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

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Abstract: Ultrafiltration and ion exchange are among the pretreatment processes selected for the Waste Treatment Plant at the U.S. Department of Energy's Hanford Site. Envelope B AZ-101 waste may contain tributyl phosphate (TBP) and normal paraffin hydrocarbon (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 TBP and NPH (dodecane) in Simulated Low-Activity Waste Solution on Ultrafiltration and Ion Exchange. The first study dealt with ultrafiltration. 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 the organics may have on these resins' high-sorption capacities for cesium and 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 both batch contact and small-scale column tests.

The batch contact work demonstrated there is no statistically significant effect of organics (TBP, dodecane, and their degradation products) on cesium and rhenium

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sorption by SuperLig® 644 and SuperLig® 639 resins, respectively, from AZ-101 simulant solution. Both the cesium and rhenium column breakthrough/elution profile curves for simulants with and without organics were virtually identical, which is an indication of a no-organics effect.

INTRODUCTION

The River Protection Project-Waste Treatment Plant (RPP-WTP) is to design and build a high-level nuclear waste treatment facility at the U.S. Department of Energy's (DOE) Hanford Site in Richland, Washington. The Waste Treatment Plant (WTP) is to process millions of gallons of radioactive waste stored in tanks at the Hanford Site. The unit operations associated with the high-level nuclear waste treatment include ultrafiltration, precipitation, evaporation, ion exchange, and vitrification. Ion exchange is identified as the preferred treatment process for removal of cesium-137 and technetium-99 from the Hanford waste.

Envelope B AZ-101 waste may contain tri-butyl phosphate (TBP) and normal paraffin hydrocarbon (NPH)–dodecane as dissolved species and also as a separate phase. SuperLig® 644 and SuperLig® 639 resins are effective in removing cesium-137 and technetium-99, respectively, from the Hanford Envelope B waste.

It is not known whether TBP and NPH (dodecane), referred to here as organics, may have any effect on the ability of the SuperLig® 644/639 resins to remove cesium-137/technetium-99 from the waste solution. The objective of this study was therefore to evaluate the effect the above organics may have on the sorption behavior of SuperLig® 644 and SuperLig® 639 resins using AZ-101 filtrates from an earlier ultrafiltration work (1). Batch contact and small-scale column tests were employed in the study.

EXPERIMENTAL

Materials

The SuperLig® 644 and SuperLig® 639 resins were obtained from IBC Advanced Technologies, Inc. (American Fork, UT). SuperLig® 644 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, 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 (2). It was received in neutral form and used as received.

The resins were air dried at room temperature and characterized as follows:

1. The F-factor (solids fraction remaining after water loss through vacuum drying) 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 for ~24 hours in a Napco (Winchester, VA) model 5851 vacuum oven (<40 torr absolute pressure) at 50 ± 2°C to constant mass.
2. Particle-size distribution of the air-dried, as-received resins was obtained using sieves.

The simulant used for this study was Envelope B AZ-101 filtrate from an earlier ultrafiltration work (1). Two types of simulants were used: AZ-101 filtrate with no organics (i.e., TBP or NPH–dodecane) and 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). Note that the AZ-101 filtrate with a prior ultrafiltration concentration of 5000 μg/mL organics was spiked with TBP. The first TBP spike involved adding a weighed amount of TBP to the simulant and shaking periodically for 3 days. The second TBP spike involved adding a weighed amount of TBP to the simulant 1 h 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 5-month lag period between the ultrafiltration and ion exchange studies.

The chemicals used were all reagent grade. Nitric acid (Fisher Chemicals, Pittsburgh, PA) and sodium hydroxide (Fisher Chemicals, Pittsburgh, PA) were used to prepare 0.5 M HNO_3, 0.1 M NaOH, and 0.25 M NaOH solutions. Deionized water was used to prepare the solutions. Deionized 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, OH) and sodium perrhenate (GFS Chemicals, Inc., Columbus, OH) were used to spike some simulant solutions in the batch contact experiments. It involved dissolving a weighed amount in the simulant of interest.

