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Removal of Technetium from Hanford Tank Waste Supernates

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Abstract: SuperLig® 639 ion exchange resin manufactured by IBC Technologies is currently being evaluated for technetium removal from Hanford tank-waste supernates as part of the design for the U.S. Department of Energy/Office of River Protection Project—Waste Treatment Plant. Small-scale testing of the SuperLig® 639 was performed with four Hanford tank-waste supernates using a dual-column configuration, each containing a 5-mL resin bed. Two tank-waste supernates exhibited a high fraction of nonextractable technetium (nonpertechnetate): AN-102/C-104 was 50% nonpertechnetate, and AP-104 was 69% nonpertechnetate. The pertechnetate removal was excellent for all tested supernates, showing an average of 99% removal for supernates that were essentially all pertechnetate and >86% removal for supernates that contained a high fraction of nonpertechnetate. The column elution was effective using 65°C water, resulting in 99% elution on average within 16 bed volumes of eluant.

INTRODUCTION

The U.S. Department of Energy's (DOE's) Hanford Site in southeastern Washington State contains 177 large underground storage tanks with approximately 55 million gallons of radioactive waste. Plans are under-way to separate the waste into high-level and low-activity waste (LAW) streams. The primary unit processes of the Hanford waste-treatment flow sheet for LAW feed are cross-flow filtration, Sr/TRU (transuranic) precipitation, cesium, and technetium ion exchange, evaporation, and vitrification. After solids are removed, the LAW feed will be passed through ion exchange columns to remove cesium and technetium. The decontaminated LAW feed will contain the bulk

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of the waste mass and will be vitrified as a low-activity glass and stored at the Hanford Site. The cesium and technetium eluted from the ion exchange columns will be mixed with tank sludge, vitrified as high-level waste, and eventually stored at a federal repository. The current flow sheet for technetium ion exchange removal includes the use of SuperLig® 639 for removing the pertechnetate form of technetium-99 (^{99}Tc) from the aqueous fraction of the waste (1). The SuperLig® 639 (SL-639) material is an organic resin that has been developed and supplied by IBC Technologies, Inc., American Fork, UT.

The Hanford tank-waste supernate is highly alkaline and consists mostly of dissolved salts and the radionuclides ^{137}Cs, ^{99}Tc, and ^{90}Sr, which, because of their long half-lives and abundance in the supernate, are primarily responsible for the observed radioactivity. SL-639 has been demonstrated to work well in the highly alkaline, high-salt environment of Hanford tank wastes (2–10).

This article presents the laboratory column-testing results from actual waste testing of Hanford tank supernate from Tanks 241-AP-101, 241-AN-102 blended with C-104 solids filtrate, leach, and wash solutions, 241-AP-104, and 241-AZ-101.

EXPERIMENTAL SECTION

Resin

SL-639 (Lot#010227CTC-9-23), a proprietary organic ligand attached to a polystyrene substrate, was obtained from IBC Advanced Technologies (American Fork, UT). SL-639 exchanges pertechnetate via a reversible equilibrium involving the formation of a ligand-$NaTcO_4$ complex. The presence of sodium in the complex results in a neutral compound. The SL-639 resin has a particle density of 1.07 g/mL, and the mean particle range, determined from the sieve data, was 460–670 nm. A small volume of a gamma tracer, ammonium pertechnetate ($NH_4^{95m}TcO_4$ in HCl), was added to monitor the pertechnetate in solution. The ^{95m}Tc provides a strong gamma emission peak at 205 KeV. Sodium hydroxide solutions were prepared by appropriate dilutions from a 50 wt% NaOH reagent solution in deionized (DI) water using volumetric glassware. Nitric acid solutions were prepared by diluting concentrated nitric acid in DI water using volumetric glassware. All chemicals used were of reagent grade.

Column System

The column system consists of two small columns containing the sorbent resin, a small metering pump, three valves, a pressure gauge, and a pressure-relief valve. The pump inlet tube was manually switched between the waste feed and various process solutions.

The columns are Spectra Chrom^{TM} chromatography columns made of glass with adjustable plungers on the bottom and the top. The adjustable plungers at the top of each column were used to minimize the volume of solution above each of the resin beds. The resin beds were gently packed with approximately 1 cm of quartz glass wool to prevent the resin from floating during contact with the feeds. The inside diameter of the columns is 1.5 cm, which corresponds to a volume of 1.77 mL/cm of length. The columns are jacketed with a clear plastic to provide temperature regulation and a safety shield. The columns are connected in series with the first column referred to as the lead column and the second column referred to as the lag column. An Accu® piston pump (SciLog, Middleton, WI) was used to deliver feed to the columns. The volume actually pumped through the system is determined using the effluent mass (including analytical samples) and the fluid density. A pressure-relief valve on the pressure gauge remained below 5 psi during the run. The system apparatus volume was measured to be 20 mL (four bed volumes [BVs]) with approximately 10 mL (2 BVs) volume holdup from the feed line to the lead column. Both the resin-bed height and quartz glass-wool height were carefully monitored throughout the loading and elution process. There was no observed change in the height of either material, indicating that there was very little shrinkage or swelling of the resin. If there was a resin BV change during the run, the change was less than 0.1 mL, or less than 2% of the total BV.

Preparation of the As-Received Feed Solution

Column testing was performed on four Hanford tank-waste supernates: 241-AP-101, 241-AN-102 blended with C-104 solid filtrate, leach and wash solutions, 241-AP-104, and 241-AZ-101. (The prefix "241" is common to all Hanford tanks and will not be used hereafter.) Tanks AP-101 and AP-104 are designated as Envelope A tank-waste feeds, Tank AZ-101 is a high-cesium tank and is designated as an Envelope B tank, and Tank AN-102 supernate is designated as an Envelope C supernate. The Envelope A designation represents the bulk of the double-shell tank waste. Envelope B designates a waste that is a high-cesium waste, and Envelope C designates a waste that contains organic complexants, thus providing a higher concentration of TRUs and other radionuclides.

The AP-101 supernate was received at a sodium concentration of 5.6 M and diluted to 4.8 M Na with 0.10 M NaOH. The feed was filtered and processed for cesium removal before starting this testing. Table 5 shows a selected composition of the as-received AP-104 feed, the processed product, and the eluate. The technetium ion exchange feed had a measured density of 1.257 g/mL.

The AN-102 supernate was received along with associated solids. All samples were homogenized, resulting in a material that contained approximately 2 wt % solids. This as-received AN-102 supernate was blended with C-104 filtrate and C-104 solids leach and wash solutions. This combined feed had a sodium concentration of 3.2 M, so it was evaporated with gentle heating (50°C) under a nitrogen sparge until the sodium concentration reached 5.2 M. Solids did form upon cooling but were identified as mainly sodium nitrate, sodium nitrite, aluminum trihydroxide (gibbsite), sodium oxalate, and zeolites. The blended and evaporated feed was processed for strontium and TRU removal and filtered. After filtration, the feed was processed for cesium removal by ion exchange before technetium processing. Table 6 shows a selected composition of the blended AN-102/C-104 feed, the processed product, and the column eluate. The technetium ion exchange feed had a measured density of 1.240 g/mL.

