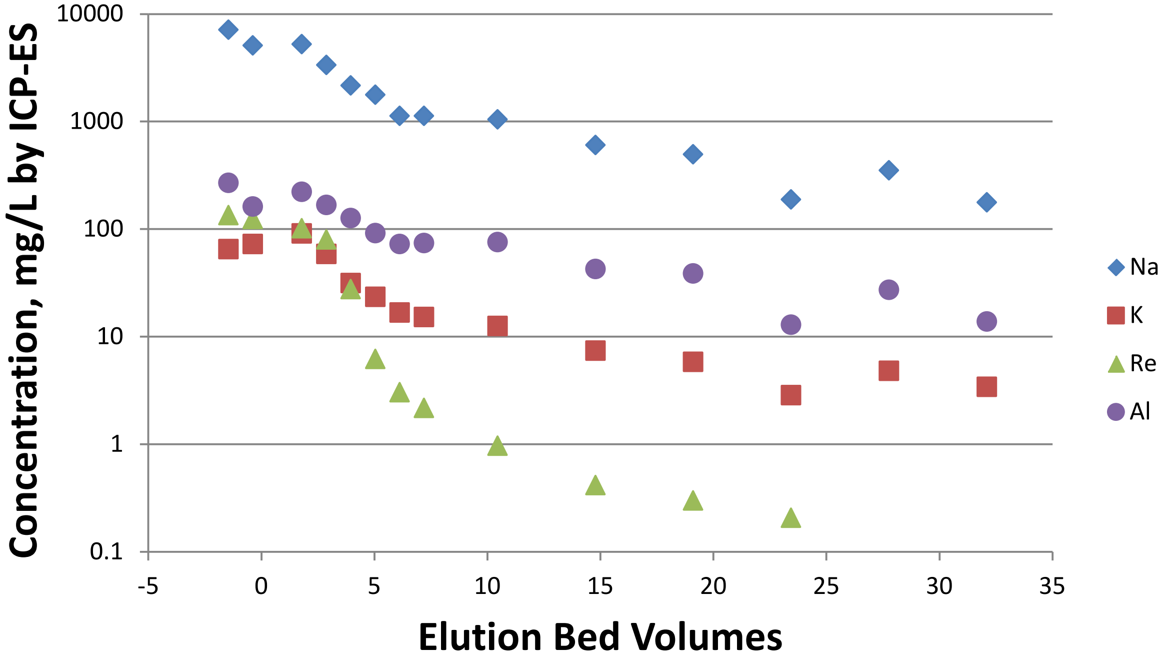

Figure 3-19, Figure 3-20, and

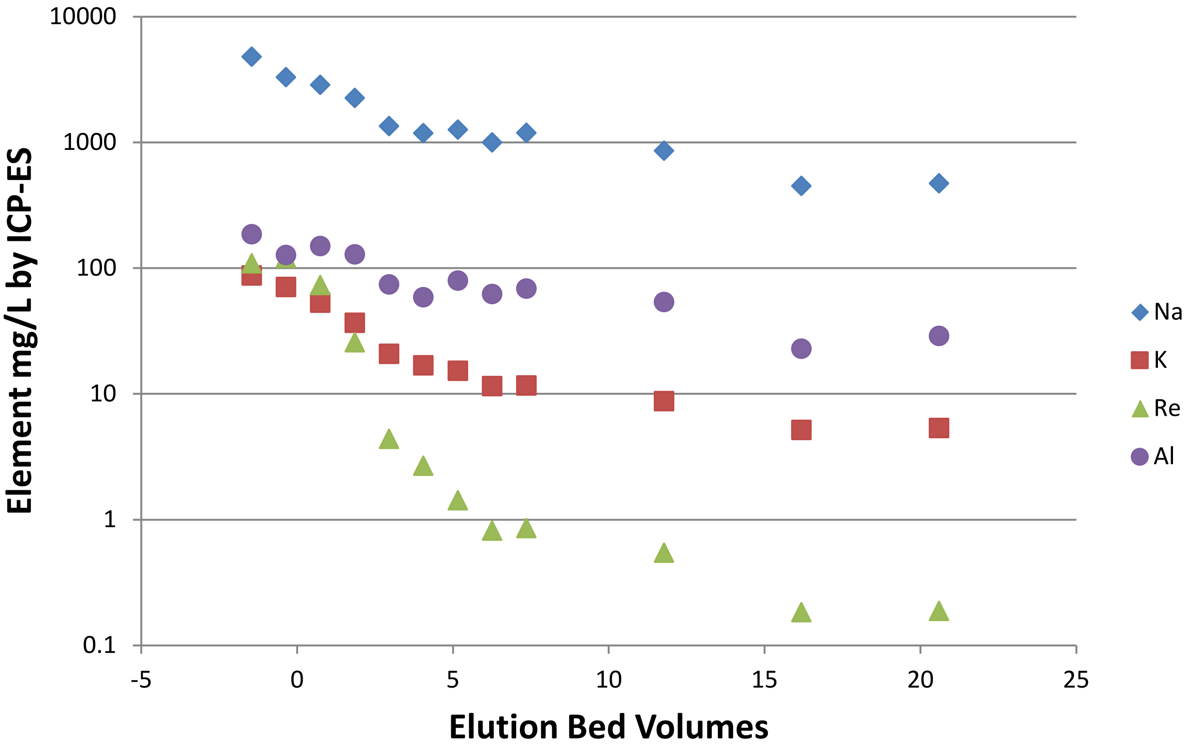

Figure 3-21 show the lead column elutions for the three engineering scale tests Campaigns 1, 2, and 3, respectively. Note that the x-axis shows negative bed volumes initially, showing that elution fluid contained significant eluted elements during displacement. As noted above, displacements were done at room temperature while elution used water at 55 °C, and displacement and elution steps were all performed in the same in lead-lag series as the loading steps. Maximum rhenium concentrations were seen during the transition from displacement to elution. Those concentrations were about 10 times the feed rhenium concentration in loading. Initial sodium concentrations reflected the 0.25 M (~5500 mg/L) content of the displacement fluid.

It is observed that the aluminum elutes more slowly than the rhenium, paralleling the sodium and potassium curves. Further investigation is needed to determine if some aluminum precipitates, presumably as a hydroxide, during elution. This could absorb on or coat the beads and impact performance during subsequent cycles.

Elution data from the lag column are in Appendix E. The data are complicated by the fact that eluting liquid from the lead column flowed through the lag column, so those elution data represent elution of the two-column (in series) system.