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 a Teflon®-lined screw cap. A Mettler-Toledo (Columbus, OH) analytical balance (model AG285) with an accuracy of ±0.001 g was used to weigh the samples. The bottles were equilibrated in an Incubated Benchtop Shaker (model C24, New Brunswick Scientific Company, Edison, NJ) for 72 ± 1 h at a shaking speed of 275 rpm and temperature of 25 ± 2°C.

At the end of the 72-hour equilibration period, the resin-solution mixtures were separated by filtration. Nalgene (Rochester, NY) 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.

Ion Exchange Column Apparatus

The ion exchange column apparatus consisted of two (designated as lead and lag columns) glass columns, two fraction collectors, a constant-temperature water circulating bath, and several metering pumps. The column apparatus was set up 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, TX) 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, TX) 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, whereas the screens were used as supports for the resins. Temperature regulation in the columns was achieved with a constant-temperature circulating water bath (Model DC10-P5, ThermoHaake, Newington, NH) 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 a Fluid Metering Incorporated (FMI, Syosset, NY) positive displacement pump (model RP-P) equipped with a Scilog Inc. (Middletown, WI) piston pump head (model RH00). The piston pump head (1/8-inch ID) 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 23mL/minute.

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 (1/16-inch ID × 1/8-inch OD) supplied with Teflon quick-disconnect fittings (Cole-Palmer Instrument Company, Vernon Hills, IL) at the ends.

Column Tests

A known mass of air-dried, as-received resin (SuperLig® 644 or SuperLig® 639) was soaked in deionized water using a 10 : 1 liquid : solid volume ratio at room temperature for about 1 hr. This was followed by pouring all the resin slurry into the column while simultaneously tapping the glass column wall 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.

The temperature for all the column operations was 25 ± 1°C except SuperLig® 639 resin elution process step, which was run at 65 ± 2°C. Note that in addition to circulating water at 65°C through the column jackets, heated deionized 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.

Table 1 gives details of the experimental conditions, including when the lead and lag columns were connected in series or ran in parallel. Samples of the column effluent were collected periodically for analysis. The overall error for all the analyses was within ±20%. Note that the effluent from the cesium lag column was the feed for the rhenium lead column.

RESULTS AND DISCUSSION

Resin Characterization

Particle-size distribution, F-factor, and bed density of air-dried, as-received resins are given in Table 2. Both resins had few fines. The bulk of the resins was between 300 and 600 μm (i.e., 94 wt% for SuperLig® 644 and 80 wt % for SuperLig® 639).

Table 1. Experimental conditions for SuperLig® 644/639 resins and AZ-101 simulant with and without organics

Process step	Solution	Bed volumes of solution processed	Flow rate, BV/hr	Time per process step, hr
Lead and Lag Columns in Parallel				
Resin Preconditioning	0.25-M NaOH	12 [12]	3 [3]	4 [4]
Lead and Lag Columns in Series				
Loading	AZ-101 simulant	100 [200]	1.5 [1.5]	66.7 [133.3]
Feed Displacement	0.10-M NaOH	6 [6]	3 [3]	2 [2]
Post-Feed Water Rinse	Deionized water	6 [n/a]	3 [n/a]	2 [n/a]
Lead and Lag Column in Parallel				
Elution of SuperLig® 644	0.5-M HNO_3	20	1	20
Elution of SuperLig® 639	Deionized water at 65 ± 2°C	[25]	[1]	[25]
Post-Elution Water Rinse	Deionized water	6 [n/a]	1 [n/a]	6 [n/a]

Temperature of each process step = 25 ± 1°C unless indicated otherwise.
Bed volume (BV) of column without organics = 13 [6.1] mL (in simulant solution).
Bed volume (BV) of column with organics = 15 [6.1] mL (in simulant solution).
n/a = not applicable.
Note: [ ] applies to SuperLig® 639 resin.

Table 2. Resin characterization data for air-dried, as-received resins

Particle size, μm	SuperLig® 644 Weight%	SuperLig® 639 Weight%
>840	0.00	1.00
600–840	2.11	18.97
425–600	52.93	72.59
300–425	41.47	7.29
212–300	3.29	0.12
62–212	0.20	0.04
	SuperLig® 644	SuperLig®639
F-factor	0.58	0.91
Dry basis bed density in AZ-101 simulant, g/mL	0.21	0.53

Simulant Characterization

As mentioned earlier, the simulants for this work were filtrates from an ultrafiltration study (1). Table 3 gives the composition of the major constituents 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 5-month storage time.