The AP-104 feed was received at an acceptable sodium concentration; however, the density was slightly too high (1.263 g/mL). The supernate was diluted approximately 13% with 0.01 M NaOH. The resulting solution had a sodium concentration of 4.92 M. The feed was filtered and processed for cesium removal before starting this testing. The cesium was removed in two stages, one using 183 mL supernate and a second using 1710 mL. These two fractions were analyzed separately after ion exchange and then were combined. The combined supernate was not analyzed separately. Table 7 shows a selected composition of the large-volume cesium-decontaminated AP-104 feed, which does not vary significantly from the small-volume cesium-decontaminated supernate. The table also shows the technetium-processed product (effluent) and the column eluate. The technetium ion exchange feed had a measured density of 1.241 g/mL.

The AZ-101 feed was received at a sodium concentration of 4.8 M and used without adjustment of the sodium concentration. The feed was filtered and processed for cesium removal by ion exchange before starting this testing. Table 8 shows a selected composition of the as-received AZ-101 feed, the processed product, and the eluate. The technetium ion exchange feed had a measured density of 1.229 g/mL.

Column Processing

A subsample of the as-received resin was soaked in a 10-fold excess volume of DI water for 2 h; the water was decanted; and the resin was soaked a second time in 1.0 M NaOH for 2 h and then decanted. The resin (in 1.0 M NaOH) was transferred to a 10 mL graduated cylinder and allowed to settle overnight. The resin BV was adjusted to 5.0 ± 0.05 mL, slurried, and quantitatively transferred to the ion exchange column. The settled resin-bed height was 3.1 cm, with a BV of 5.0 mL and a length-to-diameter ratio of 2.1. The ratio of the column diameter to the diameter of the resin was approximately 20–30, which is large enough to avoid wall effects.

The feed solutions were pumped at a flow rate of 3 BV/hour through the resin beds, and the effluent was collected from the bottom of the lag column.

After the available feed was consumed, the feed was displaced from the lead column by processing 3 to 7 BVs of 0.10-M NaOH at 3 BV/hour. The long feed displacement was necessary because of the presence of the quartz glass wool at the top of each resin bed. The lead column only was processed from this point forward. The lead-column resin was rinsed with 3 BVs of DI water at 3 BV/hour. Heated water, 65°C, was cycled through the column jacket for 15 minutes to ensure that the resin bed had equilibrated to 65°C. The appropriate equilibration time had been determined before assembling the column system in the radiological hood. Pertechnetate was eluted from the lead column using DI water at a flow rate of 1 BV/hour. The eluate was collected in 0.5 BV increments for the first 7 BVs to better define the elution peak and then reduced to every 1 BV until the measured eluate ^{95m}Tc sample concentration was 1% of the original feed ^{95m}Tc concentration (1% C/C_0). After completion of elution, the lead-column resin bed was regenerated with 3 BVs of 0.25 M NaOH at 3 BV/hour. At this point, the lead column was placed in the lag-column position, and the noneluted lag column was placed in the lead-column position.

The ratio of sample ^{95m}Tc counts to the original feed counts ($^{95m}TcO_4^-$ C/C_0) was determined in all samples by counting the ^{95m}Tc gamma emission at 205 KeV with a portable gamma spectrometer equipped with a Ge flat-crystal detector. The analytical samples were weighed to within ± 0.0001 g and counted for ^{95m}Tc. The ratio of sample ^{95m}Tc counts to the original feed counts (C/C_0) was determined for all samples. The counting data were normalized to 2.0 mL of solution using the appropriate feed density. In addition, the total technetium (^{99}Tc) levels were determined by ICP-MS in selected samples, encompassing the entire processing scheme after the run was concluded. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used to determine sodium and other elemental concentrations for samples from the feed displacement and regeneration steps. Free hydroxide ion concentrations were determined by titration with standard hydrochloric acid solutions for the feed displacement and regeneration samples. The effluent and eluate composites were also analyzed for total organic and inorganic carbon, for anions by ion chromatography, and for $^{99}TcO_4^-$ by separation and beta scintillation counting.

AP-101 Diluted Feed: Column Loading and Elution

A total of 1100 mL of diluted AP-101 supernate was processed for technetium removal. Figure 1 shows the ^{99}Tc loading curves for the lead and lag columns. The data are presented as the breakthrough of technetium [i.e., the ratio of technetium coming out of the column (C) to what was introduced to the column (C_0)]. After processing 220 BVs of feed (1100 mL), the ^{99}Tc lead and lag column final breakthrough ratios, C/C_0, were approximately 5.2% and 0.5%,

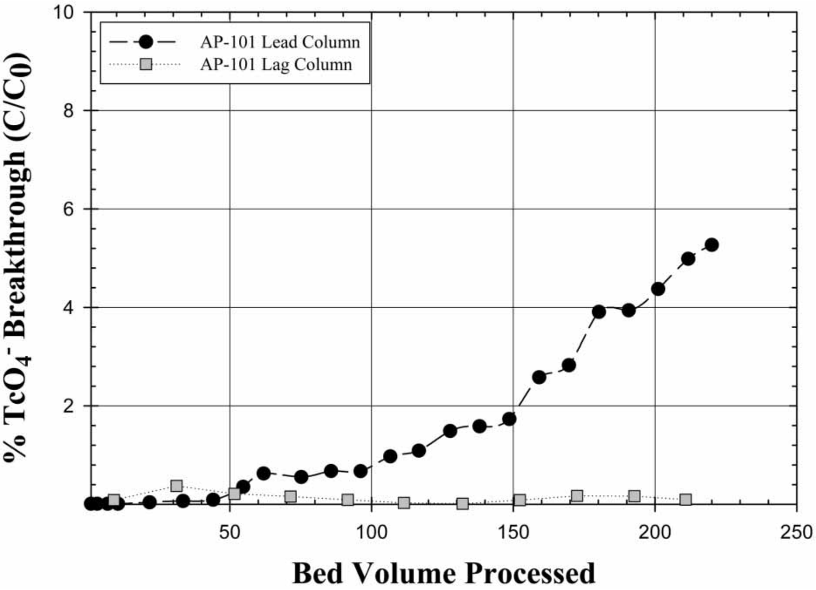

Figure 1. AP-101 technetium loading breakthrough curves, lead and lag columns.

respectively. The effluent ^{99}Tc decontamination factor (DF) was 105, as measured by the concentration of ^{99}Tc present in the initial and processed feed. The ^{99}Tc concentration in the effluent composite was 0.477 μCi/L, and the initial concentration was 50.1 μCi/L, providing an overall ^{99}Tc removal of 99%, which meets the success criteria of $\geq$98% removal of technetium.