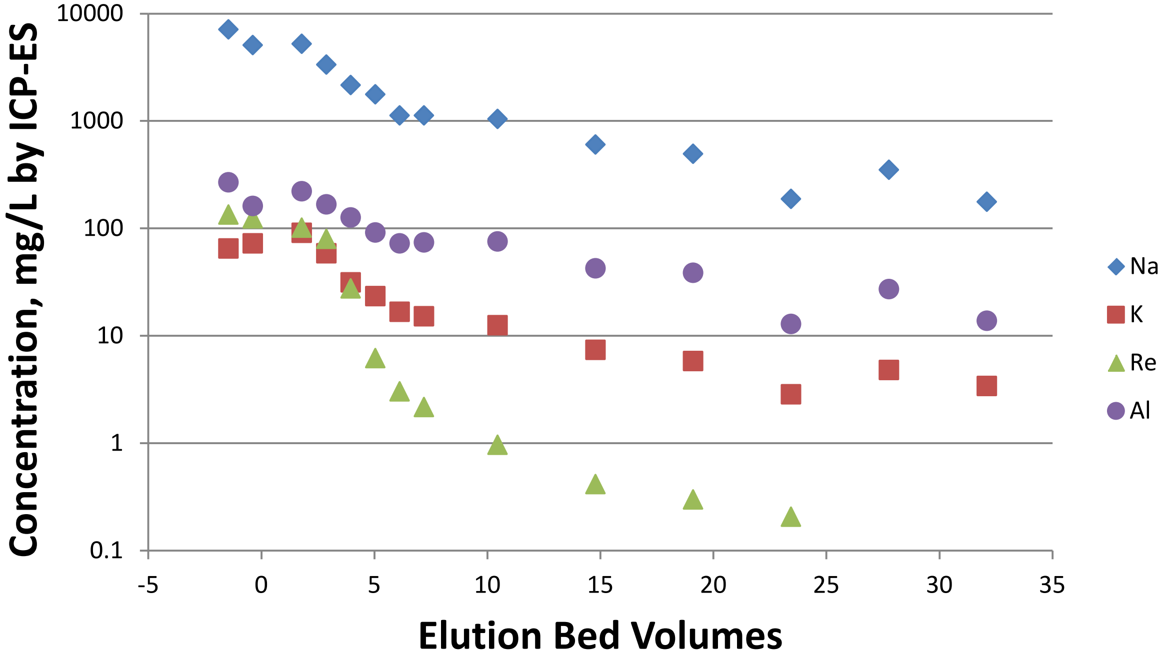

Figure 3-19. Lead Column Elution, Campaign 1

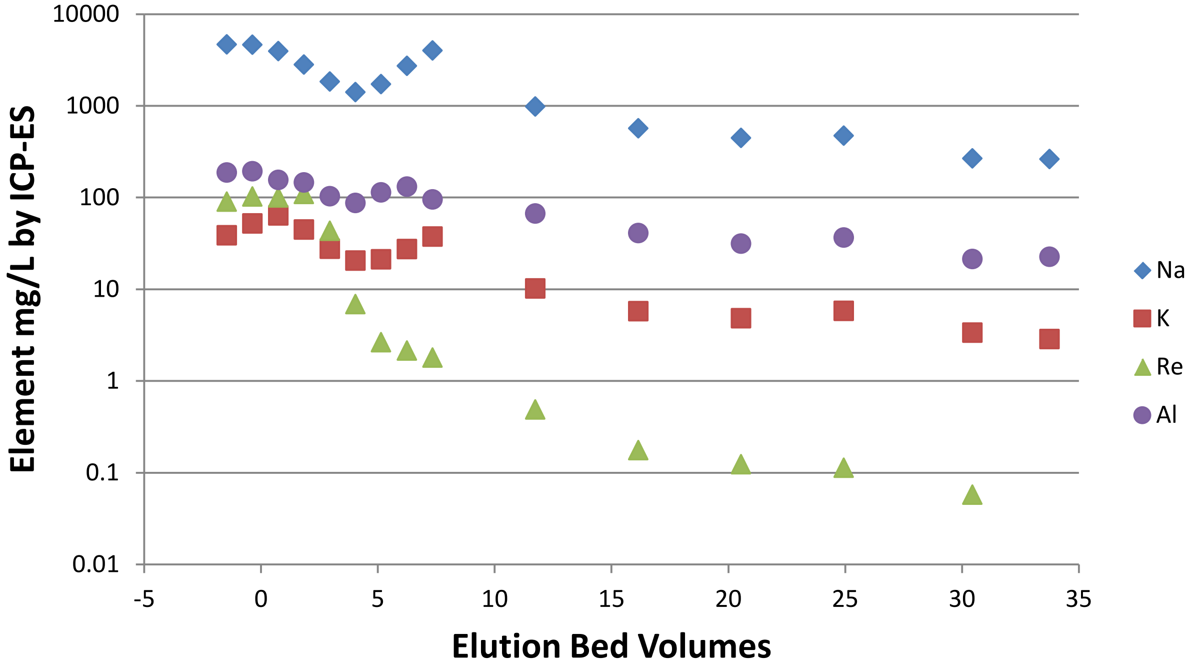

Figure 3-20. Lead Column Elution, Campaign 2

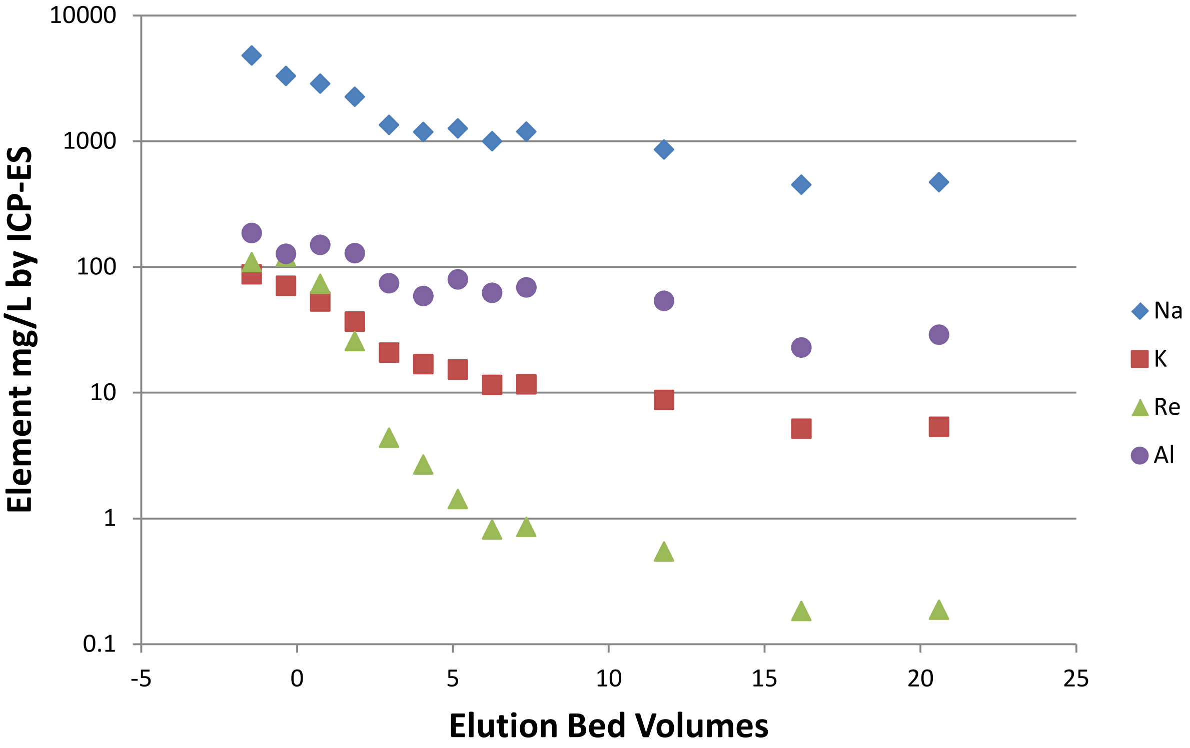

Figure 3-21. Lead Column Elution, Campaign 3

4.0 Conclusions

Operation of floating resin beds appears to be physically practical. Upflow unrestrained, upflow restrained, and downflow restrained styles of bed management were tested on the engineering scale (0.9 liter beds, 2.9” diameter), with little variation in loading profile outcome. The beds appeared to pack at a reasonably constant density after cycling.

- Density-driven (floating or sinking) resin bed motion is as a unit.
- Bed management did not affect resin bed performance. Lead and lag breakthroughs from the three engineering scale campaigns are very repeatable despite different methods of bed management.
- Loading breakthrough is relatively fast.
- Elution commences in the displacement step, where sodium molarity drops rapidly.
- Rhenium elutes most effectively compared to sodium, potassium, and aluminum from the feed.

However, the column performance with this high density simulant is poorer than predicted by computer modeling. The specific reason for this is not yet known, but possible causes include precipitation of solids in the resin, inaccurate projections due to ionic strength effects, resin degradation, bubbles causing uneven flow patterns, or flow channeling in the beds. Further testing would be needed to determine the exact cause. Reaching 50% breakthrough for the lead column at ~50 BV is probably not operationally practical at this time, since this would mean short loading cycles with frequent elutions.

The overall system pressure increased during tests, but the cause was not determined. Replacing the down-stream filter during Test #1 did not impact the pressure. It is speculated that solids were accumulating in the system and restricting flow. It is possible that if trace solids formed, they would sorb onto the resin, reducing breakthrough performance.

The effect of very high (7.8 M) sodium feed on the resin performance raises questions about both capacity and kinetics. Kinetics, specifically pore diffusion, is an issue; however, pore diffusion along will not yield the breakthrough curves observed in either lab or engineering scale test rigs. Capacity reduction, perhaps resulting in exclusion of certain pore regions, along can yield the breakthrough curves observed. Channeling, based on a series of simulations, did not yield the observed breakthrough curves and the measured pressure drops also did not confirm that channel was a dominant factor. The increased reduction in performance in going from small to engineering scale should be just hydrodynamics but modeling efforts were not able to isolate the cause.