Table 3. Composition of AZ-101 filtrates received from the ultrafiltration study

Constituent	Simulant with no organics	Simulant with organics
	Moles/L	Moles/L
Al	0.080	0.097
Cr	0.009	0.012
K	0.109	0.115
Na	4.57	4.83
F^-	0.083	0.084
NO_3^-	1.03	1.11
NO_2^-	1.24	1.31
PO_4^-	0.025	0.021
SO_4^-	0.188	0.180
Free OH^-	0.134	0.225
	μg/mL	μg/mL
Cs	24.8	33.6
Re	36.3	39.3
TBP	<0.12	<0.12
NPH–dodecane	<0.12	<0.12
	g/mL	g/mL
Density	1.23	1.22

Data with " < " symbols are detection limits.

To evaluate the degradation and adsorption hypotheses, it was decided (1) to spike the simulant with organics 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. This is the first TBP spike mentioned in the experimental section. 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.

Cesium Batch Contact Tests with SuperLig® 644 Resin

The sorption capacity of the resins was evaluated using batch contact approach. This was achieved using the original unspiked simulant and two cesium-spiked simulants giving a total of three different concentrations. Table 4 is a summary of cesium batch contact test data for simulant with and without organics using SuperLig® 644 resin. The batch distribution coefficient, Kd, was determined with the equation below.

$$\mathrm{Kd} = [(\mathrm{C_o} - \mathrm{C_f}) * \mathrm{V}] / [\mathrm{C_f} * \mathrm{m} * \mathrm{F}]$$

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

Even though the initial cesium concentrations for the simulant with and without organics are different, they are reasonably close to allow comparison

Table 4. Cesium batch contact data for AZ-101 simulant with and without organics using SuperLig® 644 resin at 25°C

Initial cesium concentration, μg/mL (No organics/ with organics)	Final cesium concentration, μg/mL (No organics/ with organics)	Simulant with no organics (Kd, mL/g)	Simulant with organics[a] (Kd, mL/g)	T-Test significant level
23.1/30.3	1.58/2.27	$(2.32 \pm 0.32)10^3$	$(2.11 \pm 0.21)10^3$	0.12
23.3/30.4	1.45/2.09	$(2.59 \pm 0.38)10^3$	$(2.23 \pm 0.24)10^3$	–
88.7/95.3	10.6/12.2	$(1.24 \pm 0.03)10^3$	$(1.17 \pm 0.03)10^3$	0.38
89.9/94.8	10.7/15.7	$(1.25 \pm 0.03)10^3$	$(0.83 \pm 0.02)10^3$	–
442/449	181/200	$(2.46 \pm 0.03)10^2$	$(2.13 \pm 0.03)10^2$	0.24
436/446	187/240	$(2.25 \pm 0.03)10^2$	$(1.48 \pm 0.02)10^2$	–

[a] Initial TBP concentration = 0.7 μg/mL. Initial NPH (dodecane) concentration = < 0.12 μg/mL.

Liquid to solid ratio = 171 mL/g.

F-factor = 0.58.

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.

To answer this question, the T-test null hypothesis was done on corresponding Kd data in Table 4 (i.e., simulant without and with organics). The last column in Table 4 gives T-test significant levels of at least 0.12 for all three sets of initial cesium concentrations. Generally, T-test significant levels should be less than 0.05 to indicate significance (3). 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.

A multiple-regression analysis of the combined data set in Table 4 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.

The TBP concentration in the simulant with organics for the batch contact experiments in Table 4, including the controls, was below the detection limit of 0.12 μg/mL. Since the AZ-101 simulant used to generate the data was spiked with TBP to an initial concentration of 0.7 μg/mL, at least the controls should have indicated the presence of TBP. It seems the major contributing factor is the decomposition or degradation of TBP. The decomposition of TBP in NaOH solutions is relatively fast (4, 5). The decomposition of TBP in solutions similar to the current simulant is first order with a half-life of $12.6\,\text{h} = 0.53$ days (5). This implies that the TBP concentration will reduce from 0.7 μg/mL to the detection limit of 0.12 μg/mL in less than 1.5 days. For example, the batch contact experiments were started 4+ 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 3 days, not counting the over 3 weeks lag time before TBP analysis.