Both the lead and lag columns were monitored during loading; however, only the lead column was eluted. Figure 2 shows the elution profile. The peak ^{99}Tc concentration of the eluate was 105 times the ^{99}Tc concentration in the feed and was found in the second BV. After this, the elution proceeded relatively quickly; 17 BVs of eluant were required for the ^{99}Tc concentration to drop below $C/C_0 = 0.01$. The ^{99}Tc concentration of the composited eluate was 454 μCi/L, which correlates to a C/C_0 of 9.0, meaning the eluate was nine times more concentrated in ^{99}Tc than the feed.

Table 1 shows the recovery for ^{99}Tc during the ion exchange processing. A total of 91.9% of the ^{99}Tc can be accounted for in the composite solutions during the column processing.

AN-102/C-104 Blended Feed: Column Loading and Elution

A total of 680 mL of blended AN-102/C-104 feed was processed for technetium removal. Figure 3 shows the ^{99}Tc loading curves for the lead and lag

Table 1. Recovery for technetium during processing of AP-101 using composite solution data[a]

Column processing step	Technetium activity, µCi (mg)		Percent of ^{99}Tc in total feed
Feed	55.4	(3.27)	100
Effluent composite[b]	0.52	(0.030)	0.94
Lead-column eluate	50.4	(2.97)	91.0
Lead-column regeneration	0.0069	(0.0004)	0.01
Total technetium recovered	50.9	(3.00)	91.9

[a] Based upon ^{99}Tc analysis of final solutions.

[b] Effluent composite contains effluent, loading samples, water rinse, and feed-displacement solutions.

columns. After processing 136 BVs of feed (680 mL), the ^{99}Tc lead and lag column final breakthrough ratios, C/C_0, were 46% and 43%, respectively. The initial feed technetium concentration was 50% nonpertechnetate, which would not have been retained by the SL-639 resin. The final effluent DF was 1.8, as measured by the concentration of ^{99}Tc present in the initial and processed feed. The ^{99}Tc concentration in the effluent composite was 44.1 µCi/L, and the initial concentration was 79.5 µCi/L, providing an overall ^{99}Tc removal of 44.5%, which meets the success criteria of $\geq$25%

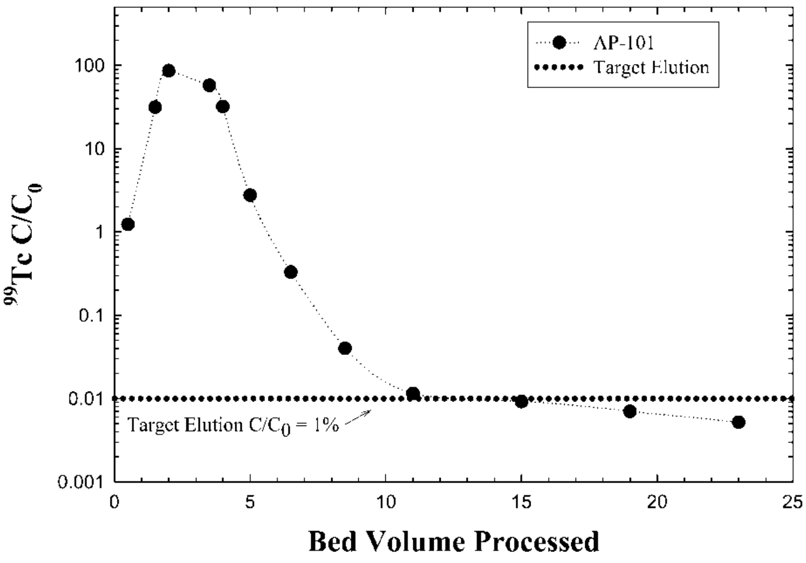

Figure 2. AP-101 elution of technetium from lead column.

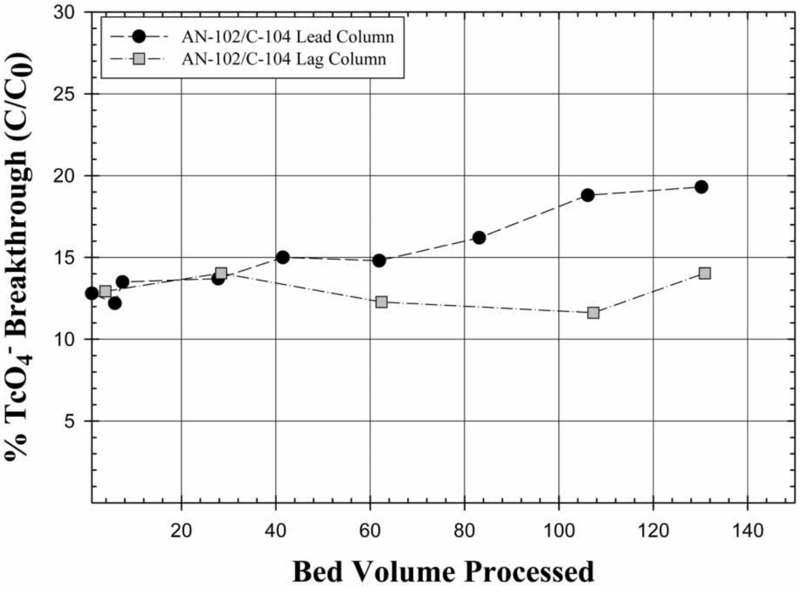

Figure 3. AN-102/C-104 technetium loading breakthrough curves, lead and lag columns.

removal of technetium. The concentration of TcO_4^- in the effluent composite was 5.45 μCi/L, and the initial concentration of TcO_4^- was 39.9 μCi/L. The effluent composite concentration demonstrates a pertechnetate removal of 86%, or an overall TcO_4^- DF of 7.3.

Figure 3 indicates that there was immediate breakthrough of pertechnetate on the lead and lag column (13%). This value was confirmed using two different determinations of pertechnetate; however, it is puzzling. The pertechnetate breakthrough increases only slightly on the lead column (13–19%) and remains essentially steady on the lag column (13–14%). This demonstrates that the lag column is efficiently retaining any pertechnetate that passed through the lead column. Thus, it appears that the high initial breakthrough is actually an elevated baseline, which is caused by an unidentified interferent.

Figure 4 shows the elution profile for the AN-102/C-104 pertechnetate. The peak ^{99}Tc concentration was 48 times the ^{99}Tc concentration in the feed and was found in the second BV. After this, the elution proceeded relatively quickly; 16 BVs of eluant were required for the ^{99}Tc concentration to drop below $C/C_0 = 0.01$. The ^{99}Tc concentration of the composited eluate was 180 μCi/L, which correlates to a C/C_0 of 4.5, meaning that the eluate was four and a half times more concentrated in ^{99}Tc than the feed.