At this time, it is recommended that LAW feed dilution to ~5 M [Na^+] is assumed in any planning for using this resin for this application. It is well established that the technology is highly effective at the lower concentration, so it is prudent to assume that operation at the higher concentration cannot be pursued until more testing is completed. If an intermediate concentration is desired, it should be noted that there is a density between the 5 and 7.8 M sodium concentrations where the resin would be neutrally buoyant, and a well-packed bed would not form as desired. Presumably, this would be adverse to breakthrough performance and is not advisable at this time.

5.0 Future Work

Further testing would be needed to determine whether this high density liquid causes an inherently fast breakthrough, or whether it was caused by an artifact of the experiment or equipment.

6.0 References

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Russell, R.L., Westsik, Jr., J.H., Swanberg, D.J., Eibling, R.E., Cozzi, A.D., Lindberg, M.J., Josephson, G.B., Rinehart, D.E., Letter Report: LAW Simulant Development for Cast Stone Screening Tests, PNNL-22352, March, 2013

Appendix A. Recipe for HTWOS 8 M Na Salt Simulant

Preparation Instructions for 210 liters of HTWOS 8 M Na Salt Simulant for EDL TcIX (Actual concentration of Na in recipe is 7.8 M) Engineering Scale Testing Tasks at Savannah River National Laboratory by Mike Williams of SRNL (803-725-2551) or Michael.Williams@srnl.doe.gov who is the Cognizant Technical Function (CTF) for approval of any chemical substitutions for this recipe.

	8 M Na Simulant Salt Solution			
	Chemical Composition and Recipe			
	Chemical Additions for 210 liter Batch			
Batch Sheet		chemical	weight	
Chemical Name		Formula	gms	MW
Water		H2O	10500.0	18.02
Potassium Nitrate		KNO3	1087.03	101.09
Sodium Chloride		NaCl	807.52	58.44
Sodium Fluoride		NaF	434.72	41.99
Sodium Sulfate (anhydr.)		Na2SO4	3997.01	142.02
Water for Rinsing		H2O	10500.0	18.02
Mix the chemicals to dissolve and then add				
Sodium Hydroxide*	50 wt%	NaOH	73012.80	40
Aluminum Nitrate Nonahydrate		Al(NO3)3.9H2O	37734.33	375.04
Caution: Heat Generated by this Step				
*Additional adjustment of sodium hydroxide and sodium nitrate may be needed to achieve Table 1-1 below				
COA Analyte Target Molar Conc.				
Mix to ensure Aluminum is reacted and dissolved. Then add				
Water		H2O	10500.0	18.02
Sodium Phosphate Dodecahydrate		Na3HPO4.12H2O	6098.65	380.12
Sodium Acetate Trihydrate		NaCH3COO.3H2O	1717.47	136.08
Water for Rinsing		H2O	10500.00	18.02
Mix until dissolved.				
Add				
Sodium Carbonate		Na2CO3	9526.38	105.99
Water		H2O	21000.0	18.02
Mix thoroughly to dissolve				
Add				

Sodium Nitrate			NaNO3	18593.94	84.98
Sodium Nitrite			NaNO2	12765.69	68.98
Water Add to 1.34 gm/ml		Density	H2O	*	18.02
			Target Mass =	620.4	pounds
			Not to exceed or	281.4	kg
		Target	Specific Gravity=	1.340	
Table1-1			*adjust final water addition to volume		
COA	Target Molar				
Analyte	Concentration				
K	0.051				
NO3	2.53				
Na	7.80				
NO2	0.88				
Al	0.48				
free OH	2.43				
CO3	0.43				
SO4	0.13				
Cl	0.066				
F	0.049				
Acetate	0.06				
PO4	0.076				