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

1. The simulant with organics spiked earlier was respiked to 1.0 μg/mL TBP (solubility limit is 1.1 μg/mL). The respiking was done about 1 h before the start of any batch contact or column experiment. It is 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 (4).

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 tenth bed volume (BV). 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) was 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.

The Kds for SuperLig® 644 resin of the repeated batch contact test (item #2) were essentially the same as the corresponding Kds in Table 4. This implies, again, that TBP and its degradation products have no significant effect on cesium removal from AZ-101 simulant.

Table 5 gives data for simulant that was spiked with TBP and analyzed immediately after spiking. The data 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.

Figure 1 shows log-log plots of Kd vs. final cesium concentration for the data in Table 4 with linear regression lines through each set of data points. Interpolation (vertical lines) using initial cesium concentration of 24 μg/mL for simulant with no organics and 32 μg/mL for simulant with organics, gives Kds of 695 mL/g and 541 mL/g, respectively. The equivalent Kd for simulant with organics based on initial cesium concentration of 24 μg/mL is 634 mL/g. The λ value, which is a prediction of the number of bed

Table 5. 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

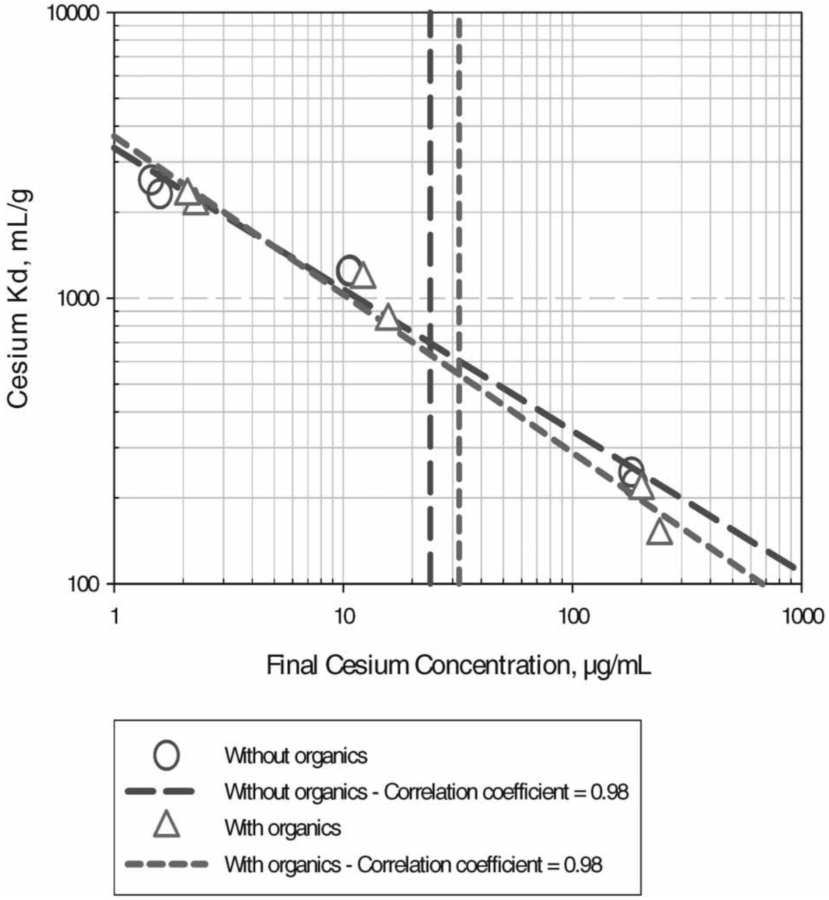

Figure 1. Cesium Kd isotherms for AZ-101 simulant and SuperLig® 644 resin.

volumes required to reach 50% breakthrough in a column operation, is given by $\lambda = \text{Kd}^*$ dry basis resin bed density.