Table 2. Recovery for technetium during processing of AN-102/C-104 using composite solution data[a]

Column processing step	Technetium activity, μCi (mg)		Percent of ^{99}Tc in total feed
Feed	49.7	(2.93)	100
Effluent composite[b]	28.9	(1.70)	58.1
Lead column eluate	19.1	(1.13)	38.4
Lead column regeneration	<0.0011	(<0.00006)	<0.002
Total technetium recovered	48.0	(2.83)	97

[a] Based upon ^{99}Tc analysis of final solutions.

[b] Effluent composite contains effluent, loading samples, DI water rinse, and feed-displacement solutions.

Table 2 shows the recovery for ^{99}Tc during the ion exchange processing. A total of 96.5% of the ^{99}Tc can be accounted for in the composite solutions during the column processing.

AP-104 Diluted Feed: Column Loading and Elution

A total of 1773 mL of diluted AP-104 supernate was processed for technetium removal. Figure 5 shows the ^{99}Tc loading curves for the lead and lag columns.

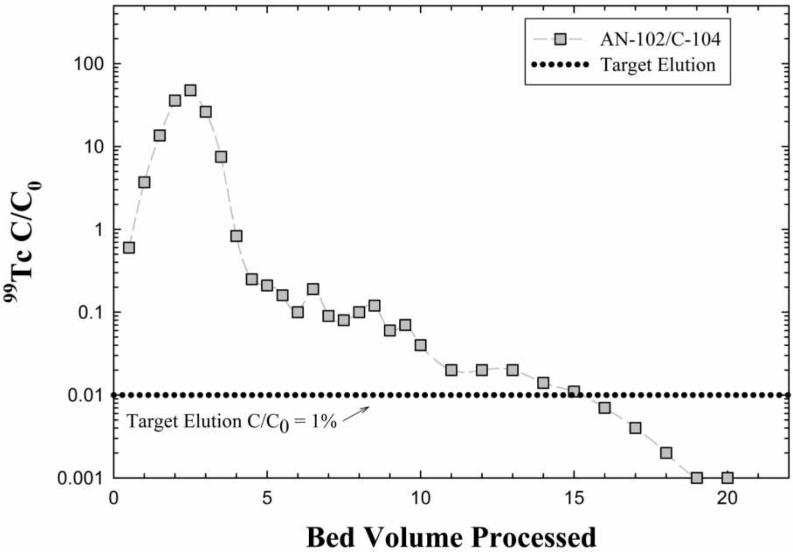

Figure 4. AN-102/C-104 elution of technetium from lead column.

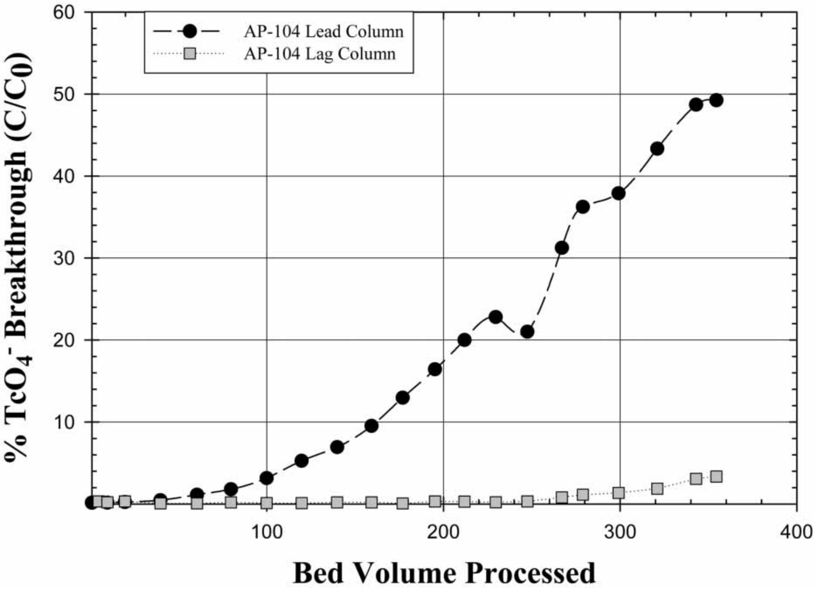

Figure 5. AP-104 technetium loading breakthrough curves, lead and lag columns.

After processing 355 BVs of feed (1773 mL), the ^{99}Tc breakthrough was 88% on the lead column and 73% on the lag column. The initial feed was 31% pertechnetate. The TcO_4^- breakthrough, based upon the $^{95m}TcO_4^-$ counting data, was approximately 49% on the lead column and 3.3% on the lag column. The concentration of ^{99}Tc in the effluent composite was 106 μCi/L, and the concentration of ^{99}Tc in the initial feed was 158 μCi/L. The effluent composite concentration demonstrates a total technetium removal of 32%, providing a final DF of 1.5 for the effluent. The concentration of TcO_4^- in the effluent was 5.85 μCi/L, and the concentration of TcO_4^- in the initial feed was 48.9 μCi/L. The effluent composite concentration demonstrates a pertechnetate removal of 88%. Since this waste feed was designated as an Envelope A feed, the Tc removal goals were to remove $\geq$98% of the total technetium. The 32% removal of ^{99}Tc does not meet the target criteria for removal of $\geq$98% of the total technetium. However, Tank 241-AP-104 waste is identified as complexant concentrate waste (10) and in the presence of complexants, a significant fraction of the technetium present in the waste can be present in the nonpertechnetate form, which cannot be removed using the SL-639 resin. The removal goal of complexant concentrate wastes (normally designated as Envelope C waste feeds) is to remove a total of 25%, or greater, of the total technetium. The technetium processing resulted in the removal of 32% of the total technetium, meeting the success criteria for an Envelope C feed.

Both the lead and lag columns were monitored during loading; however, only the lead column was eluted. Figure 6 shows the elution profile. The peak ^{99}Tc concentration of the eluate was 83 times the ^{99}Tc concentration in the feed and was found in the second BV. There was a hump in the TcO_4^- elution centered at 20 BVs, which is likely due to a closed sampling valve. A total of 23 BVs of eluant was required for the ^{99}Tc concentration to drop below $C/C_0 = 0.01$. The TcO_4^- concentration of the composited eluate was 540 μCi/L, which correlates to a C/C_0 of 11.0 based upon the initial TcO_4^- concentration of 48.9 μCi/L.

Table 3 shows the recovery for ^{99}Tc during the ion exchange processing. A total of 96% of the ^{99}Tc can be accounted for in the composite solutions during the column processing.

