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Evaluating the Effects of Tri-Butyl Phosphate (TBP) and Normal Paraffin Hydrocarbon (NPH) in Simulated Low-Activity Waste Solution on Ion Exchange

OCTOBER 18, 2002

SAVANNAH RIVER TECHNOLOGY CENTER

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Completeness of Testing

This report describes the results of work and testing specified by Test Specification: TSP-W375-00-00036, Rev. 1. and Test Plan: WSRC-TR-2002-00143, Rev. 0. The work and any associated testing followed established quality assurance requirements and was conducted as authorized. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Results required by the test plan are reported. Also reported are any unusual or anomalous occurrences that are different from starting hypotheses. The test results and this report have been reviewed and verified.

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List of Acronyms

BV	bed volume
C/C_o	analyte concentration in column effluent divided by analyte concentration in feed
DF	decontamination factor
DI	de-ionized water
DL	detection limit
FBRM	focused beam reflectance measurement
H-form	hydrogen form
IC	ion chromatography
ICP-AES	inductively coupled plasma atomic emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
Na-form	sodium form
MRQ	minimum reportable quantity
NPH	normal paraffin hydrocarbon
PSD	particle size distribution
RSD	relative standard deviation
TBP	tri-butyl phosphate
TC	total carbon
TIC	total inorganic carbon
TOC	total organic carbon
WTP	waste treatment plant
λ	lambda - the number of BVs of solution processed at 50% breakthrough

1.0 Summary

Ultraflitration and ion exchange are among the pretreatment processes selected for the WTP at the Hanford Site. Envelope B AZ-101 waste may contain TBP and NPH - dodecane, as dissolved species and also as a separate phase.

This study is the second part of a two-part study on Evaluating the Effects of Tri-Butyl Phosphate (TBP) and Normal Paraffin Hydrocarbon (NPH) in Simulated Low-Activity Waste Solution on Ultraflitration and Ion Exchange. The first study dealt with ultraflitration.

The second part involved using filtrates from the ultrafiltration work to perform resin sorption experiments using SuperLig® 644 and SuperLig® 639 resins. SuperLig® 644 resin has a high selectivity for cesium while SuperLig® 639 resin is highly selective for rhenium as perrhenate (the surrogate for pertechnetate). What is unknown is the effect organics may have on these resins high sorption capacities for cesium/rhenium.

The goal of the study was to evaluate the effectiveness of the resins to remove cesium and rhenium from AZ-101 simulant containing organics by comparing to the baseline case, i.e. AZ-101 simulant containing no organics using a two-fold experimental approach: (1) Batch equilibrium contact tests, and (2) Small-scale column tests.

The batch contact tests measured sorption Kds. The Kds were used to predict the effective resin capacity. This was achieved through generation of sorption isotherms using three initial concentrations of the species of interest (cesium or rhenium) per testing condition.

The small-scale column tests, which closely mimic plant conditions, generated loading and elution profile data used to determine whether removal targets and design requirements were met. It involved a two-column system connected in series for loading and parallel for eluting.

The batch contact work clearly demonstrated there is no statistically significant effect of organics (TBP, dodecane and their degradation products) on cesium and rhenium sorption by SuperLig® 644 and SuperLig® 639 resins respectively from Envelope B AZ-101 simulant solution. See Table 1.1 for a summary of the results.

The rhenium column breakthrough curves for simulants with and without organics were virtually identical. This implies organics do not negatively impact rhenium removal with SuperLig® 639 resin. The λ_{Re} values exceeded 100 BV at 50% breakthrough. Also the total DF target of 50 for envelope B waste was exceeded for rhenium. See Tables 1.2 and 1.3 for summaries of the results.

Rhenium elution with de-ionized water at 65 °C was adequate overall with no discernible organics effects. The BVs at $C/C_o = 0.01$ for both lead and lag column elution using simulants with and without organics ranged from 7 to 25.

Due to a small breakthrough for cesium, λ_{Cs} and total DF_{Cs} could not be obtained for cesium column runs for both simulants with and without organics. However, the column breakthrough data for simulants with and without organics were basically the same up to 86 BV; indicating a no organics effect on cesium removal using SuperLig® 644 resin for at least 86 BV. Both the cesium column runs for simulants with and without organics exceeded 75 BV at 50% breakthrough.

Cesium elution with 0.5 M HNO_3 at 25 °C from SuperLig® 644 resin was efficient with lead column BVs at $C/C_o = 0.01$ of 10 for both simulants with and without organics. The identical BVs indicate cesium elution was not affected by organics.

Table 1.1 Batch Contact λ Values.

	Simulant Without Organics	**Simulant With Organics**
λ_{Re}	171	171
λ_{Cs}	146	133

Table 1.2 Column Loading λ and Total DF Values.

	Simulant Without Organics	**Simulant With Organics**
λ_{Re}	195	190
Total DF_{Re}	> 360	345
λ_{Cs}	Not determined	Not determined
Total DF_{Cs}	> 1199*	> 1596**

* Based on 100BVs (or < 0.08% breakthrough)
** Based on 86 BVs (or < 0.06% breakthrough)

Table 1.3 Column Elution BV Values at $C/C_o = 0.01$.

	Simulant Without Organics	**Simulant With Organics**
	Lead & Lag Columns	**Lead & Lag Columns**
BV_{Re}	25 & 13	20 & 7
BV_{Cs}	10 & $C/C_o << 0.01$ throughout	10 & $C/C_o << 0.01$ throughout

2.0 Introduction

Ultraflitration and ion exchange are among the pretreatment processes selected for the WTP at the Hanford Site. Envelope B AZ-101 waste may to contain TBP and NPH - dodecane, as dissolved species and also as a separate phase.

This study is the second part of a two-part study on the effects of TBP and NPH referred to here as organics on ultraflitration and cesium/rhenium ion exchange. The first study dealt with ultraflitration[1].

The second part used filtrates from the ultrafiltration work and SuperLig® 644 and SuperLig® 639 resins to conduct sorption experiments.

The objectives were to:

1. Determine the effects on the equilibrium batch contact Kds for cesium and rhenium using SuperLig® 644 and SuperLig® 639 resins respectively due to the presence of TBP and NPH in simulated waste solution.

2. Determine the effects of TBP and NPH on cesium and rhenium column loading and elution.

The report deals mainly with batch and column test procedures used for the study followed by a discussion of results. The work was done according to the "Task Technical and Quality Assurance Plan for Evaluating the Effects of Tri-Butyl Phosphate (TBP) and Normal Paraffin Hydrocarbon (NPH) in Simulated Low-Activity Waste Solution on Ion Exchange"[2]. The Task Technical and Quality Assurance Plan was also derived from "Test Specification for Evaluating Effect of Tri-Butyl Phosphate and Normal Paraffin Hydrocarbon in Simulated Low-Activity Waste Solution on Ultrafiltration and Ion Exchange Systems"[3].

3.0 Experimental

3.1 Materials

3.1.1 Resins

The SuperLig® 644 and SuperLig®639 resins were obtained from IBC Advanced Technologies, Inc. (American Fork, Utah). SuperLig® 644 (Batch # = I-D5-03-06-02-35-60) is a cation-exchange resin that is selective for cesium. It is a proprietary polymeric organic material. It was received in hydrogen form and used in its as-received condition with no pretreatment.

The SuperLig® 639 resin (Batch # = I-R2-03-27-02-20-45), on the other hand, is an ion-pair exchanger that is selective for rhenium (the surrogate for technetium). It essentially removes a neutral salt (i.e. sodium perrhenate ion-pair) from solution[4]. It was received in neutral form and used as-received.

3.1.2 Simulant

The simulant used for this study was Envelope B AZ-101 filtrate from an earlier ultrafiltration work[1]. About 1.8 liters of three different AZ-101 filtrates were received.

Simulant 0: AZ-101 filtrate with no organics (i.e. no TBP or NPH - dodecane).
Simulant H: AZ-101 filtrate with a prior ultrafiltration concentration of 5000 μg/mL organics (i.e. 2500 μg/mL TBP and 2500 μg/mL NPH - dodecane).
Simulant L: AZ-101 filtrate with a prior ultrafiltration concentration of 50 μg/mL organics (i.e. 25 μg/mL TBP and 25 μg/mL NPH - dodecane).

Note that only simulant 0 and simulant H above were used for the study. According to Task Technical and Quality Assurance Plan[2], simulant L was only to be used if simulant H had indicated organics affected the removal of cesium or rhenium from AZ-101 simulant. The simulant supernate recipe is given in Table A.6 in the Appendix.

3.1.3 Chemicals

The chemicals used were all reagent grade. Nitric acid (Fisher Chemicals, New Jersey) and sodium hydroxide (Fisher Chemicals, New Jersey) were used to prepare 0.5 M HNO_3, 0.1 M NaOH and 0.25 M NaOH solutions. De-ionized water was used to prepare the solutions. De-ionized water was also used in some of the column process steps (e.g. resin rinsing and rhenium elution from SuperLig® 639 resin).

Cesium nitrate (GFS Chemicals, Inc., Columbus, Ohio) and sodium perrhenate (GFS Chemicals, Inc., Columbus, Ohio) were used to spike some simulant solutions in the batch contact experiments. It involved dissolving a weighed amount in the simulant of interest.

AZ-101 filtrate with a prior ultrafiltration concentration of 5000 μg/mL organics (simulant H) was spiked with TBP. The first TBP spike involved adding a weighed amount of TBP to simulant and shaking periodically for three days. The second TBP spike involved adding a weighed amount of TBP to simulant one hour before the start of batch contact or column experiments with periodic shaking. These spikes replenished dissolved TBP that had degraded in the caustic simulants during the months on the shelf.

3.2 Resin Characterization

For the procedures described below, as-received resins (SuperLig® 644 and SuperLig® 639) that have been air-dried at room temperature were used unless otherwise stated. "Air-dried" in this report means that all free liquid had been removed. "Vacuuming at 50°C" was used to remove all possible moisture for F-factor and metals content determinations.

The procedures for bulk density, L-Factor, and I_{Na}-Factor were similar to those used by Fiskum et al.[5]

The bulk density was determined by weighing approximately 4 g of air-dried as-received SuperLig® 644 resin or 5 g of air-dried as-received SuperLig® 639 resin into a 10-mL graduated cylinder and measuring the volume after tapping the cylinder walls to obtain uniform packing.

The F-Factor (solids fraction remaining after water loss) of air-dried as-received resin was determined by weighing in duplicate approximately 0.3 g of SuperLig® 644 resin or 1 g of SuperLig® 639 resin and drying the resin in vacuum at 50°C to constant mass.

The L-Factor (solids fraction remaining after conversion of as-received resin to H-form) was determined by contacting in quadruplicate about 0.3 g of the air-dried as-received resin (SuperLig® 644) with 10 to 15-mL of 0.5 M HNO_3 for at least 1 hour. This was followed by filtering the resin-HNO_3 mixture into a tared 0.45-µm nylon Nalgene (Rochester, New York) filter unit under vacuum, washing the resin with 10 to 15-ml of de-ionized water to neutral pH at room temperature, and finally drying the resin in air at room temperature to a constant mass. The F-Factor of the air-dried H-form resin was determined by drying in duplicate the resin in vacuum at 50 °C to constant mass.

The I_{Na}-Factor (mass increase after conversion from H-form to Na-form) was obtained by converting the H-form SuperLig® 644 resin from the L-factor determination step to Na-form. This was achieved by contacting in duplicate about 0.2 g of the H-form resin with 10 to 15-mL of 0.25 M NaOH for at least 1 hour. This was followed by filtering the resin-NaOH mixture with a tared 0.45-µm nylon Nalgene filter unit under vacuum, washing the resin with 10 to 15-ml of de-ionized water to neutral pH at room temperature, and finally drying the resin in vacuum at room temperature to a constant mass.

