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TECHNETIUM REMOVAL FROM HANFORD AND SAVANNAH RIVER SITE ACTUAL TANK WASTE SUPERNATES WITH SUPERLIG® 639 RESIN

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ABSTRACT

SuperLig$^{®}$ 639 elutable, organic resin has been selected for technetium (as pertechnetate ion) removal from Hanford Site radioactive waste samples as part of the River Protection Project - Waste Treatment Plant (RPP-WTP) design. In support of the RPP-WTP flow sheet development, column tests have been performed at the Savannah River Technology Center with SuperLig$^{®}$ 639 resin using actual Hanford Site tank waste samples. The resin was shown to be highly effective at pertechnetate removal from these caustic, high-sodium, aqueous waste samples. Pertechnetate ion was subsequently eluted from the columns with water. An additional column test conducted on a Savannah River Site waste sample revealed exceptional performance, presumably due to the fact that lower concentrations of competing anions (primarily nitrate) were present in the sample.

INTRODUCTION

Millions of gallons of high-level radioactive waste (a legacy by-product of the production of nuclear materials for national defense needs during the past 50 years) are stored in underground tanks in the U. S. Department of Energy's (DOE) Hanford Site awaiting pretreatment and safe disposal. Numerous processes involving the addition of many chemical reagents resulted in the generation of various waste streams which were combined in underground storage tanks. The tanks contain varying amounts and types of solids and millions of gallons of aqueous supernate. While all of the supernate is alkaline and primarily contains dissolved sodium salts, significant compositional variation is observed between tanks. The principal radioactive constituents in the waste are ^{137}Cs ($t_{1/2}$ = 30 y), ^{99}Tc ($t_{1/2}$ = 2 x10^{6} y), and ^{90}Sr ($t_{1/2}$ = 29 y), which are primarily responsible for the radioactivity due to their long half-lives and high fission yields.

The design process flowsheet proposed for pretreatment of Hanford Site tank waste supernates removes ^{137}Cs, ^{99}Tc, and ^{90}Sr from the bulk of the waste and concentrates these species into smaller volume streams. The bulk of the decontaminated waste is to be vitrified and disposed as low-activity waste glass. The concentrated radionuclides are to be combined with high-level waste tank sludge solids and vitrified into high-level waste glass. To achieve this goal, novel process schemes and suitable ion exchange and precipitation technologies are continuing to be developed and tested.

Technetium removal from simulated Hanford Site tank wastes by ion exchange materials has been widely investigated. (1-6) Recent studies have demonstrated that a material designated as SuperLig® 639 was very effective for technetium removal from actual Hanford Site tank wastes. (7-12) SuperLig® 639 resin contains a polystyrene substrate with an attached proprietary organic ligand, which is highly selective for pertechnetate ion in alkaline sodium salt solutions. SuperLig® 639 is currently the baseline material for technetium removal from Hanford Site waste because of its high selectivity, elutability, and availability in an engineered form that is suitable for use in column configuration.

This paper presents the results of laboratory-scale column experiments performed to demonstrate the removal of technetium with SuperLig® 639 resin from actual radioactive waste samples retrieved from underground tanks in Hanford, WA. Tests with Hanford Site samples were performed with two columns in series (lead/lag configuration). Columns were sized based on small-scale batch contact tests, with the goal of obtaining technetium breakthrough profiles from the lead column while simultaneously maintaining sufficiently low breakthrough from the lag column to satisfy the design technetium decontamination criteria. The three samples tested are representative of the three general categories which have been assigned to Hanford Site waste supernates (based on chemical compositions) for processing through the River Protection Project - Waste Treatment Plant (RPP-WTP). An additional column test was performed on a Savannah River Site (SRS) tank sample in order to evaluate resin performance with this waste type, although there are currently no plans to remove technetium from SRS waste.

EXPERIMENTAL

Waste Sample Histories and Characterization

Hanford Site samples

The column testing was performed using actual Hanford tank waste samples. The waste samples were retrieved from Hanford tanks 241-AN-103, 241-AZ-102 and 241-AN-102, which are representative of the waste supernate categories designated as Envelopes A, B, and C, respectively. The Envelope A and C waste samples were diluted to 5-6 M Na^+ (sodium is the dominate cationic species in all Hanford supernate samples) prior to column testing in order to be consistent with the current RPP-WTP design processing conditions for these waste types. The prefix “241” is common to all Hanford Site tanks and will not be used further.