Requirements:

1. All chemicals added are based on 100% Assay (purity). The waters of hydration for chemicals charged shall be as shown in the recipe and the supplier shall obtain approval from the CTF if availability of the stated water of hydration is an issue. For example, sodium sulfate shows no waters of hydration in the recipe. An adjustment would be needed if the sodium sulfate decahydrate (10 waters) is available based on purity and cost. The issue may arise with the availability of other salts in various hydrated forms like sodium oxalate or sodium carbonate. Individual chemicals charged shall be adjusted based on actual Assay and compensated in the water charge to achieve the final Target Molar Concentration. “Free Flowing” sodium nitrite shall not be used because it contains an adulterant. All reagents should be free of other additives, especially surfactants and anti-caking agents. All chemicals used in this simulant shall be 98% or higher Assay (purity). If a chemical used is less than 98% Assay (purity), the SRNL CTF shall be notified for approval prior to its use. For Chemical Assay (purity) >99.9%, no mass adjustment calculation is required. Prior to use, ensure that the sum of the assayed lead (Pb) concentration in each chemical will result in a solution that is less than 5.0 mg/L lead.
2. Equipment, including the mixing tank, used for production of simulant should be thoroughly cleaned and inspected for cleanliness before the beginning of each Batch/Lot. Triple rinsing (i.e., 3 vessel volumes to be used) of all process equipment and mixing tanks using DI water is required. The presence of even trace amounts of immiscible organic species must be avoided. Trace amounts of soluble organic species such as detergents and chelators can have a significant effect on the chemical behavior of the simulant. Any inorganic species that may cause precipitation of any of the simulant components must also be avoided. An example would be alkaline earth elements.
3. Water used must be filtered to 0.5 microns and de-ionized (DI).

4. All tanks and processing equipment shall be sufficiently cleaned so that no impurities are introduced into the simulant. The preparation tankage must tolerate high caustic and high temperatures generating by the caustic addition (near boiling). **The aluminum nitrate and NaOH addition creates a great deal of heat and caution is needed not to add too much NaOH too fast.** All equipment contacting the simulant must be chemically compatible and aluminum metal especially must be avoided as it is dissolved by caustic.
5. Sodium nitrite should be added only after aluminum nitrate solids are thoroughly dissolved in sodium hydroxide to avoid formation of poisonous NO2 fumes.
6. Rayon or equivalent grade 50 wt% NaOH (caustic soda) may be used after adjustment of the water added to account for the water in the 50 wt% NaOH and silicon present, if greater than 2 ppm.
7. Aluminum nitrate [Al(NO3)3.9H2O] is the usual source of aluminate ion. Use of aluminum nitrate requires addition of extra sodium hydroxide and less sodium nitrate based on the following stoichiometry.

   Al(NO3)3 + 4 NaOH = NaAlO2 + 3NaNO3 + 2 H2O

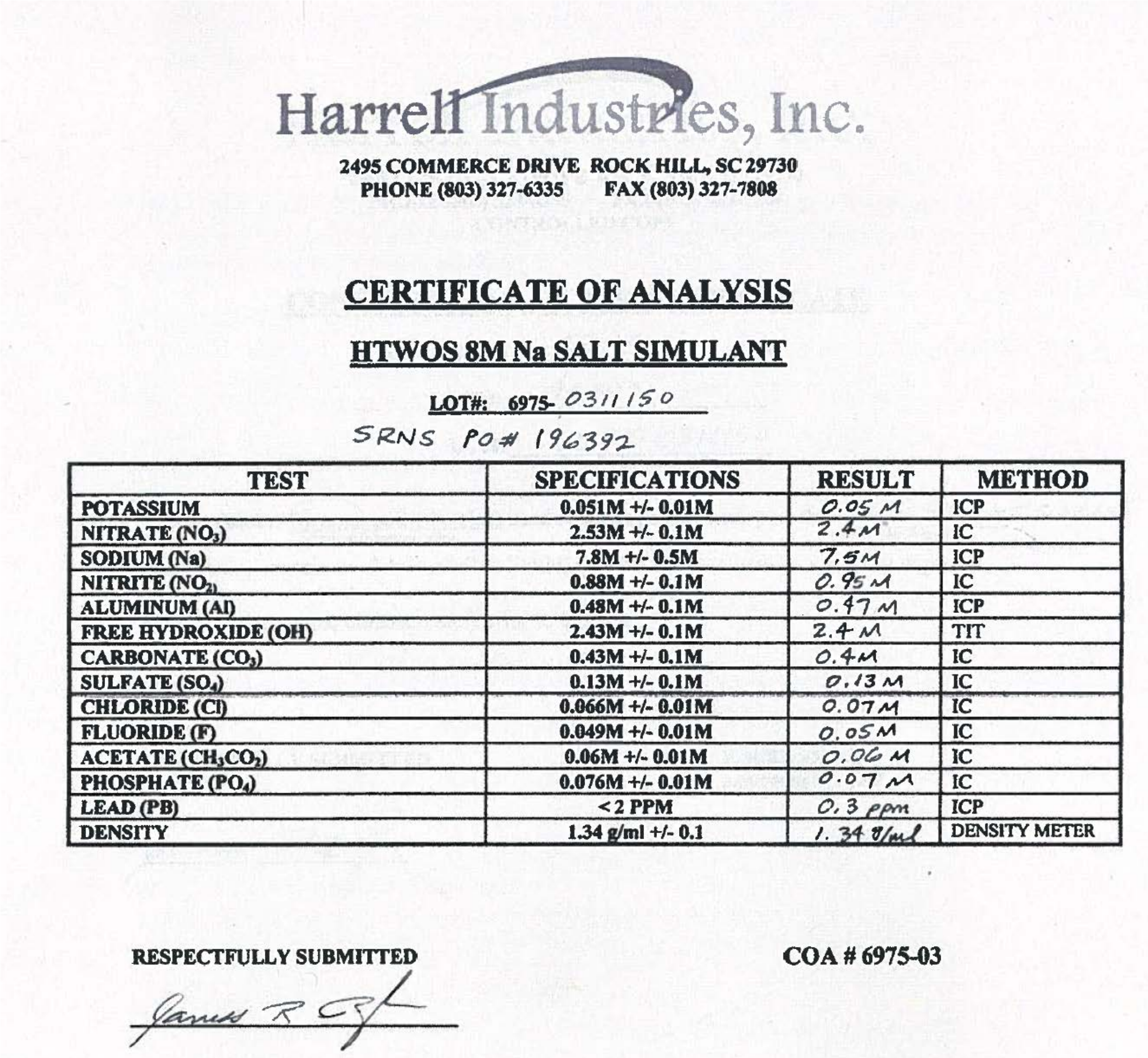
   Aluminum nitrate yields an acidic solution in water and can react with sodium nitrite to form NO2 gas. Thus, the preferred order of addition is to dissolve sodium hydroxide first, followed by aluminum nitrate. Sodium nitrite is added only after the aluminum nitrate is completely dissolved in excess sodium hydroxide.
8. Chemicals should be stored indoors. Exposure of chemicals to excessive moisture should be avoided.
9. The supplier shall maintain traceability of each chemical used in production of HTWOS 8 M Na Simulant back to chemical certificates of analysis. Each production Batch/Lot shall be traceable to composite sample and certificates of analysis.
10. The supplier shall follow the order of chemical addition in the Preparation of 200 liters of HTWOS 8 M Na Simulant and verify that all chemicals, including deionized water, are added in the proper quantity for this batch size.
11. When high purity chemicals are used in the preparation, typically less than 0.05%(weight) of solids fail to dissolve (insoluble). Larger amounts of insoluble solids could be formed if lower purity chemicals are used in the preparation.
12. After mixing, the solutions should be allowed to cool to 23-26 degrees C and held at that temperature range for at least 72 hours before filtering (minimize absorption of carbon dioxide from air, which can form solids).
13. The solution must be filtered to 10 micron (nominal) and placed in new, cleaned polydrums for shipment.
14. Sample and analyze the solution for all COA analytes in Table 1-1 plus lead.
15. Prepare a Certificate of Analysis, COA, for the Analytes listed in the HTWOS 8 M Na Simulant. Include specific gravity of the HTWOS 8 M Na Simulant product and Lot/Batch number with reference to the Batch Sheet which is attached.
16. Water used must be de-ionized (100-micromhos per cm or less) and filtered (DI).
17. All tanks and processing equipment shall be sufficiently cleaned so that no impurities are introduced into the simulant.
18. Shipping Instructions for HTWOS 8 M Na Simulant after approval received from SRNL CTF:

1	210 liters minimum of Simulant to be placed in a minimum of one 55 gallon bung polydrum or			
	two 30 gallon polydrums containing about 105 liters each.			
2	The Simulant can be produced in multiple Batches, but the final material			
	produced for the drums shall be blended.			

3	The Simulant drums are to be palletized and loaded on one SRNS LTL		
	Carrier truck(s) for delivery and off-loading at 731-1N at SRS for QA Receipt		
	Inspection by 3/19/15.		
4	The drums are to be new and cleaned (triple water rinse) before Simulant		
	addition		

19. Documentation Required:
    - Drums/containers shall be marked with the following information: A) HTWOS 8 M Na Simulant, B) Supplier's name, C) SRNS PO Number, D) Date Loaded, E) Batch/Lot Number, and F) Drum/Container No. __ of __(Number of drums/containers).
    - Certificate of Drum/Container Cleanliness.
    - Include the following for HTWOS 8 M Na Simulant for EDL: 1) Certificate of Analysis of Finished Product for COA Analytes, 2) Certificate of Materials used, 3) One set of completed Chemical Batching Record and Logs for each Batch/Lot Shipped.

Appendix B. Certificate of Analysis



Harrell Industries, Inc.

2495 COMMERCE DRIVE ROCK HILL, SC 29730
PHONE (803) 327-6335 FAX (803) 327-7808

CERTIFICATE OF ANALYSIS

HTWOS 8M Na SALT SIMULANT

LOT#: 6975- 0311150

SRNS PO# 196392

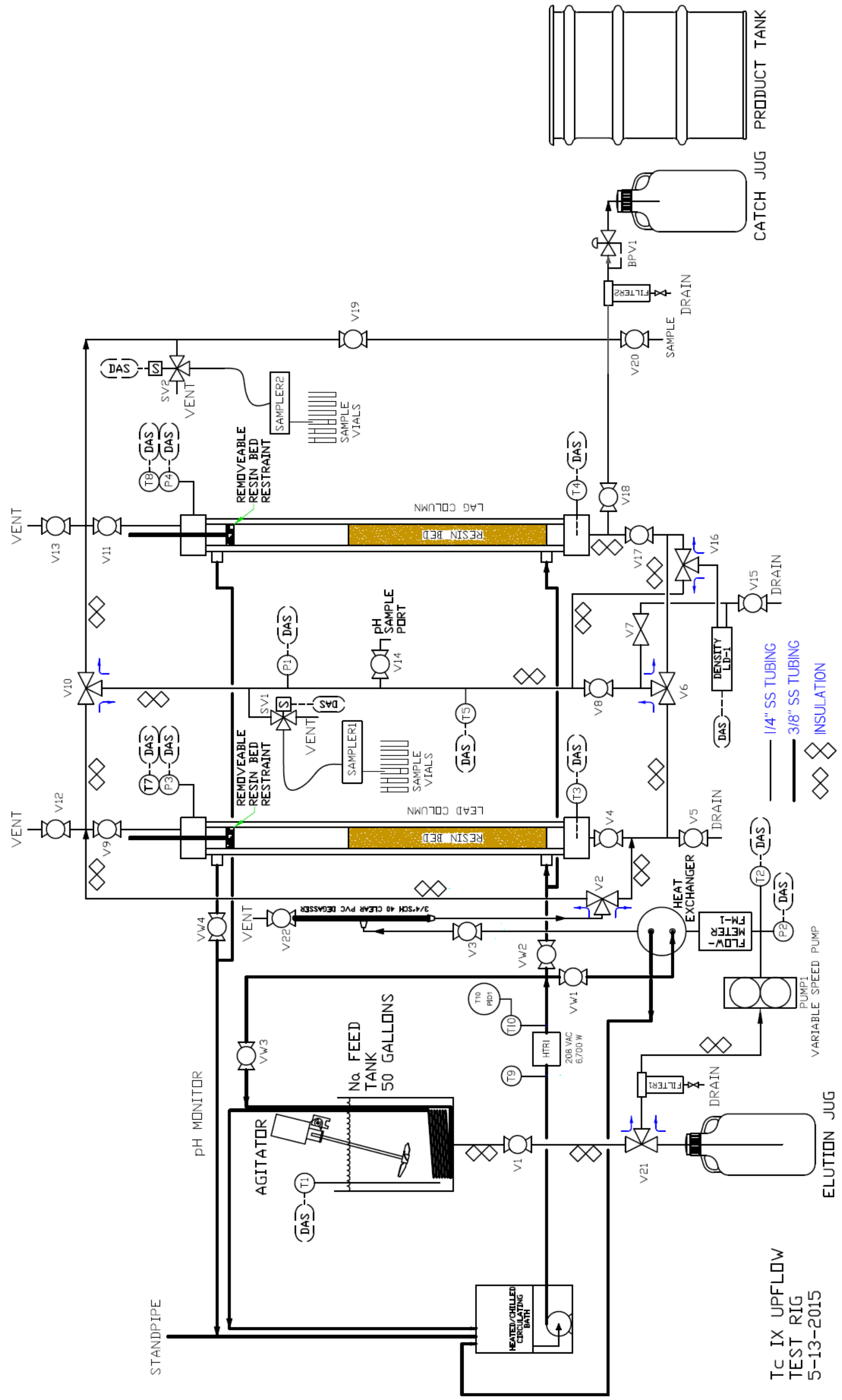
TEST	SPECIFICATIONS	RESULT	METHOD
POTASSIUM	0.051M +/- 0.01M	0.05 M	ICP
NITRATE (NO_3)	2.53M +/- 0.1M	2.4M	IC
SODIUM (Na)	7.8M +/- 0.5M	7.5M	ICP
NITRITE (NO_2)	0.88M +/- 0.1M	0.95M	IC
ALUMINUM (Al)	0.48M +/- 0.1M	0.47 M	ICP
FREE HYDROXIDE (OH)	2.43M +/- 0.1M	2.4 M	TIT
CARBONATE (CO_3)	0.43M +/- 0.1M	0.4M	IC
SULFATE (SO_4)	0.13M +/- 0.1M	0.13 M	IC
CHLORIDE (Cl)	0.066M +/- 0.01M	0.07M	IC
FLUORIDE (F)	0.049M +/- 0.01M	0.05M	IC
ACETATE (CH_3CO_2)	0.06M +/- 0.01M	0.06 M	IC
PHOSPHATE (PO_4)	0.076M +/- 0.01M	0.07 M	IC
LEAD (PB)	< 2 PPM	0.3 ppm	ICP
DENSITY	1.34 g/ml +/- 0.1	1.34 g/ml	DENSITY METER