AZ-101 Concentrated Feed: Column Loading and Elution

A total of 1590 mL of AZ-101 evaporated feed was processed for technetium removal. Figure 7 shows the ^{99}Tc loading curves for the lead and lag columns. After processing 318 BVs of feed (1590 mL), the ^{99}Tc lead and lag column final breakthroughs were 31% and 0.1%, respectively. The effluent DF was 205, as measured by the concentration of ^{99}Tc present in the initial and processed feed. The ^{99}Tc concentration in the effluent composite was

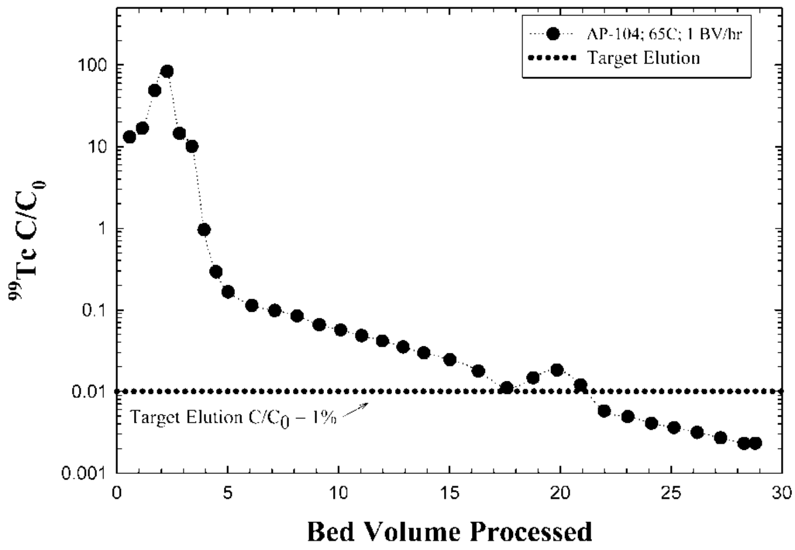

Figure 6. AP-104 elution of technetium from lead column.

Table 3. Recovery for technetium during processing of AP-104 using composite solution data[a]

Column processing step	Technetium activity, μCi (mg)		Percent of ^{99}Tc in feed
Feed	279.2	(16.45)	100
Effluent composite[b]	177.7	(10.47)	79.8
Lead column eluate	90.9	(5.36)	40.8
Total technetium recovered	268.6	(15.83)	96.2

[a] Based upon ^{99}Tc analysis of final solutions, except where noted.

[b] Effluent composite contains collected effluent, loading samples, feed displacement, and resin rinse samples.

1.83 μCi/L, providing an overall ^{99}Tc removal of 99.5%, which exceeds the design criteria of ≥98% removal of technetium.

Figure 8 shows the elution profile of the AZ-101 pertechnetate. The peak ^{99}Tc concentration of the eluate was 81 times the ^{99}Tc concentration in the feed and was found in the second BV. The elution dropped slightly after this and then leveled out until the eighth BV. At this point, the ^{99}Tc concentration dropped quickly: 17 BVs of eluant were required for the ^{99}Tc concentration to drop below $C/C_0 = 0.01$. The ^{99}Tc concentration of the

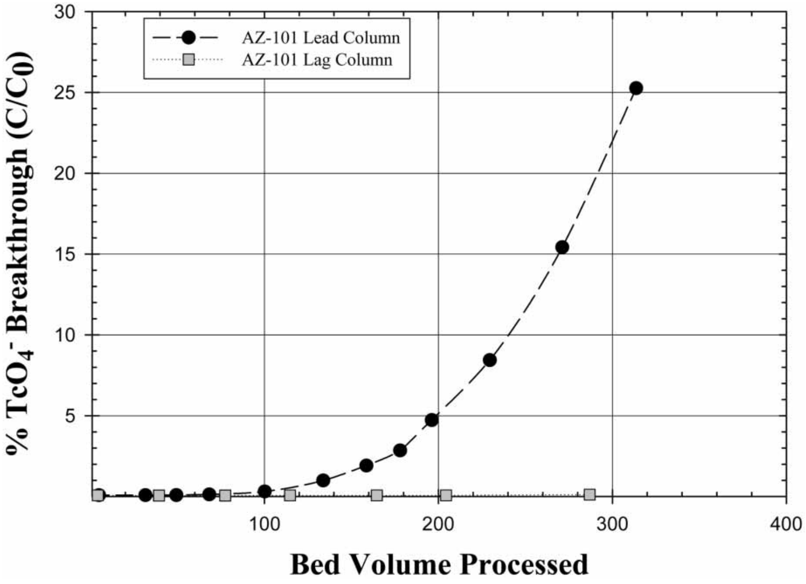

Figure 7. AZ-101 technetium loading breakthrough curves, lead and lag columns.

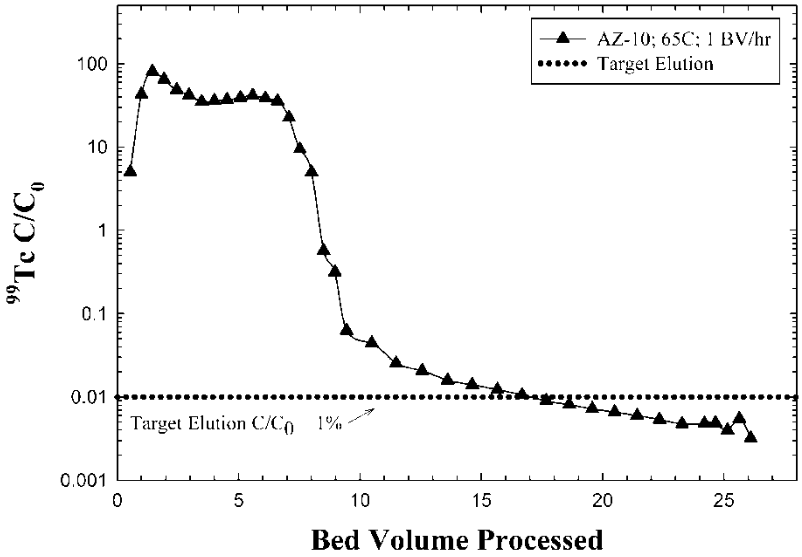

Figure 8. AZ-101 elution of technetium from lead column.

composited eluate was 4578 μCi/L, which correlates to a C/C_0 of 12.2, meaning the eluate was 12 times more concentrated in ^{99}Tc than the feed.

Table 4 shows the recovery for ^{99}Tc during the ion exchange processing. A total of 98.6% of the ^{99}Tc can be accounted for in the composite solutions during the column processing.

Table 4. Recovery for technetium during processing of AZ-101 using composite solution data[a]

Column processing step	Technetium activity, μCi	(mg)	Percent of ^{99}Tc in feed
Feed	596.6	(35.2)	100
Effluent composite[b]	2.92	(0.17)	0.5
Lead column feed displacement[c]	0.74	(0.043)	0.1
Lead column rinse[d]	2.25	(0.13)	0.4
Lead column eluate	582.6	(34.3)	97.7
Lead column regeneration[d]	0.025	(0.0015)	0.004
Total technetium recovered	588.5	(34.68)	98.6

[a] Based upon ^{99}Tc analysis of final solutions, except where noted.

[b] Effluent composite contains collected effluent and loading samples.

[c] Value (0.74 μCi) is based upon analysis of one-half the collected samples, and interpolation of the remaining one-half.

[d] Rinse and regeneration sample values both are a sum of the analysis of two solutions.