Metals content (Na and K) analysis was performed on vacuum-dried as-received (unused) resins and vacuum-dried used resins from the column experiments (SuperLig® 644 and SuperLig® 639).

Dry particle size analysis using sieves was performed on the air-dried as-received resins (SuperLig® 644 and SuperLig® 639).

Wet particle size analysis using Focused Beam Reflectance Measurement (FBRM) instrument (model M400L, Lasentec, Redmond, Washington) was performed on air-dried as-received resins and used resins (both in DI water) from the column experiments (SuperLig® 644 and SuperLig® 639).

3.3 Batch Contact Tests

Batch contact runs were conducted by adding 10 mL of simulant solution with known concentration of cesium or rhenium to a known mass (0.1 g) of air-dried as-received resin (i.e. SuperLig® 644 or SuperLig® 639) in a 15-mL glass bottle equipped with Teflon®-lined screw cap. A Mettler-Toledo (Columbus, Ohio) analytical balance (model AG285) with an accuracy of ± 0.001 g was used to weigh the samples. The bottles were equilibrated in a bench top Mix-Max orbital shaker (model C24, New Brunswick Scientific Company, Edison, New Jersey) for 72 ± 1 hours at a shaking speed of 275 rpm and temperature of 25 ± 2 °C. High precision (0.01 °C) thermometers traceable to the National Institute of Standards and Testing (NIST) were mounted in polyethylene bottles containing de-ionized water to record the temperature in the orbital shaker[6].

At the end of the 72-hour equilibration period, the resin-solution mixtures were separated by filtration. Nalgene (Rochester, New York) 0.45-μm nylon filters connected to a vacuum and trap assembly were used for the filtration. Aliquots of the filtrate were placed in glass vials with Teflon®-lined screw caps for analyses. The amount of cesium or rhenium sorbed was determined from the initial and final concentrations of cesium or rhenium in solution.

Control runs were conducted along with and in the same manner as the batch contact runs described above. A control is a simulant solution containing no resin and is utilized to determine the initial simulant concentration of the desired constituent.

Three different initial simulant concentrations were used for each resin type (i.e. SuperLig® 644 or SuperLig® 639). Two of the three initial simulant concentrations were obtained by spiking with cesium nitrate for SuperLig® 644 resin or sodium perrhenate for SuperLig® 639 resin. All batch contact runs were conducted in duplicate. Glass containers were used throughout to prevent organics adsorbing to plastics.

3.4 Column Operation

3.4.1 Ion Exchange Column Apparatus

The ion exchange column system consisted of two (lead and lag) glass columns, two automatic fraction collectors, water circulating bath, and several metering pumps. The column apparatus was setup in a chemical hood. The pump inlet tubings were manually switched between simulant and the other process solutions.

The borosilicate glass columns (Spectrum Chromatography, Houston, Texas) had an inside diameter of 1.45 cm (i.e. 1.65 mL/cm of height) and graduations on the walls to facilitate measurement of resin bed height and height of liquid above resin bed. The glass columns were equipped with adjustable polypropylene plungers (model 124108, Spectrum Chromatography, Houston, Texas) at the top and 200 mesh stainless steel screens at the bottom. The plungers were used to control the height of liquid above the resin beds, while the screens were used as supports for the resins. Temperature regulation in the columns was achieved with a circulating water bath (Model DC10-P5, ThermoHaake, Newington, New Hampshire) looped with the column glass jackets. Calibration was done to ensure that the desired column temperature was reached. The outer walls of the columns and jackets were coated with polyvinyl chloride to help minimize hazard in case of breakage.

Solutions were introduced down flow through the columns using Fluid Metering Incorporated (FMI, Syosset, New York) positive displacement pump (model RP-P) equipped with Scilog Inc. (Middletown, Wisconsin) piston pump head (model RH00). The piston pump head (1/8-in I.D.) was made of stainless steel and was rotated by a 450-rpm optically encoded servo-controlled motor. The maximum flow rate for the pump was 23 mL/min[6].

Spectrum Chromatography IS-95 Interval Samplers located at the outlet of each column were utilized to collect aliquots of samples either manually or automatically. All the individual units (i.e. pumps, columns, fraction collectors) from the solution reservoir bottles to the effluent bottles were connected with polyethylene tubings (1/8-in ID) supplied with Teflon quick-disconnect fittings (Cole-Palmer Instrument Company, Vernon Hills, Illinois) at the ends.

3.4.2 Column Tests

A known mass (see Table 3.1) of air-dried resin (SuperLig® 644 or SuperLig® 639) was soaked in de-ionized water using a 10:1 liquid:solid volume ratio at room temperature for about one hour. This was followed by pouring all the resin slurry into the column while simultaneously tapping the glass column walls to ensure uniform resin bed packing. The resin packing procedure was the same for both SuperLig® 644 and SuperLig® 639 resins. The major difference was that quartz wool and glass beads were placed on top of the SuperLig® 639 resin bed to prevent SuperLig® 639 resin from floating in the simulant. Note that the glass beads were on top of the quartz wool.

Table 3.1 Mass of SuperLig® 644 and SuperLig® 639 Resins Used per Column.

	Simulant Without Organics	**Simulant With Organics**
	SuperLig® 644 Resin	**SuperLig® 644 Resin**
Lead column resin mass, g	4.8079	4.8082
Lag column resin mass, g	4.8084	4.8083
	SuperLig® 639 Resin	**SuperLig® 639 Resin**
Lead column resin mass, g	3.5207	3.5290
Lag column resin mass, g	3.5280	3.5294

The temperature for all the column operations was 25 ± 2 °C except SuperLig® 639 resin elution process step which was run at 65 ± 3 °C. Note that in addition to circulating water at 65 °C through the column jackets, heated de-ionized water at 65 °C was fed into the columns. The height of the resin bed, the height of the liquid above the resin bed, flow rate, and temperature of water in the circulating bath were measured periodically.

Tables 3.2, 3.3 and 3.4 give details of the experimental conditions including when the lead and lag columns were connected in series or ran in parallel. Note that there are two tables for SuperLig® 644 resin and one table for SuperLig® 639. The resin BV for SuperLig® 644 resin turned out to be different for the runs without and with organics.

Table 3.2 Experimental Conditions for SuperLig® 644 and Simulant Without Organics.

Process Step	**Solution**	**Total Volume Processed**		**Flow Rate**		**Time per Step**	
		mL	**BV**	**mL/min**	**BV/hr**	**hr**	**min**
Lead and Lag Column Conditioning, Parallel Columns							
Bed Preconditioning	0.25 M NaOH	120	12	0.5	3.0	4	240
Reconnect Lead and Lag Columns in Series							
Loading	AZ-101 simulant	1300	100	0.33	1.5	66.7	4000
Feed Displacement	0.10 M NaOH	78	6	0.65	3.0	2	120
Post-Feed Water Rinse	DI water	78	6	0.65	3.0	2	120
Lead and Lag Column Elution, Parallel Columns							
Elution	0.5 M HNO3	260	20	0.22	1.0	20	1200
Post- Elution Water Rinse	DI water	78	6	0.22	1.0	6	360

Temperature of each process step = 25 ± 2 °C.
Bed volume (BV) for each column = 13 mL (in simulant).
Note: The above calculations were based on actual column BV of 13 mL except bed preconditioning which was based on assumed column BV of 10 mL.

Samples of the effluent were collected periodically per the sampling and analysis scheme given in Tables 3.5 and 3.6 for the column runs conducted (i.e. SuperLig® 644 resin/simulant with and without organics and SuperLig® 639 resin/simulant with and without organics). The overall error for all the analyses is within ± 20%.

At the end of the last process step, the resins were removed from the columns and divided into two portions. One portion was vacuum-dried at 50 °C for metals content (Na and K) analysis. The other portion was used as-is for wet particle size analysis using Focused Beam Reflectance Measurement (FBRM) instrument.

The column runs were smooth overall except the target resin bed volume of 10 mL for SuperLig® 644 resin was exceeded (13 and 15 mL for runs without and with organics respectively) because the resin was new, and only preliminary shrink/swell data were available at the time.

Table 3.3 Experimental Conditions for SuperLig® 644 and AZ-101 Simulant With Organics.

Process Step	**Solution**	**Total Volume Processed**		**Flow Rate**		**Time per Step**	
		mL	**BV**	**mL/min**	**BV/hr**	**hr**	**min**
Lead and Lag Column Conditioning, Parallel Columns							
Bed Preconditioning	0.25 M NaOH	120	12	0.5	3.0	4	240
Reconnect Lead and Lag Columns in Series							
Loading	AZ-101 simulant	1290	86	0.375	1.5	57.3	3440
Feed Displacement	0.10 M NaOH	90	6	0.75	3.0	2	120
Post-Feed Water Rinse	DI water	90	6	0.75	3.0	2.	120
Lead and Lag Column Elution, Parallel Columns							
Elution	0.5 M HNO3	300	20	0.25	1.0	20	1200
Post- Elution Water Rinse	DI water	90	6	0.25	1.0	6	360

Temperature of each process step = 25 ± 2 °C.
Bed volume (BV) for each column = 15 mL (in simulant).
Note: The above calculations were based on actual column BV of 15 mL except bed preconditioning which was based on assumed column BV of 10 mL.

Table 3.4 Experimental Conditions for SuperLig® 639 and AZ-101 Simulant With and Without Organics.

Process Step	**Solution**	**Total Volume Processed**		**Flow Rate**		**Time per Step**	
		mL	**BV**	**mL/min**	**BV/hr**	**hr**	**min**
Lead and Lag Column Conditioning, Parallel Columns							
Bed Preconditioning	0.25 M NaOH	73	12	0.31	3	4	240
Reconnect Lead and Lag Columns in Series							
Loading	AZ-101 simulant	1222	200	0.15	1.5	133.3	8000
Feed Displacement	0.10 M NaOH	36	6	0.3	3.0	2	120
Lead and Lag Column Elution, Parallel Columns							
Elution	DI water @ 65 ± 3 °C	150	25	0.1	1.0	25	1500

Temperature of each process step = 25 ± 2 °C unless indicated otherwise.
Bed volume (BV) for each column = 6.1 mL (in simulant).

Table 3.5 Sampling and Analysis Scheme for SuperLig® 644 and AZ-101 Simulant With and Without Organics.

Process Step	**Lead Column**	**Lag Column**	**Analytical Sample Volume, mL**	**Analysis**
0.25 M NaOH Preconditioning	n/a	n/a	n/a	n/a
Loading	5th BV and 10 BV increments thereafter	5th BV and 10 BV increments thereafter	*3	Na, K using ICP-AES, Cs using ICP-MS, and chloride, fluoride using IC
Loading Effluent Composite	n/a	1 composite	**4	Cs using ICP-MS, other metals using ICP-AES, and nitrate, nitrite, chloride, fluoride using IC
Feed Displacement	n/a	1 composite	4	Cs using ICP-MS
Post-Feed Water Rinse	n/a	1 composite	4	Cs using ICP-MS
Elution	1 BV increments for first 8 BVs and 2 BV increments thereafter	1 BV increments for first 8 BVs and 2 BV increments thereafter	2	Cs using ICP-MS
Elution Effluent Composite	1 composite	1 composite	26	Cs using ICP-MS, other metals using ICP-AES, nitrate, nitrite, chloride, fluoride, sulfate, phosphate using IC, TIC/TOC using furnace oxidation, and acid concentration using titration
Post- Elution Water Rinse	1 composite	1 composite	4	Cs using ICP-MS
Resin at the end of run	0.6 gram	0.6 gram	n/a	Na and K using ICP-AES
Resin at the end of run	Rest of resin	Rest of resin	n/a	PSD by FBRM method

ICP-MS = Inductively coupled plasma mass spectrometry
ICP-AES = Inductively coupled plasma atomic emission spectrometry
GC-MS = Gas chromatography mass spectrometry
IC = Ion chromatography
TOC = Total organic carbon
TIC = Total inorganic carbon
PSD = Particle size distribution
FBRM = Focused Beam Reflectance Measurement

n/a = not applicable

* For the run with organics, an additional 11 mL of sample was collected manually at the 10th BV for TBP analysis using GC-MS.