RESPECTFULLY SUBMITTED

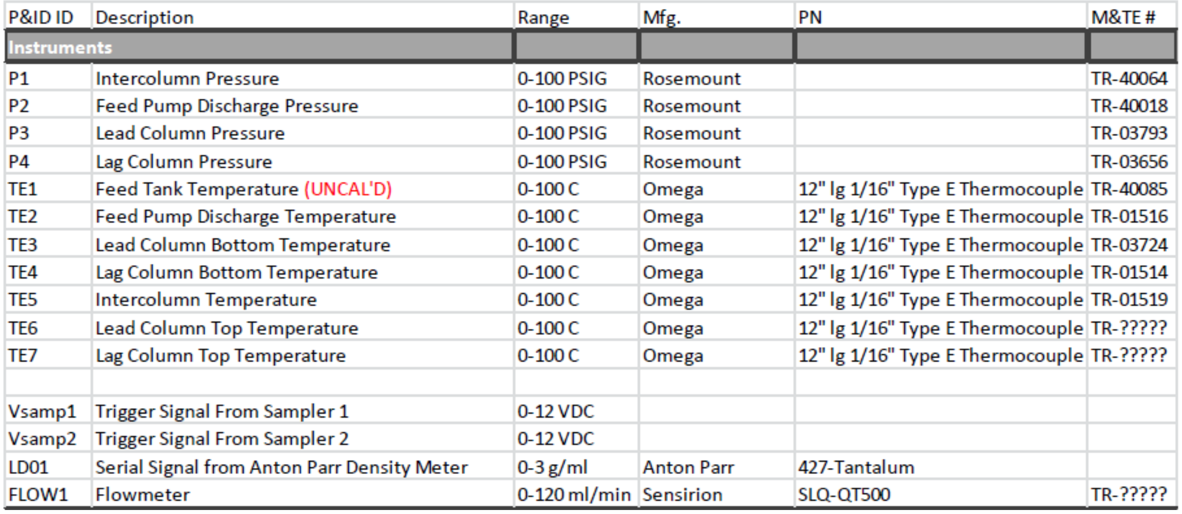
James R

COA # 6975-03

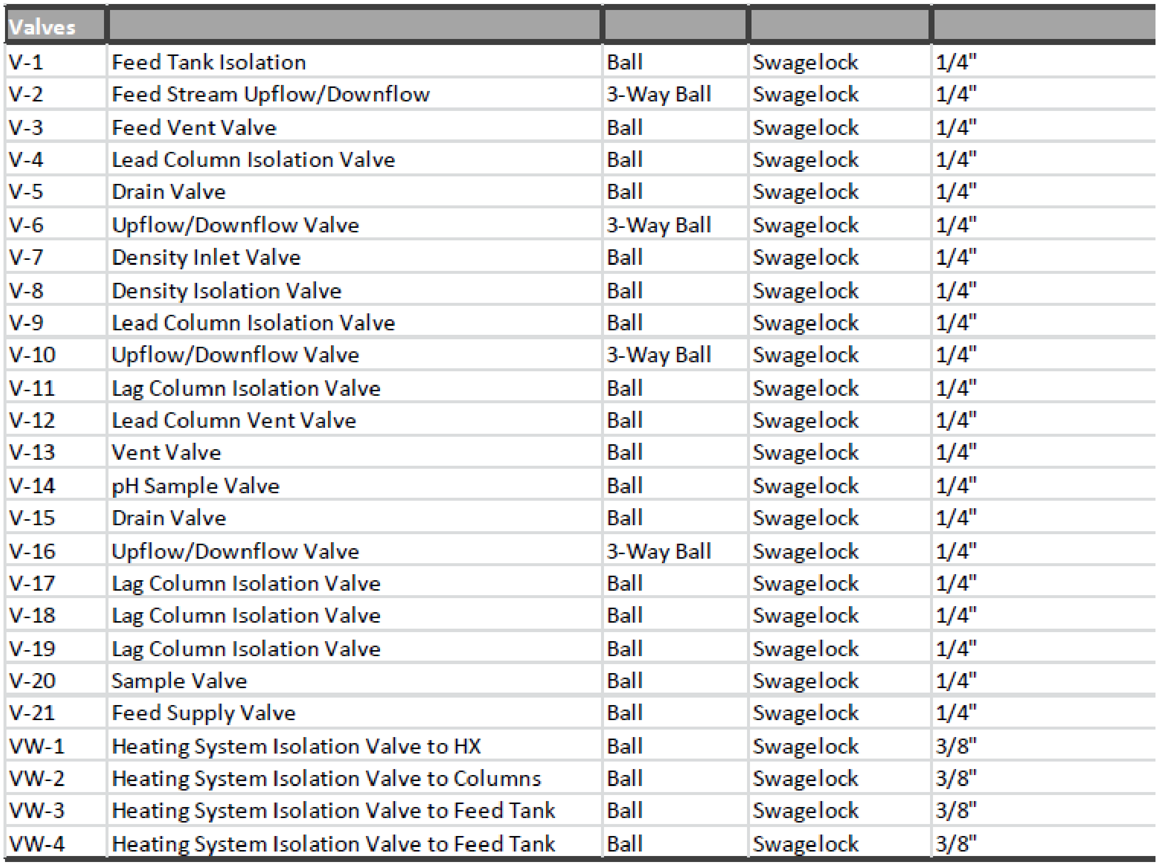
Appendix C. Engineering-scale IX rig Piping & Instrument Diagram