RESULTS

AP-101 Results: Supernate and Product-Solution Composition

AP-101 tank supernate was diluted to provide an ion exchange feed that was approximately 5-M sodium. The diluted AP-101 supernate was processed for cesium removal before technetium processing. The main components of the AP-101 column feed, column effluent, and column eluate are shown in Table 5. The total anion normality is 5.90 N, and the cation normality is 5.56 N. This difference is within 6% and is well within the analytical uncertainty (10%).

The column-effluent composite consists of the processed AP-101 feed combined with small volumes of the feed-displacement solution (0.25 M NaOH) and the water rinse of the resin. The inclusion of these two process solutions resulted in an effluent that was diluted approximately 5% from the original feed. Thus, only concentration changes beyond 5% are considered meaningful. The potassium (11%), chromium (7%), and nitrate (18%) showed a meaningful concentration change during processing, indicating that these components are likely retained by the SL-639 resin. SL-639 does

Table 5. Main composition of diluted AP-101 ion exchange feed and products

Analyte	AP-101 feed[a]	AP-101 effluent	AP-101 eluate
^{99}Tc, μCi/L	50.1	0.48	454 (2.7E − 04 M)
TcO_4^-, μCi/L	42	0.32	—
Na^+	4.81E + 00	4.85 E + 00	1.54E − 02
K^+	7.5E − 01	6.6 E − 01	<1.3E − 03
AlO_2^{-b}	2.5E − 01	2.3E − 01	5.19E − 04
Cl^-	4.1E − 02	3.9E − 02	6.21E − 05
CO_3^{-2c}	4.9E − 01	4.4E − 01	2.7E − 03
CrO_4^{-2b}	2.7E − 03	2.5E − 03	2.69E − 03
NO_2^-	7.8E − 01	7.4E − 01	6.74E − 04
NO_3^-	1.88E + 00	1.55E + 00	1.65E − 03
$OH^{-(c)}$	1.9E + 00	1.9E + 00	4.6E − 03
PO_4^{-3}	7.3E − 03	9.3E − 03	<1.5E − 05
SO_4^{-2}	3.2E − 02	3.1E − 02	5.31E − 05
Oxalate	2.4E − 01	1.1E − 02	1.59E − 05
Uranium	3.9E − 06	4.6E − 06	6.79E − 3

[a] The AP-101 supernate was diluted to provide an ion exchange feed that was approximately 5 M Na.

[b] Elemental Al and Cr were determined by ICP-AES. The anionic forms, AlO_2^- and CrO_4^{-2}, are assumed on the basis of waste chemistry.

[c] Hydroxide and carbonate were determined by titration. Hydroxide was assigned as the first equivalence point, and carbonate was assigned as the second equivalence point.

not act as a typical ion exchanger; rather, it is believed that the pertechnetate ion is extracted as a sodium or potassium ion pair. Thus, nitrate, which is present in the Hanford tank supernates in much higher concentrations than technetium, is believed to be a major competitor for adsorption sites. Hence, the concentration change in potassium and nitrate is not unexpected. The effluent results indicate that chromate may also be slightly retained by SL-639.

The eluate analysis indicates that the eluate is composed of sodium (0.015 M) and various anions: nitrate, chromate, aluminate, hydroxide, and carbonate. The charge balance is reasonable, the cations are 0.015 M, and anions are 0.018 M. Technetium, which is present at 2.5E-05 M, does not contribute significantly to the charge balance. There were slight amounts of radionuclides also present in the eluate composite, ^{241}Am was present at 7.22E-04 μCi/L, and ^{90}Sr was present at 1.26E-01 μCi/L, indicating that it may be possible that a slight amount of feed was present in the first elution samples. This may also explain why aluminum and chromium were present in the eluate.

AN-102/C-104 Blended Feed Results: Supernate and Product-Solution Composition

The AN-102/C-104 blended and evaporated supernate feed was first processed for Sr and TRU isotope removal by treatment with potassium permanganate and strontium nitrate (11). The supernate was filtered to remove the resulting precipitate ($SrCO_3$) and then processed for cesium removal using SuperLig®644 (12). The cesium-decontaminated product was processed for technetium removal. The main components of the AN-102/C-104 feed, the column effluent and the column eluate, are shown in Table 6. The total anion normality, 5.23 N, is larger than the cation normality, 4.82 N. This difference is within 9% and is within the analytical uncertainty (10%).

There were some significant concentration changes in the effluent components, but surprisingly, only the inorganic anions—chloride (8%), fluoride (8%), nitrate (8%), nitrite (8%), sulfate (12%), phosphate (20%), carbonate (14%), and uranium (16%)—were affected. The eluate is composed of sodium (0.012 M), potassium (0.001 M), and various anions: chloride, fluoride, nitrate, nitrite, sulfate, and carbonate. The charge balance is good; the cations are 0.014 N, and the anions are 0.014 N. Technetium, which is present at 2.1E-05 M, does not contribute significantly to the charge balance. There was a slight amount of ^{90}Sr present in the eluate, 1.08 μCi/L, indicating that it may be possible that strontium is being selectively adsorbed and released by SL-639. It is also noteworthy that uranium was not present in the eluate composite in significant quantities. Although it appears that uranium was removed from the AN-102/C-104 feed

Table 6. Main composition of blended AN-102/C-104 ion exchange feed and products

Analyte	AN-102/C-104 Blended feed[a]	AN-102/C-104 effluent	AN-102/C-104 eluate
^{99}Tc, μCi/L	79.5	44.1 (6.5E − 05)	180
TcO_4^-, μCi/L	39.9	5.45	—
Na^+	4.78E + 00	4.74E + 00	1.22E − 02
K^+	2.8E − 02	2.7E − 02	<1.3E − 03
Ca^{+2}	3.7E − 03	3.6E − 03	<1.5E − 04
AlO_2^{-b}	2.9E − 01	2.9E − 01	[3.6E − 04]
Cl^-	5.1E − 02	4.6E − 02	8.5E − 05
F^-	3.3E − 01	3.05E − 01	5.8E − 04
CO_3^{-2c}	7.6E − 01	6.5E − 01	9.2E − 03
CrO_4^{-2b}	1.9E − 03	1.9E − 03	<9.6E − 06
NO_2^-	9.0E − 01	8.3E − 01	1.1E − 03
NO_3^-	1.73E + 00	1.58E + 00	2.1E − 03
OH^{-c}	1.8E − 01	2.1E − 01	<1.0E − 02
PO_4^{-3}	2.3E − 02	1.8E − 02	<2.6E − 6
SO_4^{-2}	7.0E − 02	6.2E − 02	9.4E − 05
Oxalate	1.6E − 02	1.5E − 02	2.3E − 05
Uranium	3.5E − 06	2.9E − 06	7.5E − 09

[a] The AN-102 supernate was blended with C-104 filtrate, leach, and wash solutions and evaporated to give a solution which was ~5 M Na.