** For the run with organics, an additional 22 mL of sample was collected for TBP analysis using GC-MS.

Table 3.6 Sampling and Analysis Scheme for SuperLig® 639 and AZ-101 Simulant With and Without Organics.

Process Step	Lead Column	Lag Column	Analytical Sample Volume, mL	Analysis
0.25 M NaOH Preconditioning	n/a	n/a	n/a	n/a
Loading	5th BV and 10 BV increments thereafter	5th BV and 10 BV increments thereafter	*8	Re, Na, K, Cr using ICP-AES, nitrate, nitrite, chloride, fluoride, sulfate, phosphate using IC, and hydroxide using titration
Loading Effluent Composite	n/a	1 composite	**18	Re and other metals using ICP-AES, nitrate, nitrite, chloride, fluoride, sulfate, phosphate using IC, and hydroxide using titration
Feed Displacement	n/a	1 composite	4	Re using ICP-AES
Elution	Every 2 BV	Every 2 BV	2	Re using ICP-AES
Elution Effluent Composite	1 composite	1 composite	22	Re and other metals using ICP-AES, nitrate, nitrite, chloride, fluoride, sulfate, phosphate using IC, TIC/TOC using furnace oxidation, and hydroxide using titration
Resin at the end of run	0.6 gram	0.6 gram	n/a	Na and K using ICP-AES
Resin at the end of run	Rest of resin	Rest of resin	n/a	PSD by FBRM method

ICP-MS = Inductively coupled plasma mass spectrometry
ICP-AES = Inductively coupled plasma atomic emission spectrometry
GC-MS = Gas chromatography mass spectrometry
IC = Ion chromatography
TOC = Total organic carbon
TIC = Total inorganic carbon
PSD = Particle size distribution
FBRM = Focused Beam Reflectance Measurement

n/a = not applicable
* For the run with organics, an additional 11 mL of sample was collected manually at the 10th BV for TBP analysis using GC-MS.
** For the run with organics, an additional 22 mL of sample was collected for TBP analysis using GC-MS.

4.0 Results and Discussion

4.1 Resin Characterization

Sieve particle size distribution of air-dried as-received resins is given in Table 4.1. Both resins had few fines. The bulk of the resins was between 300 and 600 μm i.e. 94% for SuperLig® 644 and 80% for SuperLig® 639.

Table 4.1 Sieve Particle Size Distribution Data of Air-Dried As- Received Resins.

		SuperLig® 644	**SuperLig® 639**
U.S. Sieve Number	**Particle Size, μm**	**Weight %**	**Weight %**
20	> 840	nm	1.00
30	600 - 840	2.11	18.97
40	425 - 600	52.93	72.59
50	300 - 425	41.47	7.29
70	212 - 300	3.29	0.12
230	62 - 212	0.20	0.04

nm = not measured

Table 4.2 lists various properties of the SuperLig® 644 and SuperLig® 639 resins.

The L-factor is the solids fraction remaining after conversion to H form. It is given by the equation below [5]:

$$L = (m_H * F_H)/(m * F) \qquad (4.1)$$

where m_H is the mass of air-dried H form resin, F_H is the F-factor for the air-dried H form resin, m is the mass of air-dried as-received resin, and F is the F-factor for the air-dried as-received resin.

The I_{Na}-factor is the mass increase upon conversion from H form to Na form as given by the following equation[5]:

$$I_{Na} = m_{Na}/(m_H * F_H) \qquad (4.2)$$

where m_{Na} is the mass of vacuum-dried Na form resin.

The H form and Na form dry-bed resin densities are given by the following equations[5]:

$$\text{H form dry-bed resin density} = (m * F * L)/V \qquad (4.3)$$

$$\text{Na form dry-bed resin density} = (m * F * L * I_{Na})/V \qquad (4.4)$$

where V is the resin bed volume.

Table 4.2 Resin Characterization Data.

Property	**SuperLig® 644**	**SuperLig® 639**
Dry Bulk density, g/mL	0.38 (0.66 air-dried)	0.52 (0.57 air-dried)
F-factor	0.58	0.91
L-factor	0.84	n/a
I_{Na}-factor	1.17	n/a
Dry Bed Density	**g/mL**	**g/mL**
AZ-101 Simulant	0.21	0.53
0.5 M HNO_3	0.24*	n/a
0.25 M NaOH	0.19*	0.53
De-ionized Water	n/a	0.53

* Calculated using equations 4.3 and 4.4.
n/a = not applicable

4.2 Simulant Characterization

As mentioned earlier in section 3.1.2, the simulant for this work were filtrates from an ultrafiltration study[1]. Table 4.3 is the composition of the as-received filtrates. The analytical results generally compare favorably with the ultrafiltration data. The notable exception is the TBP concentration. TBP concentration in the ultrafiltration work ranged between 0.12 (detection limit) and 0.7 μg/mL. TBP concentration in the as-received filtrates was all below the detection limit of 0.12 μg/mL.

The lag time between the two analyses was about 5 months. The following were the speculations for why TBP concentration in the current analysis was below detection limit. Note that the filtrates were received in Qorpak (Bridgeville, PA) high density polyethylene (HDPE) fluorinated barrier plastic bottles with Teflon®-lined caps.

1. The TBP may have adsorbed to the walls of the plastic bottles. This is a typical phenomenon especially for hydrophobic compounds. TBP is hydrophobic.

2. The TBP may have degraded to other compounds (e.g. dibutyl phosphate, butanol, monobutyl phosphate, phosphoric acid, etc.) during the five-month storage time.

To evaluate the degradation and adsorption hypotheses, it was decided (1) to spike simulant H to 0.7 μg/mL TBP (the highest concentration obtained in the ultrafiltration study), and (2) to use glass containers with Teflon®-lined screw caps for this work. See section 3.1.3 for first TBP spike procedure. Note that NPH-dodecane was below the detection limit of 0.12 μg/mL in both the ultrafiltration study analysis and this analysis. Therefore no spiking with NPH was done.

Table 4.3 Composition of AZ-101 Filtrates Received from the Ultrafiltration Study.

Analyte	**Simulant 0, μg/mL**	**Simulant L, μg/mL**	**Simulant H, μg/mL**
Al	2150	2145	2630
Ba	< 0.024	< 0.024	< 0.024
Ca	0.14	0.12	0.23
Cd	0.62	0.64	0.51
Cr	473	471	614
Cs	24.8	25.1	33.6
Fe	1.03	1.05	0.87
K	4260	4275	4485
La	< 1	< 1	< 1
Mg	< 0.168	< 0.168	< 0.168
Na	105,000	111,000	111,000
Ni	< 0.124	< 0.124	< 0.124
P	765	772	677
Pb	< 1.38	< 1.38	< 1.38
Re	36.3	36.7	39.3
S	6805	6810	6560
Zr	1.26	1.29	0.92
Cl^-	54	61	62
F^-	1570	1625	1595
NO_3^-	63,800	68,550	68,550
NO_2^-	57,250	61,050	60,450
$PO4^-$	2345	2195	2020
$SO4^-$	18,050	18,000	17,300
OH^-, M	0.134	0.207	0.225
TIC	3127	3619	4034
TOC	75	86	<20
TC	3202	3704	4040
TBP	< 0.12	< 0.12	< 0.12
NPH – dodecane	< 0.12	< 0.12	< 0.12
Density, g/mL	1.23	1.23	1.22

Each data point is an average of duplicate measurements.
Data with "<" symbols are detection limits.

4.3 Cesium Batch Contact Tests With SuperLig® 644 Resin

The sorption capacity of the resins was evaluated using batch equilibrium contact approach. This was achieved using the original unspiked simulant and two cesium-spiked simulants giving a total of three different concentrations. Table 4.4 is a summary of cesium batch equilibrium contact data for simulant with no organics and SuperLig® 644 resin. Table 4.5 is similar data for simulant with organics.

The batch distribution coefficient, Kd, was determined with the equation below.

$$Kd = [(C_o - C_f)*V]/[\, C_f * m * F] \qquad (4.5)$$

where C_o is initial cesium concentration, C_f is final cesium concentration, V is the volume of solution, m in the mass of resin, and F is the F-factor of the resin.

As expected the percent sorbed and Kd for cesium increase with decreasing initial cesium concentration while the amount of cesium sorbed decreases with decreasing initial cesium concentration.

Even though the initial cesium concentrations for the simulant with and without organics (Tables 4.4 and 4.5) are different, they are reasonably close to allow comparison of their Kds. The Kds for the simulant without organics are consistently higher than the corresponding Kds for the simulant with organics. This may lead to the deduction that organics negatively impact the removal of cesium from AZ-101 simulant. However, the real question that needs to be posed is whether the effect is statistically significant.

Table 4.4 Cesium Batch Contact Data for AZ-101 Simulant with no Organics and SuperLig® 644 Resin at 25 °C.

Batch Contact Test	Initial Cesium Conc., µg/mL	Final Cesium Conc., µg/mL	Cesium Sorbed, %	Cesium Sorbed, µg/g	Cesium Kd, mL/g	Average Cesium Kd, mL/g	Percent RSD
Unspiked	23.1	1.58	93	3,660	2,317	2,453	7.9
Unspiked duplicate	23.3	1.45	94	3,755	2,590	-	-
Cs Spike 1	88.7	10.6	88	13,185	1,244	1,248	0.5
Cs Spike 1 duplicate	89.9	10.7	88	13,398	1,252	-	-
Cs Spike 2	442	181	59	44,569	246	236	6.4
Cs Spike 2 duplicate	436	187	57	42,045	225	-	-

Phase ratio = 171 mL/g
F-factor = 0.58
Kds are based on mass of H-form resin.
Dash denotes not applicable because average of two data points is given.

To answer this question, the T-test null hypothesis was done on corresponding data in Tables 4.4 and 4.5 (i.e. simulant without and with organics). Table 4.6 gives T-Test significant levels of at least 0.12 for all initial cesium concentrations. Generally, T-Test significant levels should be less than 0.05 to indicate significance[11]. This implies there is no significant difference between corresponding Kds for simulant without and with organics. Hence, it can be deduced that organics do not affect the removal of cesium from AZ-101 simulant using SuperLig® 644 resin.

Table 4.5 Cesium Batch Contact Data for AZ-101 Simulant with Organics* and SuperLig® 644 Resin at 25 °C.

Batch Contact Test	Initial Cesium Conc., µg/mL	Final Cesium Conc., µg/mL	Cesium Sorbed, %	Cesium Sorbed, µg/g	Cesium Kd, mL/g	Average Cesium Kd, mL/g	Percent RSD
Unspiked	30.2	2.27	92	4,790	2,110	2,196	5.5
Unspiked duplicate	30.4	2.09	93	4,769	2,282	-	-
Cs Spike 1	95.3	12.2	87	14,212	1,165	998	23.6
Cs Spike 1 duplicate	94.8	15.7	83	13,063	832	-	-
Cs Spike 2	449	200	55	42,619	213	181	25.5
Cs Spike 2 duplicate	446	240	46	35,515	148	-	-

* Simulant with a prior ultrafiltration concentration of 5000 µg/mL organics which was spiked to 0.7 µg/mL TBP.
Initial TBP concentration = 0.7 µg/mL
Initial NPH (dodecane) concentration = < 0.12 µg/mL
Phase ratio = 171 mL/g
F factor = 0.58
Kds are based on mass of H-form resin.
Dash denotes not applicable because average of two data points is given.