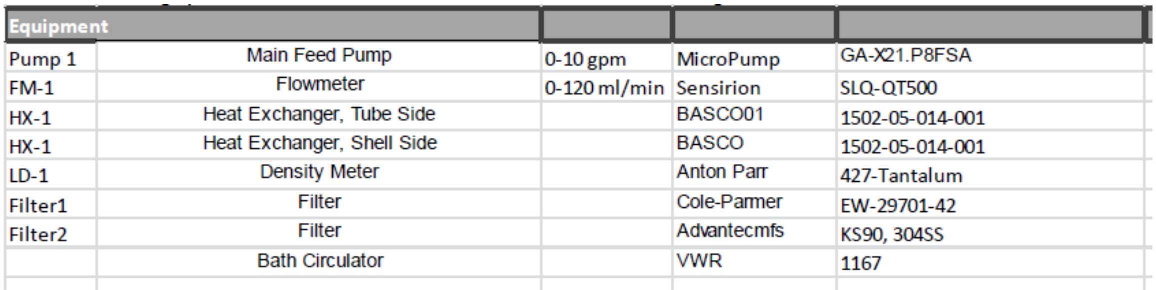
Appendix D. Engineering-scale IX rig Instrument List



P&ID ID	Description	Range	Mfg.	PN	M&TE #
Instruments					
P1	Intercolumn Pressure	0-100 PSIG	Rosemount		TR-40064
P2	Feed Pump Discharge Pressure	0-100 PSIG	Rosemount		TR-40018
P3	Lead Column Pressure	0-100 PSIG	Rosemount		TR-03793
P4	Lag Column Pressure	0-100 PSIG	Rosemount		TR-03656
TE1	Feed Tank Temperature (UNCAL'D)	0-100 C	Omega	12" lg 1/16" Type E Thermocouple	TR-40085
TE2	Feed Pump Discharge Temperature	0-100 C	Omega	12" lg 1/16" Type E Thermocouple	TR-01516
TE3	Lead Column Bottom Temperature	0-100 C	Omega	12" lg 1/16" Type E Thermocouple	TR-03724
TE4	Lag Column Bottom Temperature	0-100 C	Omega	12" lg 1/16" Type E Thermocouple	TR-01514
TE5	Intercolumn Temperature	0-100 C	Omega	12" lg 1/16" Type E Thermocouple	TR-01519
TE6	Lead Column Top Temperature	0-100 C	Omega	12" lg 1/16" Type E Thermocouple	TR-?????
TE7	Lag Column Top Temperature	0-100 C	Omega	12" lg 1/16" Type E Thermocouple	TR-?????
Vsamp1	Trigger Signal From Sampler 1	0-12 VDC			
Vsamp2	Trigger Signal From Sampler 2	0-12 VDC			
LD01	Serial Signal from Anton Parr Density Meter	0-3 g/ml	Anton Parr	427-Tantalum	
FLOW1	Flowmeter	0-120 ml/min	Sensirion	SLQ-QT500	TR-?????



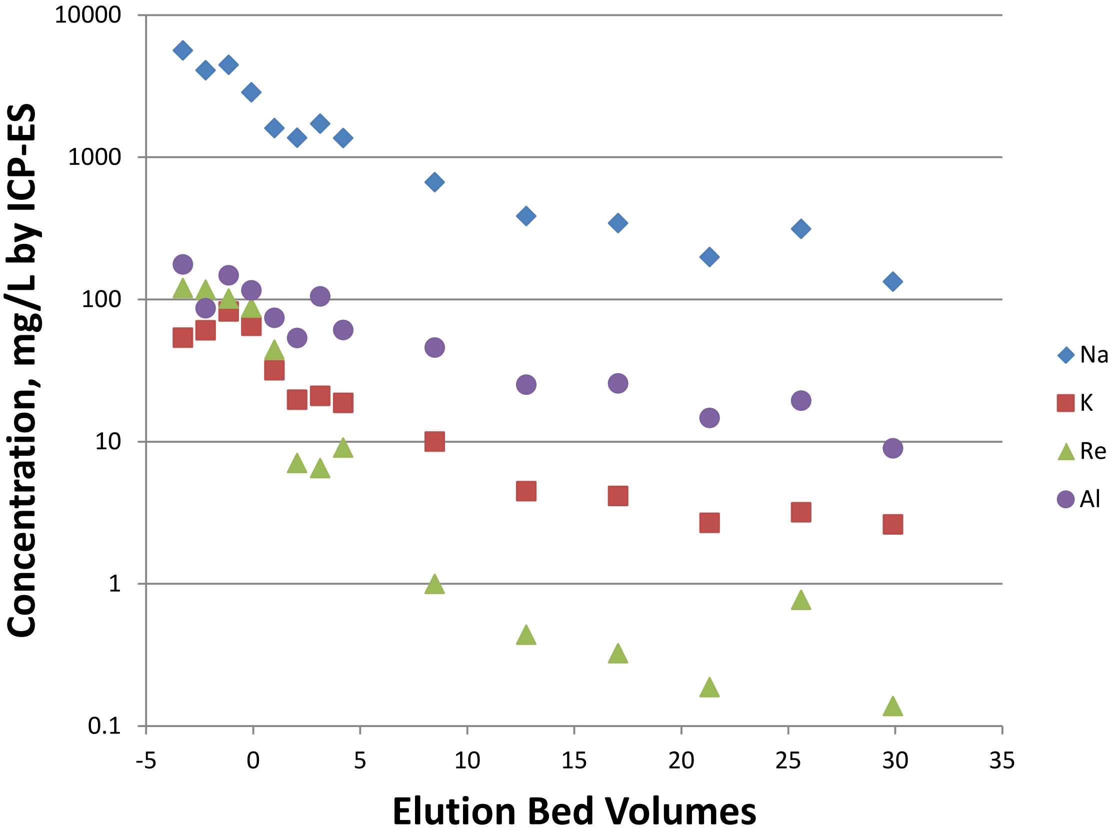
Valves				
V-1	Feed Tank Isolation	Ball	Swagelock	1/4"
V-2	Feed Stream Upflow/Downflow	3-Way Ball	Swagelock	1/4"
V-3	Feed Vent Valve	Ball	Swagelock	1/4"
V-4	Lead Column Isolation Valve	Ball	Swagelock	1/4"
V-5	Drain Valve	Ball	Swagelock	1/4"
V-6	Upflow/Downflow Valve	3-Way Ball	Swagelock	1/4"
V-7	Density Inlet Valve	Ball	Swagelock	1/4"
V-8	Density Isolation Valve	Ball	Swagelock	1/4"
V-9	Lead Column Isolation Valve	Ball	Swagelock	1/4"
V-10	Upflow/Downflow Valve	3-Way Ball	Swagelock	1/4"
V-11	Lag Column Isolation Valve	Ball	Swagelock	1/4"
V-12	Lead Column Vent Valve	Ball	Swagelock	1/4"
V-13	Vent Valve	Ball	Swagelock	1/4"
V-14	pH Sample Valve	Ball	Swagelock	1/4"
V-15	Drain Valve	Ball	Swagelock	1/4"
V-16	Upflow/Downflow Valve	3-Way Ball	Swagelock	1/4"
V-17	Lag Column Isolation Valve	Ball	Swagelock	1/4"
V-18	Lag Column Isolation Valve	Ball	Swagelock	1/4"
V-19	Lag Column Isolation Valve	Ball	Swagelock	1/4"
V-20	Sample Valve	Ball	Swagelock	1/4"
V-21	Feed Supply Valve	Ball	Swagelock	1/4"
VW-1	Heating System Isolation Valve to HX	Ball	Swagelock	3/8"
VW-2	Heating System Isolation Valve to Columns	Ball	Swagelock	3/8"
VW-3	Heating System Isolation Valve to Feed Tank	Ball	Swagelock	3/8"
VW-4	Heating System Isolation Valve to Feed Tank	Ball	Swagelock	3/8"