The waste sample from Hanford tank AN-103 was received at the Savannah River Technology Center (SRTC) at a sodium ion concentration of 11.7 M. The sample was diluted to 5.0 M Na^+ with 0.01 M sodium hydroxide solution, and filtered through 0.45-μm dead-end, nylon filters prior to the column testing. The filtrate contained the following additional major constituents: free hydroxide (1.9 M), nitrate (1.0 M), nitrite (0.9 M), and aluminum (0.84 M). Lower concentrations of other species were also observed as indicated in Table 1 for the “feed”.

The tank AN-102 waste sample was characterized by having a relatively high soluble organic content. The high organic content can be partially attributed to the presence of complexing anions that serve to solubilize strontium and transuranic (TRU) elements typically found in tank sludge solids. As a result, the AN-102 waste sample requires additional treatment for the removal of these radioactive species. The "as-received" AN-102 sample (which contained 10.2 M Na^+) was diluted with 0.01 M sodium hydroxide solution, and then subjected to precipitation to remove ^{90}Sr and transuranic elements. Cross-flow filtration (pore size: 0.1 μm) of the AN-102 precipitate slurry yielded a filtrate with a sodium concentration of 6.0 M, which was used for the column tests. The filtrate contained the following additional major constituents: nitrate (1.9 M), free hydroxide (~0.9 M), nitrite (0.83 M), and aluminum (0.27 M). The AN-102 sample also contained 4.7 E+04 mg/L total organic carbon and 1.1 E+04 mg/L total inorganic carbon. Trace amounts of other species measured are provided in Table 2 for the "feed".

The "as-received" waste sample from tank AZ-102 was relatively low in ionic strength (2.7 M Na^+). The AZ-102 sample was not diluted but was filtered through 0.45-μm dead-end, nylon filters prior to column testing. Additional major components of the filtrate included: nitrite (0.83 M), nitrate (0.27 M), free hydroxide (0.11 M), and sulfate (0.17 M). The AZ-102 sample also contained 6.1 E+03 mg/L total inorganic carbon and 6.0 E+03 mg/L total organic carbon. Trace quantities of other species were also observed as indicated in Table 3 for the "feed".

Savannah River Site sample

A sample of SRS waste tank 44F was tested for strontium and cesium removal at SRTC as part of the Alternative Salt Disposition Program for the treatment of SRS tank waste. (13) Strontium removal was achieved by a single batch contact strike with monosodium titanate (MST) followed by filtration. Cesium removal was subsequently achieved by passing the sample through crystalline silicotitanate (CST) columns. The strontium- and cesium-decontaminated sample was highly alkaline (total OH^-: 4.5 M) with a sodium concentration of 5.4 M. The sample also contained the following additional major constituents: nitrate (0.50 M), nitrite (0.48 M), and aluminum (0.24 M). Trace quantities of other species were also measured as indicated in Table 4 for the “feed”. The sample was filtered through a 0.45-µm in-line filter (Whatman Polycap® 75TF disposable capsule with a polytetrafluoroethylene membrane) prior to initiating testing with SuperLig® 639 resin to ensure that no residual MST particles were transferred with the liquid from the sample storage tank. This precaution was considered necessary based on knowledge of the storage tank history.

Resin

The material used for technetium removal from Hanford Site tank waste supernates was SuperLig® 639 resin supplied by IBC Advanced Technologies, American Fork, Utah. Resin batches 981015DHC720011 and 990420DHC720067 were used for testing. The resin was supplied as dry, 30-60 mesh spherical particles. Physical property measurements on the SuperLig® 639 resins have been previously reported (8).

Apparatus and Procedure

Hanford Site samples

Columns were prepared at SRTC from medium-wall Pyrex glass tubes with inside diameters of 1.1 cm. The outsides of the columns were coated with a layer of polyvinyl chloride to reduce hazards associated with potentially pressurizing the apparatus. Stainless steel wire screens (200 mesh) were inserted into the column bottoms to support the resin. The column top assemblies had a fill reservoir, a pressure gauge, a pressure relief valve, and a feed inlet port. The fill reservoir also served as a vent. The top was connected to the lower section by a ground glass joint and was tightly fitted by a screw cap. The column walls were graduated to allow for observation and measurement of changes in resin bed height and liquid level.

Two identical columns were connected in series (lead/lag configuration) for the column tests with the Hanford Site samples. These columns and resin beds were used to process each subsequent Hanford sample. Polyethylene tubing (3/16 inch ID) was used for the feed and effluent lines. All equipment assembly and operation was conducted remotely in shielded cells at the Savannah River Technology Center. All processing solutions were pumped down-flow through the columns using positive displacement pumps (Fluid

Metering Incorporated QG150 with ¼” and $^{3}/_{8}$” piston sizes). All experiments were conducted at ambient temperature (25 ±2 °C).