Table 4.6 T-Test on Effect of Organics on Cesium Batch Contact Kds for AZ-101 Simulant with SuperLig® 644 Resin at 25 °C.

Initial Cesium Concentration, µg/mL	Simulant with no Organics	Simulant Spiked with Organics (TBP)	T-Test Significant Level
No Organics/With Organics	Kd, mL/g	Kd, mL/g	
23.1/30.3	2,317	2,110	0.12
23.3/30.4	2,590	2,282	-
88.7/95.3	1,244	1,165	0.38
89.9/94.8	1,252	832	-
442/449	246	213	0.24
436/446	225	148	-

Kds are based on mass of H-form resin.
Dash denotes not applicable because T-Test significant level of two sets of data is given.

A multiple regression analysis of the combined data set in Tables 4.4 and 4.5 using initial cesium concentration and the presence of organics as independent variables, and final cesium concentration as the dependent variable indicated the following. At the 95% confidence level, while initial cesium concentration is significant in estimating the final cesium concentration, the presence of organics is not. Thus, the multiple regression analysis confirms the deduction drawn from the T-test null hypothesis.

Note that the concentrations of sodium, potassium, and chromium remained fairly constant during the sorption process. The percent removals for sodium, potassium, and chromium were mostly below 3%, which is within the error of measurement.

The TBP concentration in the simulant for the batch contact experiments in Table 4.5 (with organics) including the controls were below the detection limit of 0.12µg/mL. Since the AZ-101 simulant used to generate the data in Table 4.5 was spiked with TBP to an initial concentration of 0.7 µg/mL, at least the controls should have indicated the presence of TBP. This will be discussed further in the next section.

Figure 4.1 shows log–log plots of Kd versus final cesium concentration for the data in Tables 4.4 and 4.5 with linear regression lines through each set of data points. Interpolation (vertical lines) using simulant initial cesium concentration of 24 µg/mL (log value = 1.380) for simulant with no organics and 32 µg/mL (log value = 1.505) for simulant with organics, gives Kds of 695 mL/g for simulant with no organics and 541 mL/g for simulant with organics respectively. The equivalent Kd for simulant with organics based on initial cesium concentration of 24 µg/mL (log value = 1.380) is 634 mL/g.

The λ value, which is a prediction of the number of bed volumes required to reach 50% breakthrough in a column operation, is given by

$$\lambda = \text{Kd} * \text{resin dry bed density} \tag{4.6}$$

Hence, based on the same initial cesium concentration of 24 µg/mL,

λ_{Cs} for simulant with no organics = 146, and
λ_{Cs} for simulant with organics = 133.

The above λ_{Cs} values surpass 75 BV at 50% breakthrough.

4.4 Rhenium Batch Contact Tests With SuperLig® 639 Resin

The discussion here is similar to the previous section. Hence, only the salient features will be mentioned. Tables 4.7 and 4.8 are summaries of rhenium batch contact data for simulants without and with organics using SuperLig® 639 resin. Unlike the cesium batch contact data, Tables 4.7 and 4.8 do not show any consistent trend of organics affecting Kds. Rather, the trend is mixed.

Table 4.9 is a T-test null hypothesis data indicating there is no significant difference between Kds for simulants with and without organics. Significant levels for all three concentrations are 0.31 or higher.

Again, a multiple regression analysis of the combined data set in Tables 4.7 and 4.8 using initial rhenium concentration and the presence of organics as independent variables, and final rhenium concentration as the dependent variable substantiated at the 95% confidence level the above finding. Thus, organics do not affect the removal of rhenium from AZ-101 simulant using SuperLig® 639 resin, as was the case for cesium removal with SuperLig® 644 resin.

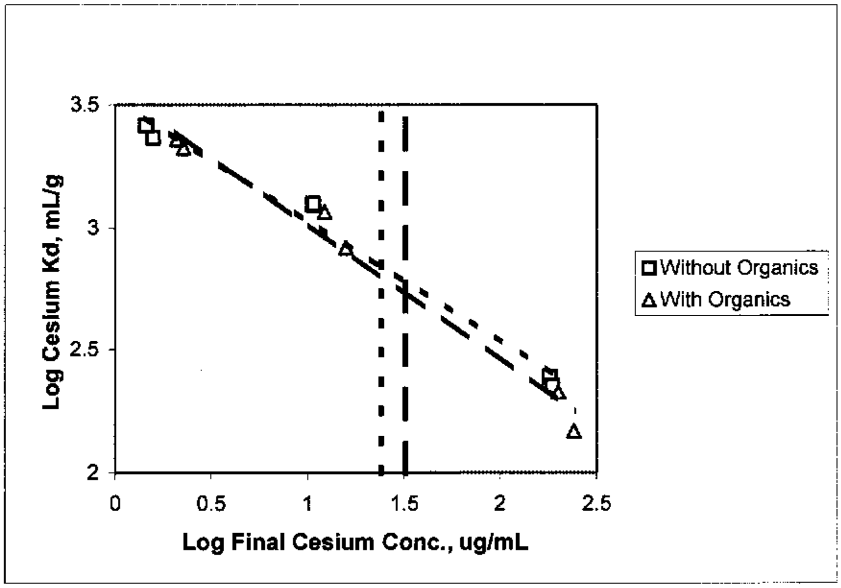

Figure 4.1 Cesium Batch Contacts for AZ-101 Simulant and SuperLig® 644 Resin.

Table 4.7 Rhenium Batch Contact Data for AZ-101 Simulant with no Organics and SuperLig® 639 Resin at 25 °C.

Batch Contact Test	Initial Rhenium Conc., µg/mL	Final Rhenium Conc., µg/mL	Rhenium Sorbed, %	Rhenium Sorbed, µg/g	Rhenium Kd, mL/g	Average Rhenium Kd, mL/g	Percent RSD
Unspiked	36.0	8.0	78	3,062	383	388	1.9
Unspiked duplicate	35.5	7.7	78	3,026	393	-	-
Cs Spike 1	109	25.5	77	9,183	360	365	1.7
Cs Spike 1 duplicate	108	24.7	77	9,114	369	-	-
Cs Spike 2	458	135	71	35,538	263	262	0.7
Cs Spike 2 duplicate	460	136	70	35,464	261	-	-

Phase ratio = 110 mL/g
F-factor = 0.91
Dash denotes not applicable because average of two data points is given.

The final concentrations of the anions (i.e. nitrate, nitrite, sulfate, phosphate, fluoride and chloride) were erratic. Percent removals ranged from –50 to +30 with duplicate runs having percent relative standard deviations of between –250 and +1250. There may be some uptake of the anions by the resin but the high initial concentration of the anions and the phase ratio used make the data unreliable for any sound deductions to be made.

Table 4.8 Rhenium Batch Contact Data for AZ-101 Simulant with Organics* and SuperLig® 639 Resin at 25 °C.

Batch Contact Test	**Initial Rhenium Conc., µg /mL**	**Final Rhenium Conc., µg /mL**	**Rhenium Sorbed, %**	**Rhenium Sorbed, µg/g**	**Rhenium Kd, mL/g**	**Average Rhenium Kd, mL/g**	**Percent RSD**
Unspiked	37.4	8.43	77	3,200	380	364	5.9
Unspiked duplicate	37.8	9.03	76	3,152	349	-	-
Cs Spike 1	113	25.8	77	9,484	368	358	3.9
Cs Spike 1 duplicate	112	26.9	76	9,359	348	-	-
Cs Spike 2	462	133	71	36,248	273	268	2.2
Cs Spike 2 duplicate	456	134	71	35,383	264	-	-

* Simulant with a prior ultrafiltration concentration of 5000 µg/mL which was spiked to 0.7 µg/mL TBP.
Initial TBP concentration = 0.7 µg/mL
Initial NPH (dodecane) concentration = < 0.12 µg/mL
Phase ratio = 111 mL/g
F-factor = 0.91
Dash denotes not applicable because average of two data points is given.

Table 4.9 T-Test on Effect of Organics on Rhenium Batch Contact Kds for AZ-101 Simulant and SuperLig® 639 Resin at 25 °C.

Initial Rhenium Concentration, µg/mL	**Simulant with no Organics**	**Simulant Spiked with Organics (TBP)**	**T-Test Significant Level**
No Organics/With Organics	Kd, mL/g	Kd, mL/g	
36.0/37.4	383	380	0.46
35.5/37.8	393	349	-
109/113	360	368	0.73
108/112	369	348	-
458/462	263	273	0.31
460/456	261	264	-

Dash denotes not applicable because T-Test significant level of two sets of data is given.

As mentioned in the previous section, the TBP concentration in solution for the batch contact experiments in Table 4.8 (with organics) including the controls were below the detection limit of 0.12 μg /mL. This it will be discussed in the next section.

Log–log plots of Kd versus final rhenium concentration for the data in Tables 4.7 and 4.8 with linear regression lines through each set of data points are given in Figure 4.2. Interpolation (vertical line) using the simulant initial rhenium concentration of 37 μg/mL (log value = 1.568) for both simulant with no organics and simulant with organics gives Kd of 323 mL/g. This results in the following λ values (see equation 4.6).

λ_{Re} for simulant with no organics = 171
λ_{Re} for simulant with organics = 171

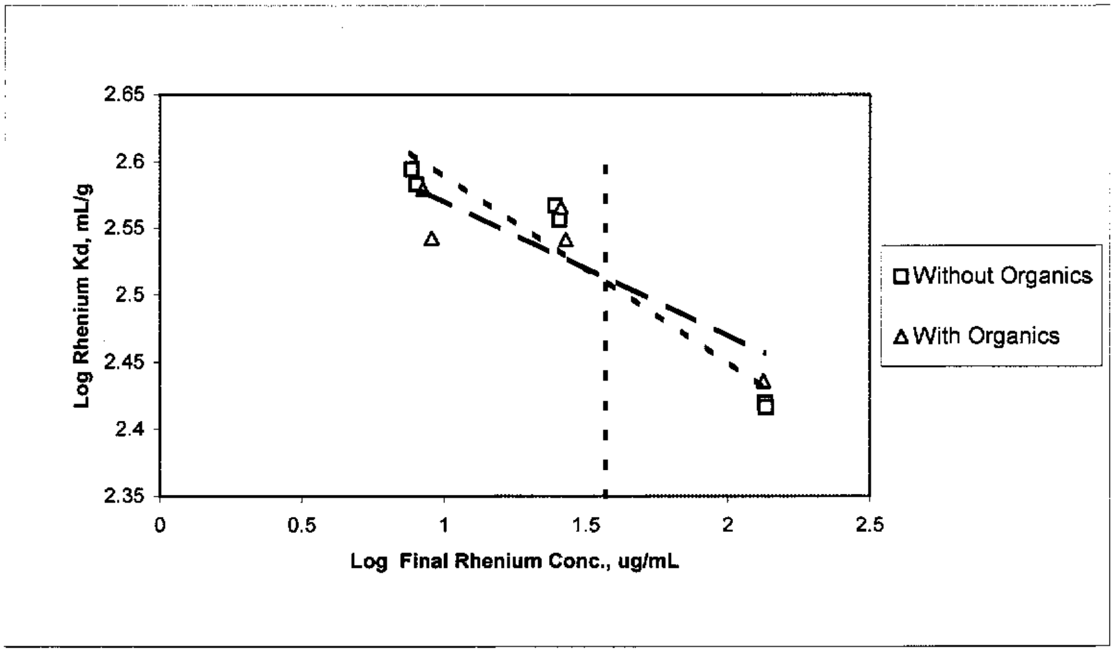

Figure 4.2 Rhenium Batch Contacts for AZ-101 Simulant and SuperLig® 639 Resin.