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 the requirement of 75 BV at 50% breakthrough for Envelop B waste (6).

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. Table 6 is a summary of rhenium batch contact

Table 6. Rhenium batch contact data for AZ-101 simulant with and without organics using SuperLig® 639 resin at 25°C

Initial rhenium concentration, μg/mL (No organics/ with organics)	Final rhenium concentration, μg/mL (No organics/ with organics)	Simulant with no organics (Kd, mL/g)	Simulant with organics[a] (Kd, mL/g)	T-Test significant level
36.0/37.4	8.0/8.43	$(3.83 \pm 0.21)10^2$	$(3.80 \pm 0.20)10^2$	0.46
35.5/37.8	7.7/9.03	$(3.93 \pm 0.22)10^2$	$(3.49 \pm 0.17)10^2$	–
109/113	25.5/25.8	$(3.60 \pm 0.08)10^2$	$(3.68 \pm 0.08)10^2$	0.73
108/112	24.7/26.9	$(3.69 \pm 0.09)10^2$	$(3.48 \pm 0.08)10^2$	–
458/462	135/133	$(2.63 \pm 0.04)10^2$	$(2.73 \pm 0.04)10^2$	0.31
460/456	136/134	$(2.61 \pm 0.04)10^2$	$(2.64 \pm 0.04)10^2$	–

[a] Initial TBP concentration = 0.7 μg/mL. Initial NPH (dodecane) concentration= <0.12 μg/mL.

Liquid to solid ratio = 111 mL/g.

F-factor = 0.91.

data for simulants without and with organics using SuperLig® 639 resin. Unlike the cesium batch contact data, the rhenium data do not show any consistent trend of organics affecting Kds; rather, the trend is mixed. The T-test null hypothesis data indicate 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 Table 6 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 and their degradation products 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.

As observed in the previous section, the TBP concentration in the simulant with organics for the batch contact experiments in Table 6, including the controls, were below the detection limit of 0.12 μg/mL. Also, the Kds for SuperLig® 639 resin of the repeated batch contact test (item #3 of the previous section) were essentially the same as the corresponding Kds in Table 6.

Log-log plots of Kd versus final rhenium concentration for the rhenium data with linear regression lines through each set of data points are given in Fig. 2. Interpolation (vertical line) using initial rhenium concentration of 37 μg/mL for both simulant with no organics and simulant with organics gives Kd of 323 mL/g. This results in the following λ values: λ_{Re} for simulant with no organics = 171 and λ_{Re} for simulant with organics = 171.