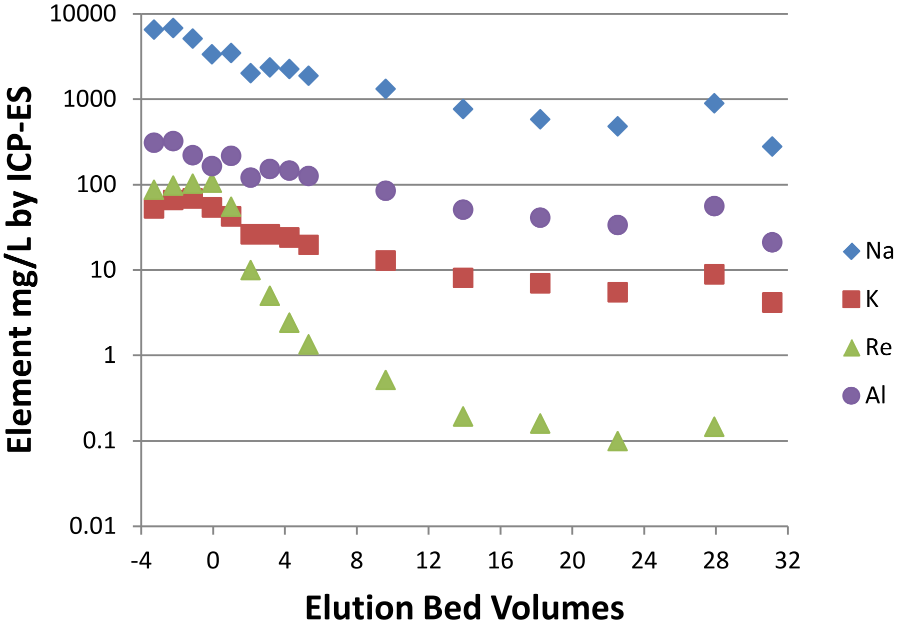
Equipment				
Pump 1	Main Feed Pump	0-10 gpm	MicroPump	GA-X21.P8FSA
FM-1	Flowmeter	0-120 ml/min	Sensirion	SLQ-QT500
HX-1	Heat Exchanger, Tube Side		BASCO01	1502-05-014-001
HX-1	Heat Exchanger, Shell Side		BASCO	1502-05-014-001
LD-1	Density Meter		Anton Parr	427-Tantalum
Filter1	Filter		Cole-Parmer	EW-29701-42
Filter2	Filter		Advantecmfs	KS90, 304SS
	Bath Circulator		VWR	1167

Appendix E Lag Column Elution Plots

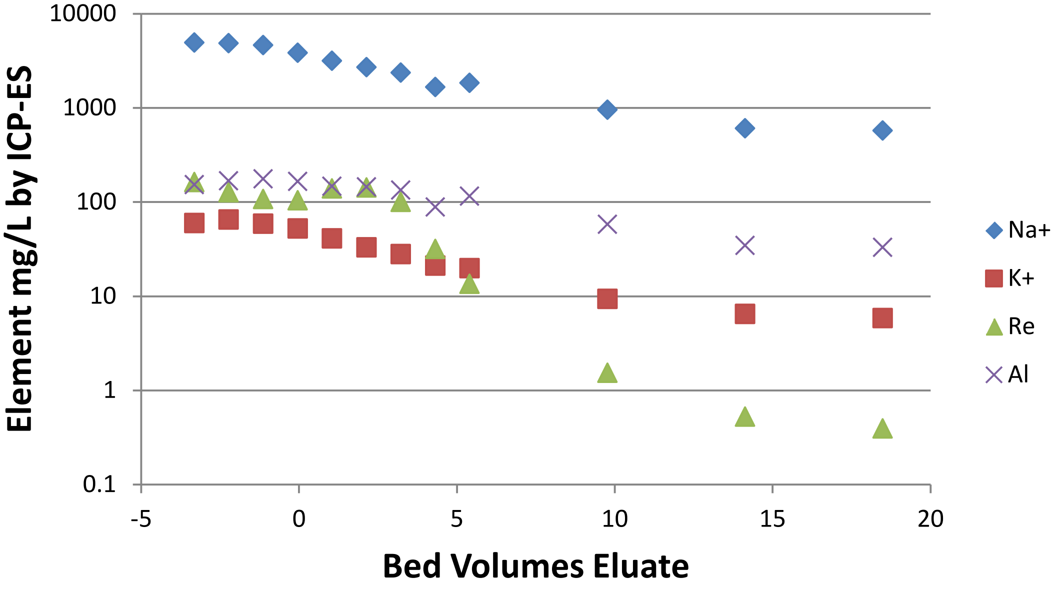
Campaign 1



Campaign 2



Campaign 3



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T. B. Brown, 773-A
S. D. Fink, 773-A
C. C. Herman, 773-A
E. N. Hoffman, 999-W
F. M. Pennebaker, 773-42A
A. L. Washington, II, 773-42A
W. R. Wilmarth, 773-A
Records Administration (EDWS)

M. R. Williams, 786-5A
M. L. Restivo, 773-42A
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M. E. Stone, 999-W