4.5 Respiked Cesium and Rhenium Batch Contact Tests

Recall in the last two sections it was mentioned that the TBP concentration in solution (including the controls) for simulant spiked with TBP to 0.7 μg/mL in the batch contact experiments for both cesium and rhenium were below the detection limit of 0.12 μg/mL.

It seems the major contributing factor is the decomposition or degradation of TBP. The decomposition of TBP in NaOH solutions is relatively fast. This is based on information on rate constants for TBP decomposition from two sources[7, 8].

1. First order rate constant for TBP decomposition in 1 M NaOH at 30 °C = 0.0055/hr = 0.132/day, giving a half-life of 126 hr = 5.3 days[7].

2. First order rate constant for TBP decomposition in DSS (decontaminated salt solution) at Savannah River Site (SRS) at 30 °C = 0.055/hr = 1.32/day, giving a half-life of 12.6 hr = 0.53 days[8].

Although the degradation half-lives above differ (perhaps due to the effects of the matrix solution), both are on the order of days and clearly indicate relatively fast degradation of TBP. Note that the solubility of TBP in DSS (decontaminated salt solution) at 25 °C is 1.1 μg/mL[8]. The corresponding value in 1 M NaOH is higher (estimated to be about 97 μg/mL) [7]. The DSS (decontaminated salt solution) is roughly similar to Hanford waste.

Based on data from the above two references, the concentration of TBP versus time for a simulant with an initial concentration of 0.7 μg/mL TBP is given below in Table 4.10.

Table 4.10 TBP Decomposition Kinetics at 30 °C.

	1st Reference[7]	**2nd Reference[8]**
Concentration of TBP, μg/mL	**Time, days**	**Time, days**
0.7	0	0
0.35	5.3	0.5
0.175	10.6	1.0
0.12 (detection limit)	13.4	1.3

The 2nd reference (whose solution is similar to Hanford waste) indicates detection limit is reached in 1.3 days or conservatively the 1st reference indicates detection limit is reached in 13.4 days. This explains why all the TBP analyses for the simulants are below detection limit.

For example, the batch contact experiments were started four plus days after spiking the simulant with TBP. Hence, there may have been no TBP present in the simulant at the start of the batch contact experiments. In addition, the batch contact experiments lasted three days, not counting the over three weeks lag time before TBP analysis.

In view of the above, the following was proposed and conducted.

1. The simulant (simulant H) spiked earlier was respiked to 1.0 μg/mL TBP (solubility limit is 1.1 μg/mL). The respiking was done about one hour before the start of any batch contact or column experiment. It was the belief that this will provide a worse-case scenario due to the fact that it will have more decomposition products. Dibutyl phosphate, for instance, is believed to be considerably more resistant to decomposition in caustic solutions than TBP[7].

2. The cesium batch contact experiment using SuperLig® 644 resin was repeated at the highest initial cesium concentration (~ 448 µg/mL).

3. The rhenium batch contact experiment using SuperLig® 639 resin was repeated at the highest initial rhenium concentration (~ 459 µg/mL).

4. TBP analysis in both the batch contact and column experiments was stopped except column loading effluent samples at the 10th BV and the loading effluent composites. This was because TBP was expected to decompose before the conduction of the analysis.

5. To confirm that the TBP analytical method was not flawed, TBP was spiked into simulant and analyzed immediately thereafter.

6. It was not necessary to analyze for the TBP decomposition products (e.g. dibutyl phosphate, butanol, monobutyl phosphate, phosphoric acid, etc.). The ultrafiltration work[1] analyzed for butanol in some of the filtrates. The concentration ranged from 1 to 2 µg/mL. The decomposition of 1.0 µg/mL of TBP would not have resulted in any appreciable concentration difference from the concentration of decomposition products already in the simulant.

Table 4.11 shows batch contact data for simulant "respiked" to 1.0 µg/mL TBP for both SuperLig® 644 and SuperLig® 639. The data are compared with their corresponding "spiked" data (from Tables 4.6 and 4.9) along with T-Test significance levels.

Table 4.11 T-Test on Effect of Respiking AZ-101 Simulant H with TBP and Conducting Batch Contact Tests an Hour Later at 25 °C.

SuperLig® 644 Resin			
Initial Cesium Concentration, µg/mL	**Simulant Spiked with TBP**	**Simulant Respiked with TBP**	**T-Test Significant Level**
Spiked/Respiked	Kd, mL/g	Kd, mL/g	
449/437	213	208	1.0
446/440	148	153	-
SuperLig® 639 Resin			
Initial Rhenium Concentration, µg/mL	**Simulant Spiked with TBP**	**Simulant Respiked with TBP**	**T-Test Significant Level**
Spiked/Respiked	Kd, mL/g	Kd, mL/g	
462/470	273	354	0.13
456/470	264	389	-

The "spiked" and "respiked" Kds for SuperLig® 644 resin are essentially the same. This implies, again, that TBP and its degradation products have no significant effect on cesium removal from AZ-101 simulant.

The "respiked" Kds for SuperLig® 639 resin, on the other hand was higher than the corresponding "spiked" Kds. However, the T-Test significance level value indicates no appreciable difference between the two Kds. Hence, TBP and its degradation products have no significant effect on rhenium removal from AZ-101 simulant.

To confirm that the TBP analytical method was not flawed, simulant was spiked with TBP and analyzed immediately after spiking. The analytical results in Table 4.12 clearly show that the below detection limit values obtained in the batch contact experiments and in the earlier filtrate characterization analyses were due to TBP decomposition and that the analytical method is capable of detecting TBP if it is not degraded.

Table 4.12 Data for TBP Analysis Done Immediately After Spiking.

	Spiked TBP Concentration, µg/mL	**Analytical TBP Concentration, µg/mL**
TBP spike	1.0	1.11
TBP spike duplicate	1.0	1.05

The concentrations of sodium, potassium, and chromium were relatively constant during the "respiked" cesium batch contact runs. Also the final concentrations of the anions (i.e. nitrate, nitrite, sulfate, phosphate, fluoride and chloride) for the "respiked" rhenium batch contact runs exhibited similar behavior that was mentioned in section 4.4.

4.6 Column Tests

4.6.1 Cesium Loading on SuperLig® 644 Resin

Column loading data for cesium are shown in Table4.13. A table is provided instead of breakthrough curves because the C/C_0 values are all close to zero. As of 100 or 85 or 86 BVs (depending on the particular run), no sign of breakthrough was apparent. Runs were terminated for lack of simulant.

Note that the detection limit for all the column runs in Table 4.13 are the same but the initial cesium concentrations are different for runs with and without organics as shown in the footnote of Table 4.13. Hence, the differences in some of the C/Co values (e.g. 0.0008 versus 0.0006). Also the "Lead – With Organics" run seems to have relatively high C/Co values than the other runs. With the exception of two possible outliers, the remaining C/Co values for the "Lead – With Organics" run are less or equal to about five times the detection limit where errors or fluctuations are generally high.

Even though a small breakthrough was attained, the column breakthrough data for simulants with and without organics were essentially the same up to 86 BV. Thus, leading to the conclusion that organics (TBP, dodecane, and their degradation products) do not adversely impact cesium removal from AZ-101 simulant at 25 °C, at least within the first 86 BV. This also passes 75 BV at 50% breakthrough.

The overall or total decontamination factor (DF) for the lead and lag system based on loading effluent composite concentration (<0.02 µg/mL) for simulant with no organics is > 1199 (C_o /C = 24/<0.02). The overall or total DF (C_o /C) for the lead and lag system based on loading effluent composite concentration (<0.02 µg/mL) for simulant with organics concentration is > 1596 (C_o/C = 32/<0.02). The lack of significant breakthrough precludes comparing to any DF targets.

Note that TBP analysis of the loading effluent composite sample and the 10th BV loading effluent sample for the column run with organics were all below detection limit of 0.012 µg/mL. The concentrations of sodium, potassium, and chromium stayed relatively constant after the 5th BV.

Table 4.13 Cesium Column Loading for AZ-101 Simulant using SuperLig® 644 Resin at 25 °C.

Bed Volumes Processed	**Lead – No Organics**	**Lag – No Organics**	**Lead – With Organics**	**Lag – With Organics**
	Cesium C/C_o	**Cesium C/C_o**	**Cesium C/C_o**	**Cesium C/C_o**
5	< 0.0008	< 0.0008	0.0024	< 0.0006
10	< 0.0008	< 0.0008	0.0124	0.0006
20	< 0.0008	n/a	0.0007	< 0.0006
30	< 0.0008	< 0.0008	0.0018	< 0.0006
40	< 0.0008	< 0.0008	0.0029	< 0.0006
50	< 0.0008	< 0.0008	0.0093	< 0.0006
60	< 0.0008	< 0.0008	0.0015	< 0.0006
70	< 0.0008	< 0.0008	< 0.0006	< 0.0006
80	< 0.0008	< 0.0008	< 0.0006	< 0.0006
85	n/a	n/a	n/a	< 0.0006
86	n/a	n/a	< 0.0006	n/a
90	< 0.0008	< 0.0008	n/a	n/a
100	< 0.0008	< 0.0008	n/a	n/a

n/a = not applicable
Cesium C_o for simulant with no organics = 24 µg/mL
Cesium C_o for simulant with organics = 32 µg/mL
Resin BV in simulant with no organics = 13 mL
Resin BV in simulant with organics = 15 mL
Flow rate = 1.5 BV/hr

4.6.2 Cesium Elution From SuperLig® 644 Resin

Lead column elution profiles for runs without and with organics are shown in Figure 4.3 for cesium (see Table A.3 in the Appendix for the data). The two graphs display peaks at approximately 3 BV. The shapes of the profiles are all the same with the exception of the fluctuation at 8 BV. The BV at C/C$_0$ = 0.01 for the two graphs is 10. The presence of organics seems to have no impact on the cesium elution.

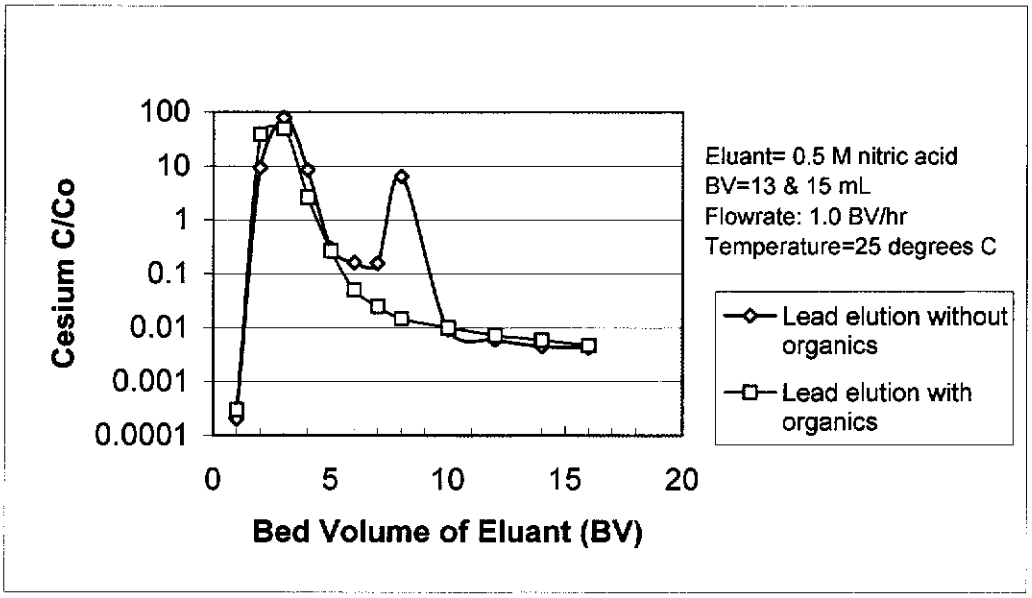

Figure 4.3 Cesium Column Elution Profiles for AZ-101 Simulant and SuperLig® 644 Resin.