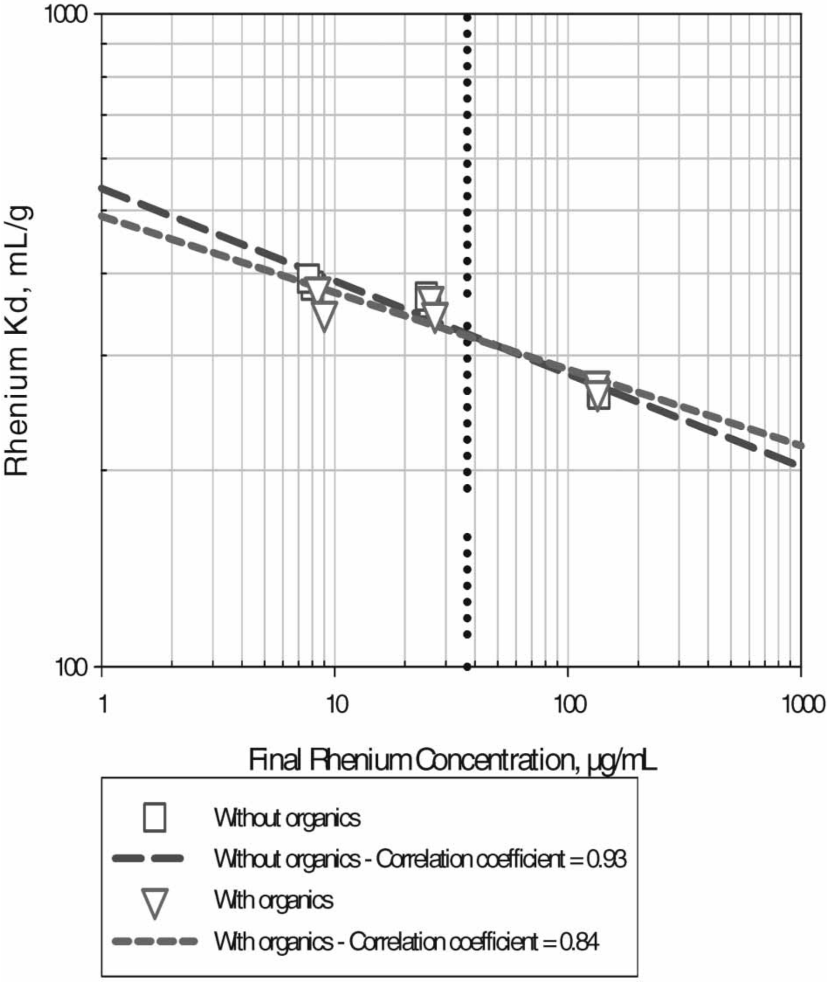

Figure 2. Rhenium Kd isotherms for AZ-101 simulant and SuperLig® 639 resin.

Cesium Loading on SuperLig® 644 Resin

Column loading data for cesium are shown in Table 7. A table is provided instead of breakthrough curves because the relative concentration (C/C_o) values are all close to zero. As of 100 or 85 or 86 bed volumes (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 7 are the same (0.02 μg/mL), but the initial cesium concentrations are different for runs with and without organics as shown in the footnote; hence, the differences

Table 7. Cesium column loading for AZ-101 simulant using SuperLig®644 resin at 25°C

Bed volumes (BV) 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.
Initial cesium concentration (C_o) for simulant with no organics = 24 μg/mL.
Initial cesium concentration (C_o) for simulant with organics = 32 μg/mL.
Resin BV in simulant with no organics = 13 mL.
Resin BV in simulant with organics = 15mL.
Flow rate = 1.5 BV/hour.

in some of the C/C_o values (e.g., 0.0008 vs. 0.0006). Also, the "Lead-With Organics" run seems to have relatively higher C/C_o values than the other runs. With the exception of two possible outliers, the remaining C/C_o values for the "Lead-With Organics" run are less than 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 bed volumes (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 the requirement of 75 BV at 50% breakthrough.

The overall 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 DF 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 tenth BV loading effluent sample for the column run with organics were all below the detection limit of 0.012 μg/mL.

Cesium Elution from SuperLig® 644 Resin

Lead column elution profiles for runs without and with organics are shown in Fig. 3 for cesium. 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 the eighth BV. The BV at $C/C_o = 0.01$ for the two graphs is 10. The presence of organics seems to have no impact on the cesium elution.