[b] Elemental Al and Cr were determined by ICP-AES. The anionic forms, AlO_2^- and CrO_4^{-2}, are assumed on the basis of waste chemistry.

[c] Hydroxide and carbonate were determined by titration. Hydroxide was assigned as the first equivalence point, and carbonate was assigned as the second equivalence point.

(6.0E-07 M), uranium is not present in the eluate in nearly that quantity (7.5E-09 M). It is unlikely that U was retained by the SL-639 resin. Kurath and Wagner (13) analyzed SL-639 resin, which had processed actual tank water material, and showed that U was not retained on the SL-639 resin.

AP-104 Results: Supernate and Product-Solution Composition

AP-104 tank supernate was diluted slightly to provide an ion exchange feed that had a density within the range 1.21 to 1.25 g/mL. This resulted in a solution that was 4.92 M sodium. The diluted AP-104 supernate was processed for cesium removal before technetium processing. The main components of the AP-104 column feed, column effluent, and column eluate are shown in Table 7. The total anion normality is 4.82 N, and the

Table 7. Main composition of diluted AP-104 ion exchange feed and products

Analyte	AP-104 feed[a]	AP-104 effluent	AP-104 eluate
^{99}Tc, μCi/L	158	106	416
TcO_4^-, μCi/L	49	5.85	540
Na^+	4.78E + 00	5.05E + 00	1.2E − 02
K^+	4.39E − 02	4.32E − 02	<1.3E − 03
AlO_2^{-b}	3.91E − 01	3.87E − 01	[1.85E − 04]
Cl^-	1.37E − 01	1.26E − 01	1.4E − 04
F^-	9.58E − 02	9.11E − 02	[1.7E − 04]
CO_3^{-2c}		2.57E − 01	4.0E − 03
CrO_4^{-2b}	7.70E − 03	7.64E − 03	<9.6E − 06
NO_2^-	1.23E + 00	1.21E + 00	6.5E − 04
NO_3^-	1.51E + 00	1.49E + 00	9.9E − 04
OH^{-d}	1.13E + 00	1.18E + 00	5.0E − 03
PO_4^{-3}	4.16E − 02	3.83E − 02	1.4E − 05
SO_4^{-2}	2.59E − 02	2.44E − 02	7.4E − 05
Oxalate	1.19E − 02	7.07E − 03	6.8E − 06
Uranium	5.08E − 7	7.98E − 07	4.1E − 09

[a] The AP-104 supernate was diluted to provide an ion exchange feed that had a density <1.25 g/mL.

[b] Elemental Al and Cr were determined by ICP-AES. The anionic forms, AlO_2^- and CrO_4^{-2}, are assumed on the basis of waste chemistry.

[c] Carbonate determined from total inorganic carbonate, reported as CO_3^{-2}; thus, the value may be biased high.

[d] Hydroxide was determined by titration.

cation normality is 4.70 N. This difference is within 3% and is well within the analytical uncertainty (10%).

The AP-104 effluent composition was as expected. It is not possible to rigorously compare the effluent composition with the technetium ion exchange feed composition because the actual technetium feed was not analyzed. The technetium feed was a combination of two cesium-decontaminated supernate fractions of which only the large-volume cesium-decontaminated product was analyzed. The feed composition shown in Table 5 is not expected to have been significantly altered as a result of combining the smaller cesium-decontamination fraction. Nonetheless, it is not clear if the observed compositional changes can be considered significant. The changes are reported for informational purposes only. Changes in sodium (6%), chloride (8%), fluoride (5%), phosphate (8%), sulfate (6%), oxalate (41%), and uranium (57%) were observed.

The eluate analysis indicates that the eluate is composed of sodium (0.012 M), potassium (0.001 M), and various anions: nitrate, nitrite, hydroxide, and carbonate. The charge balance is reasonable, the cations are

0.013 N, and the anions are 0.015 N. Technetium, which is present at 2.5E-04 M, does not contribute significantly to the charge balance. There were slight amounts of radionuclides also present in the eluate composite, ^{241}Am was present at $1.49\text{E} - 03\,\mu\text{Ci/L}$, ^{90}Sr was present at $1.91\text{E} + 00\,\mu\text{Ci/L}$, and ^{151}Sm was present at $4.50\text{E} - 02\,\mu\text{Ci/L}$. Americium-241 and strontium-90 were observed in the other eluates as well, but there was no analysis for ^{151}Sm in the other eluates.

AZ-101 Results: Supernate and Product-Solution Composition

The AZ-101 tank supernate was diluted to provide an ion exchange feed that was approximately 5 M sodium. The concentrated AZ-101 supernate was processed for cesium removal with SL-644 before technetium processing. The cesium-decontaminated product was processed for technetium removal. The main components of the AZ-101 feed, the column effluent, and the column eluate are shown in Table 8. The effluent composition was essentially unchanged during processing. The apparent concentration increase during

Table 8. Main composition of AZ-101 ion exchange feed and products

Analyte	AZ-101 feed[a]	AZ-101 effluent	AZ-101 eluate
^{99}Tc, μCi/L	375	1.6	4000
TcO_4^-, μCi/L	378	0.93	—
Na^+	4.26E + 00	4.31E + 00	9.5E − 03
K^+	9.3E − 01	9.7E − 01	1.1E − 03
AlO_2^{-b}	1.9E − 01	2.0E − 01	<4.4E − 05
Cl^-	5.6E − 03	<3.7E − 03	1.6E − 05
F^-	4.9E − 01	1.0E − 01	1.0E − 04
CO_3^{-2c}	1.0E − 02	5.7E − 01	2.0E − 03
CrO_4^{-2b}	1.0E − 02	1.1E − 02	[9.8E − 06]
NO_2^-	1.37E + 00	1.34E + 00	9.6E − 04
NO_3^-	8.5E − 01	8.5E − 01	6.9E − 04
OH^{-c}	6.3E − 01	6.6E − 01	3.0E − 03
PO_4^{-3}	1.7E − 02	1.7E − 02	1.5E − 05
SO_4^{-2}	1.8E − 01	1.7E − 01	1.3E − 04
Oxalate	1.1E − 02	1.1E − 02	1.1E − 05
Uranium	9.41E − 09	—	—

[a] The AZ-101 supernate was diluted to provide an ion exchange feed, which was approximately 5 M Na.

[b] Elemental Al and Cr were determined by ICP-AES. The anionic forms, AlO_2^- and CrO_4^{-2}, are assumed on the basis of waste chemistry.

[c] Hydroxide and carbonate were determined by titration. Hydroxide was assigned as the first equivalence point, and carbonate was assigned as the second equivalence point.

processing is likely the result of analytical uncertainties or possibly a sample-preparation error.