The C/C$_0$ values for lag column elution for cesium for runs without and with organics were all below 0.01 as shown in Table 4.14. The only exception is the no organics run at 3BV. The lag columns had little cesium loading. In fact about 99 % of the cesium in the feed was eluted from the lead columns in both the runs without and with organics.

A tabulation of lead and lag eluate composite concentrations for both runs with and without organics is shown in Table 4.15 along with the minimum reportable quantity. The composites are eluates collected between the periodic sample collection times. The major constituents apart from cesium are sodium, potassium, and nitrate. All the specified minimum reportable quantity levels set by the client were met. The high level of nitrate was from nitric acid, the eluant. It is not clear from the TIC/TOC data whether it is the result of resin degradation or from simulant.

Table 4.14 Cesium Lag Column Elution From SuperLig® 644 Resin using 0.5 M Nitric Acid at 25 °C.

Bed Volumes Processed	Lag – No Organics	Lag – With Organics
BV	**Cesium C/C_o**	**Cesium C/C_o**
1	< 0.0002	0.0047
2	0.0002	0.0013
3	0.0230	0.0020
4	0.0050	0.0069
5	0.0006	0.0029
6	0.0002	0.0015
7	< 0.0002	0.0015
8	< 0.0002	0.00013
10	< 0.0002	0.0014
12	< 0.0002	0.0014
14	< 0.0002	0.0014
16	< 0.0002	0.0014

Cesium C_o for simulant with no organics = 24 µg/mL
Cesium C_o for simulant with organics = 32 µg/mL
Resin BV in simulant with no organics = 13 mL
Resin BV in simulant with organics = 15 mL
Flow rate = 1.0 BV/hr

Table 4.15 Compositions of Lead and Lag Column Eluate Composite for SuperLig® 644 Resin.

	Run Without Organics		**Run With Organics**		
Analyte	**Lead Column Eluate, µg/mL**	**Lag Column Eluate, µg/mL**	**Lead Column Eluate, µg/mL**	**Lag Column Eluate, µg/mL**	**Minimum Reportable Quantity[2,3], µg/mL**
Al	7	2.63	7.7	4.0	75
B	5.4	5.40	4.7	4.1	2.3
Ca	1.22	1.06	8.05	1.83	150
Cd	2.0	0.49	2.94	0.22	7.5
Cr	43.0 (DL=0.1)	55.3 (DL=0.1)	36.0 (DL=0.1)	32.2 (DL=0.1)	15
Cs	88.2 (DL=0.02)	0.32 (DL=0.02)	184 (DL=0.02)	0.055 (DL=0.02)	1.5
Fe	3.9	1.63	4.43	0.58	150
K	75 (DL=1)	134 (DL=1)	165 (DL=1)	184 (DL=1)	75
La	< 1.4	< 1.4	< 1.4	< 1.4	35
Mg	< 0.168	< 0.168	0.21	0.18	300
Na	990 (DL=100)	918 (DL=100)	1485 (DL=100)	1075 (DL=100)	75
Ni	0.2	0.33	0.37	< 0.124	30
P	< 1.36	< 1.36	1.88	< 0.136	600
Pb	< 1.38	< 1.38	< 1.8	< 1.8	300
Re	nm	nm	0.25	0.12	Not specified
S	16.3	< 1	21.8	16.4	30
Cl^-	< 20	< 20	12	9	300
F^-	< 20	< 20	< 20	< 20	150
NO_3^-	28,850 (DL=1)	29,050 (DL=1)	26,200 (DL=1)	28,750 (DL=1)	3000
NO_2^-	< 100	< 100	< 100	< 100	3000
$PO4^-$	< 100	< 100	< 100	< 100	2500
$SO4^-$	40	< 50	36	21	2300
Free Acid, M	0.420	0.419	0.366	0.431	10
TIC	12.3	10.8	21.3	7.36	150
TOC	131	26.4	10.6	23.2	1500
TC	143	37.1	32.1	30.6	Not specified
Density, g/mL	1.022	1.022	1.022	1.022	n/a

DL = detection limit
nm = not measured
n/a = not applicable
Each data point is an average of duplicate measurements.
Data with "<" symbols are detection limits.

4.6.3 SuperLig® 644 Resin Bed Volume Changes

The swelling/shrinking behavior of SuperLig® 644 resin as a function of process solution is shown in Table 4.16 for the run without organics. The maximum swelling occurs in 0.1 M NaOH (the feed displacement step), and the minimum shrinking occurs in 0.5 M HNO_3 (the elution step). The resin swells about 75% from the initial packing in DI water to the loading step. From the loading step to the elution step, it shrinks approximately 24%. The run with organics also exhibited similar swelling/shrinking behavior.

Table 4.16 Bed Volume of SuperLig® 644 Resin in Various Column Process Solutions for Run Without Organics.

Process Step	Solution	Lead Column BV, mL	Lag Column BV, mL
Initial packing	DI water	7.3	7.4
Preconditioning	0.25 M NaOH	13.2	13.4
Loading	AZ-101 simulant	12.7	13
Feed displacement	0.1 M NaOH	14.4	14
Rinse	DI water	14.4	14
Elution	0.5 M HNO_3	9.7	9.9
Rinse	DI water	9.6	9.7

4.6.4 Rhenium Loading on SuperLig® 639 Resin

The lead and lag column loading breakthrough curves for rhenium using SuperLig® 639 resin for both simulant with and without organics are shown in Figure 4.4 (see Table A.4 in the Appendix for the data). The lead and lag column loading breakthrough curves for simulant with and without organics are roughly the same especially at low BVs.

The λ values (the number of bed volumes processed at $C/C_o = 0.5$) for simulant without and with organics are 195 and 190 respectively. The corresponding values (171) predicted using batch contact data agree favorably with the breakthrough curve λ values. The column data corroborates the deduction made using the batch contact data that organics (TBP, dodecane, and their degradation products) have no effect on rhenium removal from AZ-101 simulant using SuperLig® 639 resin at 25 °C. Also, the λ values exceed 100 BV at 50% breakthrough.

Note that TBP analyses of the loading effluent composite sample and the 10th BV loading effluent sample for the column run with organics were all below detection limit of 0.012 μg/mL.

The lag column loading profiles for rhenium using SuperLig® 639 resin for both simulant with and without organics are basically flat. At 200 BV, only approximately 1% breakthrough had been attained. Fairly high BVs would be required to get to 50% breakthrough.

The overall or total decontamination factor (DF) for the lead and lag system based on loading effluent composite concentration (< 0.1 and 0.11 μg/mL) for runs without and with organics is > 360 ($C_o/C = 36/< 0.1$) and 345 ($C_o/C = 38/ 0.11$) respectively. The DFs correspond to rhenium removals of at least 99.7 % for both runs without and with organics. The target technetium removal of 98% for envelope B waste is surpassed[9].

The concentration of anions was constant throughout the column runs particularly after the 5th BV.

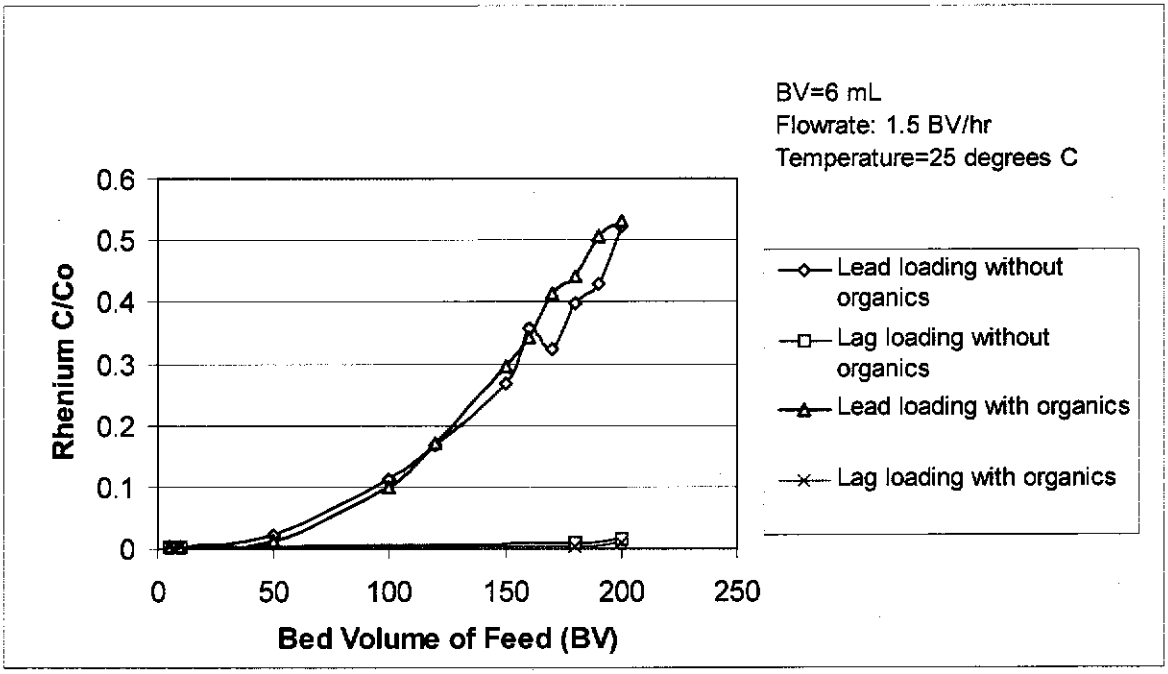

Figure 4.4 Rhenium Column Loading Profiles for AZ-101 Simulant and SuperLig® 639 Resin.

4.6.5 Rhenium Elution From SuperLig® 639 Resin

Elution profiles for rhenium from SuperLig® 639 resin using DI water at 65 °C are shown in Figure 4.5 (see Table A.5 in the Appendix for the data). All the four plots do not display any peaks. The first sample was collected at the 2nd BV, which is the first data point on the graphs. Hence, the peaks are unknown but seem to be less or equal to 2 BV. The shapes of the profiles are all the same. The BVs at $C/C_0 = 0.01$ for the four graphs are as follows.

Lead column elution without organics = ~ 25 BV
Lag column elution without organics = 13 BV
Lead column elution with organics = ~ 20 BV
Lag column elution with organics = 7 BV

The lead column elution BVs at $C/C_0 = 0.01$ are higher than the corresponding lag elution values because the lag columns had less rhenium loading than the lead columns (1% versus 53% breakthrough at 200 BV) and therefore require more BVs to elute.

The elution composite concentration (see Table 4.17) for rhenium are consistent with the above BVs at $C/C_0 = 0.01$. Therefore the observed trend is not due to the presence of organics.