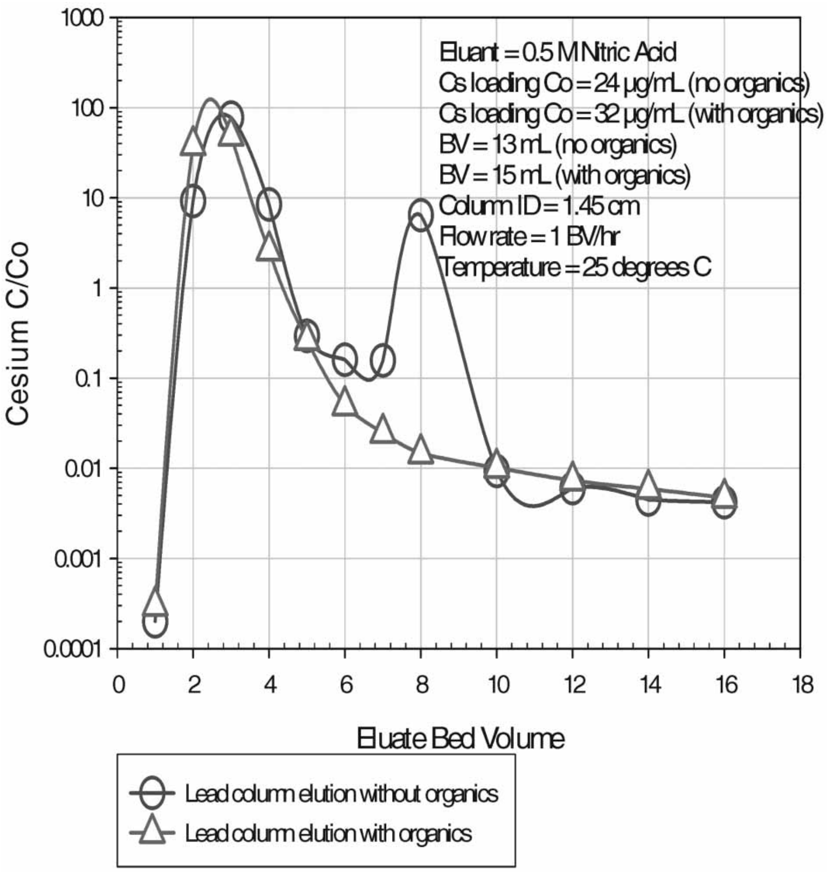

Figure 3. Cesium column elution profiles for AZ-101 simulant and SuperLig® 644 resin.

The C/C_o values for lag column elution for cesium for runs without and with organics were all below 0.01 as shown in Table 8. The only exception is the no-organics run at the third BV. 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.

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 Fig. 4. The corresponding loading breakthrough curves for simulant with and without organics are roughly the same. Remember the effluent from the cesium lag column was the feed for the rhenium lead column.

The λ values (the number of BVs processed at $C/C_o = 0.5$) for simulant without and with organics are 195 and 190, respectively. The λ values (171) predicted using batch contact data agree favorably with the breakthrough curve λ values. The column data corroborates the deduction made using the

Table 8. Cesium lag column elution from SuperLig® 644 resin using 0.5 M nitric acid at 25°C

Bed volumes (BV) processed	Lag—no organics	Lag—with organics
	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

Initial cesium concentration (C_o) for simulant with no organics = 24 μg/mL.

Initial cesium concentration (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.

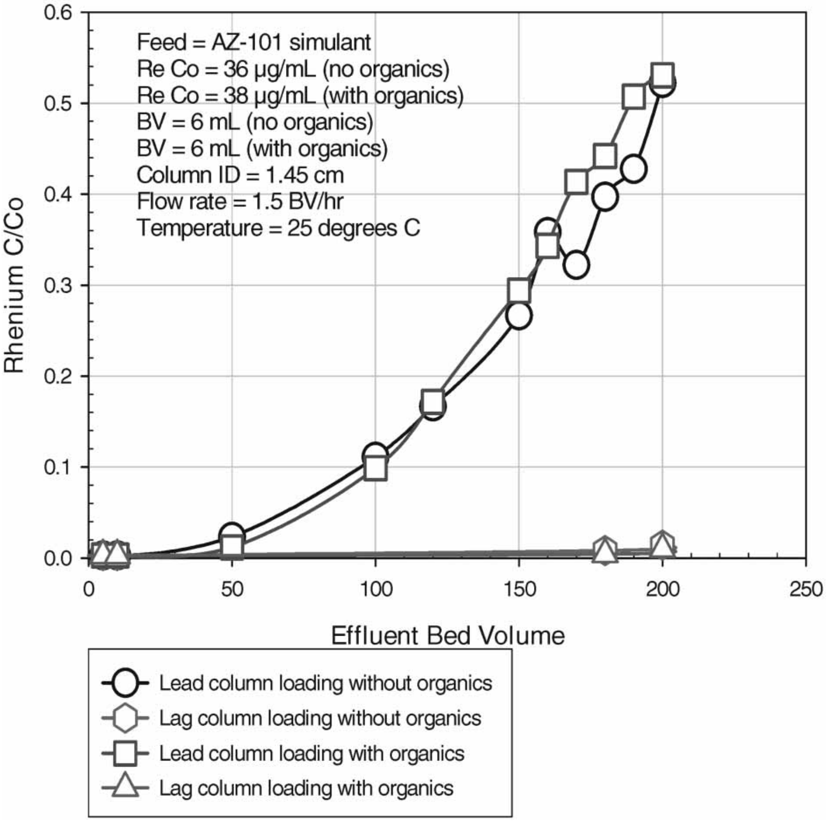

Figure 4. Rhenium column loading profiles for AZ-101 simulant and SuperLig® 639 resin.