The eluate is composed of sodium (0.010 M), potassium (0.001 M), and various anions: nitrate, nitrite, and carbonate. The charge balance is reasonably good; the cations are 0.009 N; and the anions are 0.006 N. Technetium, which is present at 9.54E − 07 M, does not contribute significantly to the charge balance. There were slight amounts of radionuclides also present in the eluate composite; ^{241}Am was present at 1.82E − 03 μCi/L, ^{3}H at 2.07E − 02 μCi/L, ^{14}C at 7.44E − 02 μCi/L, ^{90}Sr at 3.51E − 01 μCi/L, ^{238}Pu at 9.88E − 05 μCi/L, and $^{239/240}$Pu at 3.72E − 4 μCi/L. It is unlikely that SL-639 is retaining these radionuclides, with the exception of ^{90}Sr, which has also been observed in the AP-101 and AN-102/C-104 eluates.

DISCUSSION

The column loading curves demonstrated excellent removal of technetium for each tank-waste supernate tested. The breakthrough profiles are typical of slow adsorption kinetics. Table 9 shows a summary of the column performance, as well as some relevant analyte compositions for each of the tank-waste supernates. The pertechnetate removal is reported in the table rather than the ^{99}Tc removal, so the resin performance is more apparent.

Throughout the runs, especially AN-102/C-104 blended feed, initial breakthrough is relatively high because of nonpertechnetate species. These nonpertechnetate forms of technetium have been encountered before (14, 15)

Table 9. Summary of column performance and relevant feed composition

Tank	TcO_4^-, M as Tc[a]	Na, M	NO_3/Tc[b]	μCi TcO_4^- loaded[c]	% TcO_4^- removed[d]	BV to 50%/BT[e]
AP-101	2.98E − 05	4.81	6.25E+04	54.3	99.0	500
AN-102/C-104	2.38E − 05	4.78	7.28E+04	25.0	86.3	500
AP-104	2.92E − 05	4.78	5.18E+04	63.1	88.0	360
AZ-101	2.23E − 04	4.26	3.81E+03	550	99.9	360

[a] Moles of technetium as pertechnetate is calculated from the pertechnetate concentration and MW = 99.

[b] Using the feed NO_3^- concentration reported in Tables 1, 3, 5, and 7.

[c] Calculated from the area under the curve of a plot of $(1\text{-}C/C_0)[TcO_4^-]_i$ versus mL processed feed.

[d] Based upon the feed and effluent TcO_4^- concentrations.

[e] Extrapolated from column loading curves. The TcO_4^- breakthrough was quite small for AN-102/C-104 and AP-101; these values should be considered estimates only.

and typically occur in Envelope C designated tank wastes. These wastes contain a high concentration of organic (i.e., complexing) compounds. However, tanks designated as Envelope A have also been identified as containing nonpertechnetate species (6) and do in fact contain organic complexants. Blanchard and Schroeder et al. (16, 17) verified the presence of a lower valent, nonpertechneate species in Tank AW-101 (an Envelope A) supernate. The XANES data were consistent with a Tc (IV) species bound to complexants or complexant fragments through oxygen linkages. Lukens et al. (18, 19) examined the radiolysis products of pertechnetate and identified the predominant radiolysis product as insoluble $TcO_2 \cdot x\ H_2O$. A soluble pink radiolysis product produced in the presence of diols was identified as a Tc (IV) diolate. A Tc(I)-carbonyl species has also been identified.

While the form of technetium in the solutions will affect the initial breakthrough, the actual performance of the exchange material in technetium removal is affected more by the concentration of nitrate in solution. A comparison of AN-102/C-104 and AP-104 supernates, which both had high fractions of nonextractable technetium, shows that the pertechnetate removal was quite similar for both supernates. The molar compositions of these supernates are similar as are the NO_3^-/TcO_4^- ratios. A comparison of AP-101 and AN-102/C-104 supernates shows that the pertechnetate removal was similar for these supernates as well. The pertechnetate removal for AZ-101 stands out because the pertechnetate concentration was an order of magnitude higher than the other tank-waste supernates, but it exhibited the best pertechnetate removal. Although the composition of AZ-101 is different from that of the other tank-waste supernates and the ionic strength is slightly lower, the most salient difference is the NO_3^-/TcO_4^- composition. The NO_3^-/TcO_4^- ratio is an order of magnitude lower in AZ-101 than the other tank-waste supernates, indicating that the molar ratio of nitrate to pertechnetate has a strong influence on the resin performance. This dependence has been previously noted (14). Hydroxide concentration, however, has little effect on the removal pertechnetate ion. The comparison of AP-101 and AN-102/C-104 shows that even with the hydroxide concentration an order of magnitude higher, the pertechnetate removal is essentially the same. These observations indicate that free hydroxide does not have a very significant impact on the pertechnetate removal.

The elution of technetium from the resin proceeded quickly using water at 65°C. The elution peaked with 2 BVs, typically giving a peak that was 80 to 100 times greater than the original technetium feed concentration. The target elution goal was to remove technetium from the resin until the eluate contained $\leq 1\%$ of the original feed technetium concentration. This target was reached within 23 BVs for all four processed wastes. The elution for AP-104 showed significant tailing and required a 30% larger elution volume, 23 BVs, than the other processed supernates, ≤ 18. This different elution performance does not correlate clearly with the supernate composition.

The AZ-101 elution progressed to completion within 18 BVs, which is noteworthy, considering that the large concentration of technetium loaded onto the column, 550 μCi, was approximately 10 times that of the other tank wastes.

CONCLUSION

Column experiments were performed to demonstrate the effectiveness of SL-639 for removing pertechnetate ion from Hanford tank wastes. The testing examined each type of tank-waste feed anticipated during processing at the U.S. Department of Energy/Office of River Protection Project—Waste Treatment Plant: Envelopes A, B, and C. The design basis processing goal was easily met for Envelopes A, B, and C tank-waste supernates (Tanks AP-101, AZ-101, and AN-102/C-104). Supernate from Tank AP-104 contains a high fraction of nonextractable technetium (nonpertechnetate), and as such, the technetium removal should be compared to the Envelope C requirements, rather than Envelope A. The technetium removal for AP-104 supernate, 32%, meets the target goal for an Envelope C waste.

The recovery of technetium, as demonstrated by the composite solution analysis, is generally quite good, ranging from 92% to 99%. An analysis of the amount of technetium loaded onto the lead column and subsequently eluted from the column demonstrates that there is likely a very low amount of technetium retained by the resin, approximately 4 μCi. However, the spent resin was not analyzed for technetium content, so these values represent a postulated technetium retention. The molar ratio of nitrate to pertechnetate ions has a significant effect on the performance of the resin, much more so than the slight effect observed for other compositional changes. An order-of-magnitude decrease in the molar NO_3^-/TcO_4^- results in a corresponding order-of-magnitude increase in technetium retention.

The elution of technetium from SL-639 was readily accomplished using DI water at 65°C and a flow rate of 1 BV/hour. The elution peaked quickly, reaching the target elution goal of the eluate containing $\leq 1\%$ of the original feed technetium concentration, within 23 BVs. The typical elution volume, even for the highly loaded resin from AZ-101 processing, was 18 BVs.

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