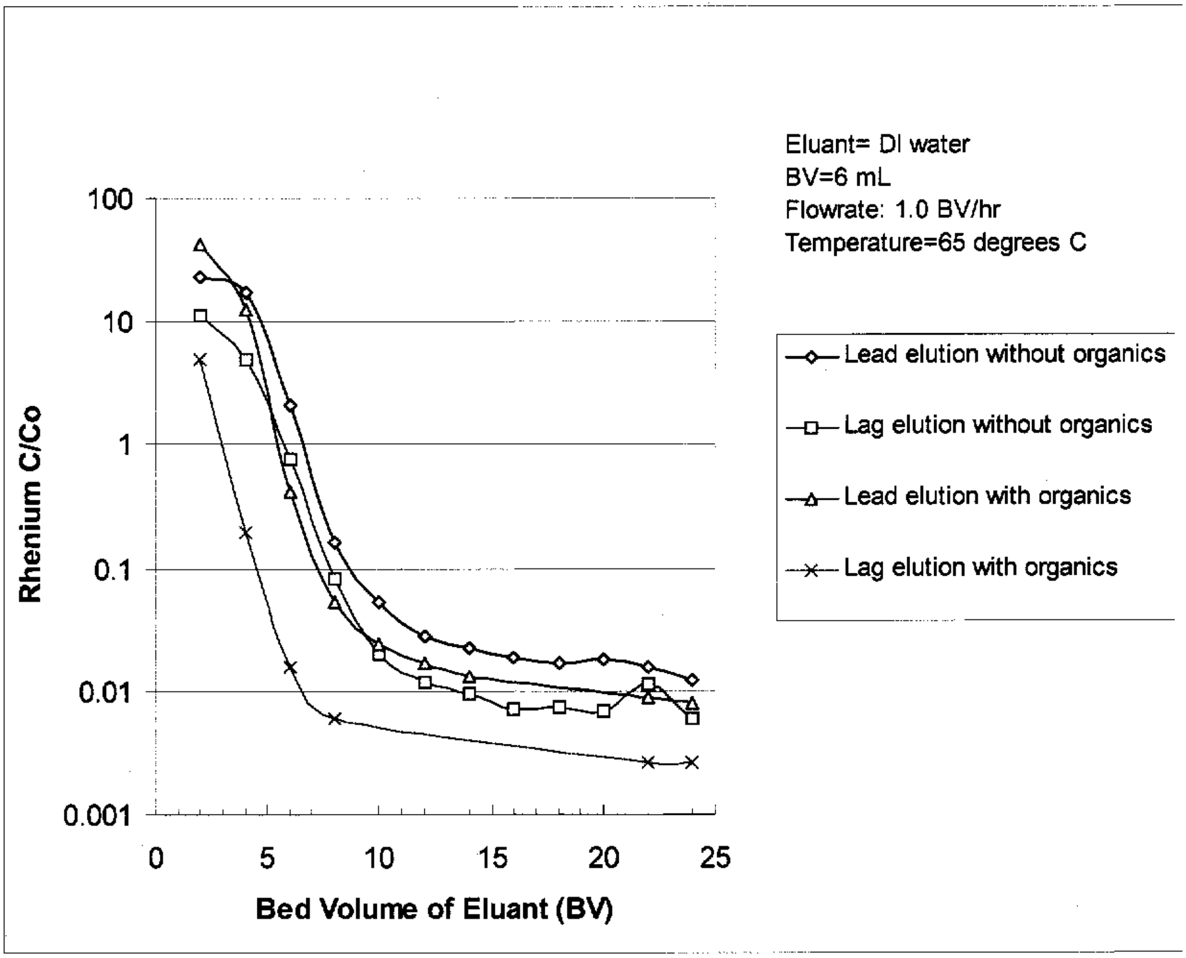

Figure 4.5 Rhenium Column Elution Profiles for AZ-101 Simulant and SuperLig® 639 Resin.

A tabulation of lead and lag eluate composite concentrations for both runs with and without organics is shown in Table 4.17 along with the minimum reportable quantity. The composites are eluates collected between the periodic sample collection times. Aside from rhenium the major constituents are sodium, potassium, nitrate, and nitrite. All the specified minimum reportable quantity levels set by the client were met.

Table 4.17 Compositions of Lead and Lag Column Eluate Composite for SuperLig® 639 Resin.

	Run Without Organics		**Run With Organics**		
Analyte	**Lead Column Eluate, µg/mL**	**Lag Column Eluate, µg/mL**	**Lead Column Eluate, µg/mL**	**Lag Column Eluate, µg/mL**	**Minimum Reportable Quantity[2,3], µg/mL**
Al	18.4	28.8	18.9	11.4	75
Ba	< 0.006	< 0.006	< 0.006	< 0.006	2.3
Ca	0.37	0.40	0.46	0.64	150
Cd	< 0.020	< 0.020	< 0.020	< 0.020	7.5
Cr	3.97	6.90	4.61	5.04	15
Cs	nm	nm	nm	nm	1.5
Fe	< 0.050	< 0.050	0.08	0.030	150
K	104 (DL=0.25)	470 (DL=0.25)	143 (DL=0.25)	363 (DL=0.25)	75
La	< 0.35	< 0.35	< 0.35	< 0.35	35
Mg	< 0.042	< 0.042	< 0.042	0.07	300
Na	1,355 (DL=10)	2,200 (DL=10)	1,440 (DL=10)	1,830 (DL=10)	75
Ni	< 0.031	< 0.031	< 0.031	< 0.031	30
P	6.5	13.2	6.30	3.9	600
Pb	< 0.345	< 0.345	< 0.345	< 0.345	300
Re	389	271	333	61	Not specified
S	54.8 (DL=0.25)	101.0 (DL=0.25)	50.4 (DL=0.25)	30.0 (DL=0.25)	30
Cl^-	14	16	< 20	< 20	300
F^-	< 20	17	< 20	< 20	150
NO_3^-	467	1,890	502	763	3000
NO_2^-	380	869	367	243	3000
$PO4^-$	< 100	< 100	< 100	< 100	2500
$SO4^-$	126	262	122	72	2300
Free OH^-, M	< 0.02	nm	0.017	0.029	1.7
TIC	318	569	nm	nm	1500
TOC	0	16	nm	nm	150
TC	318	585	nm	nm	Not specified
Density, g/mL	1.0	1.0	1.0	1.0	n/a

DL = detection limit
nm = not measured
n/a = not applicable
Each data point is an average of duplicate measurements.
Data with "<" symbols are detection limits.

4.7 Wet Particle Size of Resins

Wet particle size data gathered using the Focused Beam Reflectance Measurement (FBRM) instrument for resins used for the various column runs are shown below in Table 4.18. Also shown are data for the unused as–received resins.

For a given resin, the mean particle size is approximately the same regardless of the type of column run i.e. lead or lag, and without organics or with organics. The mean particle size of the unused as–received SuperLig® 644 resin is smaller than the mean particle size of the used SuperLig® 644 resins. For SuperLig® 639 resin, the mean particle size of the unused as–received resin is larger than the mean particle size of the used counterparts.

These differences for either SuperLig® 644 or SuperLig® 639 are relatively small. It seems the resins did not undergo any marked particle size distribution changes during the column operations, and that the presence of organics did not have any impact as well.

Table 4.18 FBRM Wet Particle Size Data for Used and Unused Resins.

Column Run of the Used Resin	**Mean Particle Size, µm**	
	SuperLig® 644 Resin	**SuperLig® 639 Resin**
Lead/No Organics	400	460
Lag/No Organics	390	440
Lead/With Organics	390	450
Lag/With Organics	400	440
Average	395	448
Percent RSD	1.5	2.1
Unused as-received resin	370	480

4.8 Metals Content of Resins

The metals content analysis of resins used for the various column runs and unused as–received resins is given in Table 4.19. On the whole for a given analyte and resin, the concentration of analyte in resin is more or less the same regardless of the type of column run or state of resin i.e. lead or lag, without organics or with organics, and used or unused resin.

There may be some differences in the concentration of analytes especially comparing the data for unused with used for a given analyte and resin. The unused resin concentrations seem to be lower than those for the used resins, but the high detection limits make it difficult to make any solid deductions. Based on the data in the table, it can be said that the column operations including the presence of organics did not affect the metals content of the resins.

Table 4.19 Metals Content Analysis of Used and Unused Resins.

SuperLig® 644 Resin					
Analyte	**Unused Resin**	**Used Resins for Without Organics Run**		**Used Resins for With Organics Run**	
	µg/g	**Lead, µg/g**	**Lag, µg/g**	**Lead, µg/g**	**Lag, µg/g**
Al	nm	< 150	< 150	< 250	< 250
Cr	nm	1456	353	2165	1285
Fe	nm	66.9	47.7	< 50	< 50
K	133	<300	< 300	< 500	< 500
Na	1230	1485	<600	< 1100	< 1480
SuperLig® 639 Resin					
Analyte	**Unused Resin**	**Used Resins for No Organics Run**		**Used Resins for With Organics Run**	
	µg/g	**Lead, µg/g**	**Lag, µg/g**	**Lead, µg/g**	**Lag, µg/g**
Al	nm	< 150	< 200	< 98	< 90
Cr	nm	29.5	59.3	< 25	< 25
Fe	nm	35.5	76	20.8	20.9
K	< 40	< 300	< 400	< 230	< 230
Na	<75	< 600	< 800	< 500	< 500

nm = not measured
Each data point is an average of duplicate measurements.
Data with "<" symbols are detection limits.

4.9 Quality Assurance

This task was conducted per the requirements of Task Technical & Quality Assurance Plan[2] that was approved by both SRTC and RPP-WTP personnel (Technical and QA personnel). These tests were not HLW form affecting. Therefore, the Quality Assurance Requirements and description (DOE/RW-033P), the principle quality assurance requirements for the Civilian Radioactive Waste Management Program, did not apply to this work. The work was performed to quality assurance requirements NQA-1-1989, and NQA-2a-1990, Part 2.7 All data were recorded in a Laboratory Notebook[10].

The original Technical Specification QA Requirement drivers were to NQA-1-1994, Basic and Supplementary Requirements, and to RW-0333P Revision 8 (if applicable), which was in effect at the time the specification was issued (6/14/01). The task, however, was conducted in accordance with the newer RPP-WTP QA requirements as specified in DOE IWO MOSRLE60, dated 6/2001.

SRTC has provided matrices to WTP demonstrating compliance of the SRTC QA program to the newer requirements as specified by WTP. Specific information regarding the compliance of the SRTC QA program with RW-0333P, Revision 10, NQA-1 1989, Part 1, Basic and

Supplementary Requirements and NQA-2a 1990, Subpart 2.7 is contained in these matrices. The QA requirements specified in the "Task Technical and Quality Assurance Plan for Evaluating the Effects of Tri-Butyl Phosphate (TBP) and Normal Paraffin Hydrocarbon (NPH) in Simulated Low-Activity Waste Solution on Ion Exchange"[2] were to these newer QA requirements. No additional QA requirements were required nor implemented in this work.

5.0 Conclusions

The conclusions of this study are as follows.

The batch contact work revealed there is no statistically significant effect of organics (TBP, dodecane and their degradation products) on cesium and rhenium sorption by SuperLig® 644 and SuperLig® 639 resins respectively from Envelope B AZ-101 simulant solution. The λ values (λ_{Cs} for simulant with no organics = 146, λ_{Cs} for simulant with organics = 133, λ_{Re} for simulant with no organics = 171, and λ_{Re} for simulant with organics = 171) predicted using the batch contact Kds all surpassed 100.