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 the requirement of 100 BV at 50% breakthrough (7).

Note that TBP analysis of the tenth 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 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 (8).

Rhenium Elution from SuperLig® 639 Resin

Elution profiles for rhenium from SuperLig® 639 resin using deionized water at 65°C are shown in Fig. 5. All four plots do not display any peaks. The first sample was collected at the second 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.

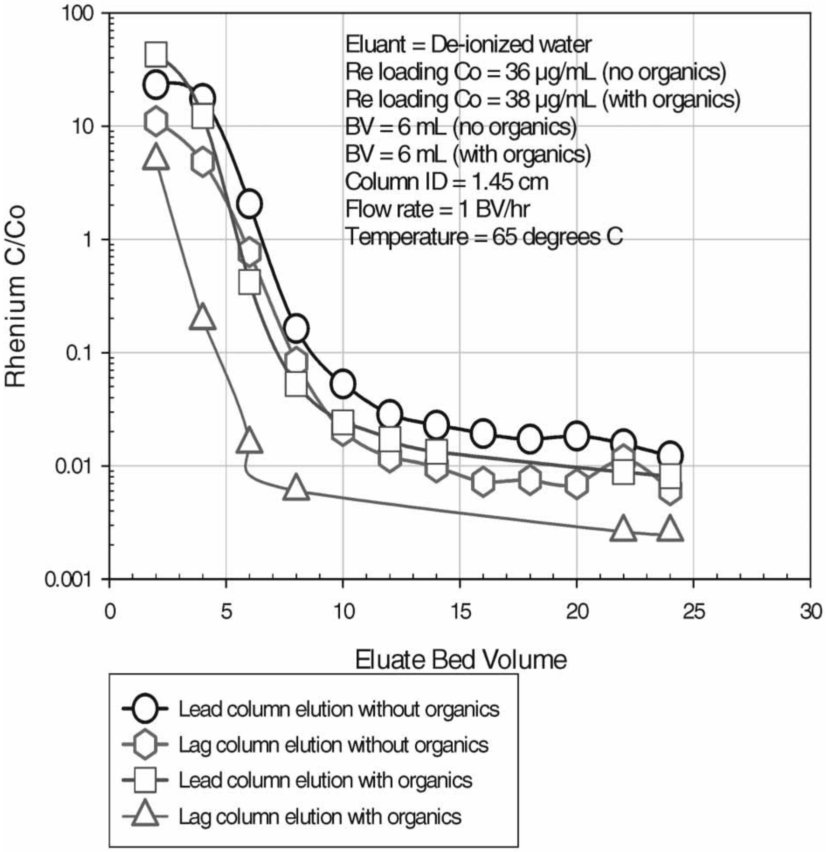

Figure 5. Rhenium column elution profiles for AZ-101 simulant and SuperLig® 639 resin.

The shapes of the profiles are all the same. The BVs at $C/C_o = 0.01$ for the four graphs are as follows:

Lead column elution without organics = $\sim$ 25 BV,

Lag column elution without organics = 13 BV,

Lead column elution with organics = $\sim$ 20 BV,

Lag column elution with organics = 7 BV.

The lead column elution BVs at $C/C_o = 0.01$ are higher than the corresponding lag elution values because the lag columns had less rhenium loading than the lead columns (1% vs. 53% breakthrough at 200 BV) and therefore require more BVs to elute. Therefore, the observed trend is not due to the presence of organics. The curves for the lead column without organics and the lead column with organics are fairly close to each other. The difference between curves for the lag column without organics and the lag column with organics may be due to the relatively small rhenium loadings (1% breakthrough) on the resin prior to elution, rather than the effect of organics.

CONCLUSIONS

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.

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 profiles indicate cesium elution was not affected by the organics.

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 these 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 Envelope B simulants.

Rhenium elution with deionized 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.

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