The rhenium column breakthrough curves for simulants with and without organics were virtually identical. Aside from the fact that the λ_{Re} values (λ_{Re} for simulant with no organics = 195, and λ_{Re} for simulant with organics = 190) obtained from the breakthrough curves were almost the same, they were also fairly close to those predicted with the batch contact data. All the above indicate organics have no impact on rhenium removal using SuperLig® 639 resin. The 99.7% rhenium removal obtained for both simulants with and without organics exceeds the 98% target for Envelop B simulants.

Rhenium elution with de-ionized water at 65 °C was adequate overall with no discernible organics effects. The BVs at $C/C_o = 0.01$ for both lead and lag column elution using simulants with and without organics ranged from 7 to 25.

Minimal cesium column breakthrough was attained for both simulants with and without organics due to insufficient simulants. Hence, λ_{Cs} values could not be obtained, let alone compare to the batch contact λ_{Cs} values. Based on 86 BV, the breakthrough data for simulants with and without organics are essentially similar, which is an indication of a no organics effect for cesium.

Cesium elution with 0.5 M HNO_3 at 25 °C from SuperLig® 644 resin was efficient with lead column BVs at $C/C_o = 0.01$ of 10 for both simulants with and without organics. The only caution in the above is that cesium loading was light because of the minimal breakthrough reached. However, the identical BVs indicate cesium elution was not affected by the organics.

All the specified minimum reportable quantity levels were met for both simulants with and without organics.

Metals content analysis and wet particle size measurements of used and unused resins indicated the column operations including the presence of organics had little effect, if any, on the metals content and particle size of the resins.

No column bed fouling was observed in any of the runs for simulants with and without organics.

6.0 References

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Appendix

Table A.1 Comparison of Compositions of Original Simulants with Column Loading Effluent Composites for SuperLig® 644 Resin.

Analyte	No Organics		With Organics	
	Initial Simulant, µg/mL	**Loading Effluent Composite, µg/mL**	**Initial Simulant, µg/mL**	**Loading Effluent Composite, µg/mL**
Al	2150	2165	2630	2680
Ba	< 0.024	< 0.024	< 0.024	< 0.024
Ca	0.14	0.42	0.23	0.82
Cd	0.62	< 0.028	0.51	< 0.028
Cr	473	442	614	607
Cs	24.8	< 0.02	33.6	< 0.02
Fe	1.03	< 0.088	0.87	< 0.088
K	4260	4505	4485	4740
La	< 1	< 1.4	< 1	< 1.4
Mg	< 0.168	< 0.168	< 0.168	< 0.168
Na	105,000	110,500	111,000	114,500
Ni	< 0.124	< 0.124	< 0.124	< 0.124
P	765	808	677	709
Pb	< 1.38	< 1.38	< 1.38	< 1.8
Re	36.3	36.6	39.3	39.0
S	6,805	6,745	6,560	6,620
Cl^-	54	157	62	106
F^-	1,570	1,596	1,595	1,725
NO_3^-	63,800	68,650	68,550	70,150
NO_2^-	57,250	62,200	60,450	61,700
$PO4^-$	2,345	2,210	2020	2,090
$SO4^-$	18,050	18,750	17,300	18,100
OH^-, M	0.134	nm	0.225	nm
TBP	< 0.12	nm	< 0.12	< 0.12
NPH – dodecane	< 0.12	nm	< 0.12	< 0.12
Density, g/mL	1.23	1.23	1.22	1.22

nm = not measured
Each data point is an average of duplicate measurements.
Data with "<" symbols are detection limits.

Different detection limits for La and Pb are given because the analyses were done on different days. La: The La analyses for the "Initial Simulant" with and without organics were done simultaneously with other Hanford simulants that contained significant amount of Sr. Hence, La detection limit was based on two wavelengths instead of three and resulted in a slightly lower quantitation limit. Pb: The Pb concentration is calculated by subtracting the Al interference from the Pb signal. Since the interference is strongly dependent on the magnitude of the Al interference, detection limits for Pb are calculated on a daily basis.

Table A.2 Comparison of Compositions of Original Simulants with Column Loading Effluent Composites for SuperLig® 639 Resin.

Analyte	No Organics		With Organics	
	Initial Simulant, µg/mL	**Loading Effluent Composite, µg/mL**	**Initial Simulant, µg/mL**	**Loading Effluent Composite, µg/mL**
Al	2150	2125	2630	2645
Ba	< 0.024	< 0.024	< 0.024	< 0.024
Ca	0.14	0.9	0.23	2.10
Cd	0.62	< 0.028	0.51	< 0.028
Cr	473	407	614	539
Cs	24.8	nm	33.6	nm
Fe	1.03	< 0.26	0.87	0.10
K	4,260	4,505	4,485	4,370
La	< 1	< 1.4	< 1	< 1.4
Mg	< 0.168	< 0.168	< 0.168	< 0.168
Na	105,000	106,000	111,000	120,500
Ni	< 0.124	< 0.124	< 0.124	< 0.124
P	765	731	677	647
Pb	< 1.38	< 1.38	< 1.38	< 1.38
Re	36.3	< 0.1	39.3	0.11
S	6,805	6,450	6,560	5,940
Cl^-	54	112	62	96
F^-	1,570	1,580	1,595	1,695
NO_3^-	63,800	65,900	68,550	65,900
NO_2^-	57,250	60,250	60,450	58,700
PO4$^-$	2,345	2,137	2020	1,990
SO4$^-$	18,050	17,700	17,300	17,550
Free OH^-, M	0.134	1.133	0.225	1.057
TBP	< 0.12	nm	< 0.12	< 0.12
NPH – dodecane	< 0.12	nm	< 0.12	< 0.12
Density, g/mL	1.23	1.23	1.22	1.22

nm = not measured
Each data point is an average of duplicate measurements.
Data with "<" symbols are detection limits.

Different detection limits for La are given because the analyses were done on different days. The La analyses for the "Initial Simulant" with and without organics were done simultaneously with other Hanford simulants that contained significant amount of Sr. Hence, La detection limit was based on two wavelengths instead of three and resulted in a slightly lower quantitation limit.

Table A.3 Cesium Lead Column Elution From SuperLig® 644 Resin using 0.5 M Nitric Acid at 25 °C.

Bed Volumes Processed	**Lead – No Organics**	**Lead – With Organics**
BV	Cesium C/C_o	Cesium C/C_o
1	< 0.0002	< 0.0003
2	9.1762	38.2146
3	77.5808	48.5513
4	8.4254	2.6155
5	0.2936	0.2650
6	0.1593	0.0501
7	0.1568	0.0247
8	0.3816	0.0147
10	0.0093	0.0101
12	0.0060	0.0073
14	0.0045	0.0059
16	0.0042	0.0047

Cesium C_o for simulant with no organics = 24 µg/mL
Cesium C_o for simulant with organics = 32 µg/mL
Resin BV in simulant with no organics = 13 mL
Resin BV in simulant with organics = 15 mL
Flow rate = 1.0 BV/hr

Table A.4 Rhenium Column Loading for AZ-101 Simulant using SuperLig® 639 Resin at 25 °C.

Bed Volumes Processed	Lead – No Organics	Lag – No Organics	Lead – With Organics	Lag – With Organics
	Rhenium C/C$_o$	Rhenium C/C$_o$	Rhenium C/C$_o$	Rhenium C/C$_o$
5	< 0.0028	< 0.0028	< 0.0028	< 0.0028
10	< 0.0028	< 0.0028	< 0.0028	< 0.0028
50	0.0232	nm	0.0117	nm
100	0.1104	nm	0.0988	nm
120	0.1656	nm	0.1717	nm
150	0.2649	nm	0.2939	nm
160	0.3560	nm	0.3433	nm
170	0.3201	nm	0.4136	nm
180	0.3947	0.0080	0.4421	0.0042
190	0.4250	nm	0.5072	nm
200	0.5189	0.0141	0.5306	0.0101

nm = not measured
Rhenium C$_o$ for simulant with no organics = 36 µg/mL
Rhenium C$_o$ for simulant with organics = 38 µg/mL
Resin BV in simulant with no organics = 6.1mL
Resin BV in simulant with organics = 6.1 mL
Flow rate = 1.5 BV/hr

Table A.5 Rhenium Column Elution From SuperLig® 639 Resin using De-ionized Water at 65 °C.

Bed Volumes Processed	Lead – No Organics	Lag – No Organics	Lead – With Organics	Lag – With Organics
	Rhenium C/C$_o$	Rhenium C/C$_o$	Rhenium C/C$_o$	Rhenium C/C$_o$
2	23.0175	10.9568	42.9129	4.9935
4	17.3321	4.8022	12.3017	0.1925
6	2.0368	0.7672	0.4187	0.0156
8	0.1620	0.0820	0.0528	0.0060
10	0.0524	0.0201	0.0242	nm
12	0.0282	0.0119	0.0172	nm
14	0.0226	0.0097	0.0133	nm
16	0.0190	0.0072	nm	nm
18	0.0171	0.0075	nm	nm
20	0.0182	0.0069	nm	nm
22	0.0155	0.0113	0.0088	0.0026
24	0.0121	0.0061	0.0081	0.0026

nm = not measured
Rhenium C$_o$ for simulant with no organics = 36 µg/mL
Rhenium C$_o$ for simulant with organics = 38 µg/mL
Resin BV in simulant with no organics = 6.1mL
Resin BV in simulant with organics = 6.1 mL
Flow rate = 1.0 BV/hr

Table A.6 AZ-101 Simulant Recipe[1].

Volume of Feed Made from this Recipe: 8 Liters
Weigh a LARGE MIXING VESSEL of at least 8000 ml capacity
ADD THE FOLLOWING COMPOUNDS:

Transition Metals and Complexing Agents	**Formula**	**Mass Needed (g)**	**Actual Wt (g)**
Aluminum Nitrate	Al(NO3)3•9H2O	1186.521	1186.52
Ammonium Nitrate	NH4NO3	11.759	11.76
Cesium Nitrate	CsNO3	0.438	0.438
Zirconyl Nitrate	ZrO(NO3)2•xH2O	0.067	0.067
Sodium Chloride	NaCl	2.631	2.633
Sodium Fluoride	NaF	32.06	32.064
Sodium Chromate	Na2CrO4	18.189	18.1912
Sodium Sulfate	Na2SO4	209.021	209.02
Sodium Perrhenate	NaReO4	0.468	0.4619

ADD	Formula	Mass Needed (g)	Actual Wt (g)
Water	H2O	1600	1600.00

MIX THOROUGHLY TO DISSOLVE THE SALTS. IN A <u>SEPARATE</u> CONTAINER MIX THE FOLLOWING:

	Formula	Mass Needed (g)	Actual Wt (g)
Sodium Hydroxide	NaOH	639.284	639.26
Potassium Hydroxide	KOH	53.085	53.09
Water	H2O	800	800.00

MIX THOROUGHLY TO DISSOLVE THE SODIUM HYDROXIDE AND POTASSIUM HYDROXIDE.

ADD	Formula	Mass Needed (g)	Actual Wt (g)
Sodium Phosphate	Na3PO4•12H2O	48.117	48.12
Water	H2O	1600	1600.00

MIX THOROUGHLY. THEN ADD THIS SOLUTION SLOWLY TO THE MIXING VESSEL WHILE MAINTAINING AGITATION.

ADD	Formula	Mass Needed (g)	Actual Wt (g)
Sodium Carbonate	Na2CO3	326.057	326.06

MIX THOROUGHLY.

ADD	Formula	Mass Needed (g)	Actual Wt (g)
Sodium Nitrate	NaNO3	10.162	10.16
Sodium Nitrite	NaNO2	780.663	780.66

MIX THOROUGHLY.

NEXT ADD THE FINAL WATER ADDITION	Formula	Mass Needed (g)	Actual Wt (g)
Water	H2O	2371.31	2371.30