A sample of SuperLig® 639 resin batch 981015DHC720011 was soaked in water and equal portions were transferred into the columns to give two resin beds, which were each 6 mL in volume. The resin beds were then preconditioned by passing 3 BV of 1.0 M sodium hydroxide solution through the columns in series over a 1 hour period. 1 bed volume (BV) was defined as the volume of the wetted and packed resin bed. SuperLig® 639 resin does not undergo significant volume changes throughout the complete processing cycle (precondition/load/wash/elute) specified in the current plant design basis.

The feed solutions were pumped at a flow rate of 3 BV/hr through the resin beds, and the effluent was collected from the bottom of the lag column. The column liquid levels were maintained at approximately 1-2 cm above the resin beds, leaving a partially pressurized air headspace in the tops of the columns. Sub-samples (~1 mL) were collected from the lead column at 10 BV increments and the lag column was sampled at 20 BV increments. Sub-samples from the lead and lag columns were analyzed for technetium (^{99}Tc) by inductively coupled plasma-mass spectroscopy (ICP-MS). The loading cycle was terminated when the available feed was consumed.

The columns were then washed in series with 0.1 M sodium hydroxide solution at a flow rate of 3 BV/hr in order to displace residual feed solution. The lead and lag columns were disconnected, and the lead column was eluted independently. Pertechnetate ion was eluted from the lead column using deionized water at a flow rate of 1 BV/hr and the eluate was collected in 2 BV portions. Sub-samples of the eluate solutions were analyzed for ^{99}Tc by ICP-MS.

The Hanford Site waste samples were processed in the following sequence: AN-103, AN-102, and AZ-102. After processing each tank sample, the resin in the lead column was eluted and then regenerated/preconditioned with 3 BV of 1.0 M NaOH at a flow rate of 3 BV/hr prior to initiating testing with the next waste sample. (**Note:** The lag column was not eluted between column tests. Therefore, the lag column ^{99}Tc breakthrough performance was the result of cumulative loading during the successive column tests with the Hanford Site waste samples. This testing method (eluting only the lead column) emulates the current plant operating process.

The composited product (effluent) and water eluate solutions from each column experiment were characterized by inductively coupled plasma - atomic emission spectroscopy (ICP-AES) and ion chromatography (IC). The total inorganic and organic carbon (TIC/TOC) content of the composite samples was determined by furnace oxidation. Uranium analysis was conducted by addition of phosphoric acid and measurement of uranyl phosphate phosphorescence after laser excitation. The analysis results are reported in Tables 1-3 for the “product” and “eluate” solutions.

Savannah River Site sample

A single column (no lag column) with a similar design to the columns used for testing Hanford Site samples, but with a 2.69 cm inside diameter, was prepared for testing the SRS sample. In order to avoid problems with resin floating during feed processing, quartz wool and glass beads were placed on top of the resin to retain the bed. A 50:50 mixture by mass of “as-received” resin batches 981015DHC720011 and 990420DHC720067 was used to prepare the resin bed. The sample was thoroughly mixed by gentle and repeated tumbling in a polyethylene bottle. 23.9899 g of this physical mixture was soaked in water for several hours and the entire slurry was then transferred to the column to give a final packed volume of 50.6 mL. Based on drying tests conducted in an oven at ambient pressure and 95 °C, the measured mass corresponds to a dry resin mass of 23.6540 g. (14)

The solution processing sequence (precondition/load/wash/elute) for the SRS sample was identical to that described above for the Hanford Site samples. However, the height of the column of liquid above the resin during processing was maintained at a level equivalent to the height of the resin bed (i.e. liquid head volume = 1 BV). This processing method was utilized to mimic the plant design for column operation. The primary consequence of operating the columns with a large liquid head is mixing effects in the head space during transitions between processing solutions. Impacts upon loading and elution profiles are expected to be small and limited to the first few bed volumes of solution processed. Target precondition, load, wash, and elution flow rates were identical to those used for the Hanford Site samples. One milliliter samples of the effluent were collected at approximately 10 BV intervals during the loading cycle. Individual 1 mL samples were collected for analysis during the water elution, as opposed to collecting the eluate in 2 BV increments (which was the case for the tests with Hanford Site samples).

RESULTS

Hanford Site Samples

The planned pretreatment process for Hanford Site tank wastes involves cesium (^{137}Cs) removal followed by technetium (^{99}Tc) removal. However, due to scheduling issues with the AN-103 sample, the technetium column experiment was performed prior to cesium decontamination. The cesium decontamination experiment was performed with SuperLig® 644 resin several weeks after the technetium loading experiment was completed. Details of the cesium removal experiment are reported elsewhere. (15) The compositions of the Cs/Tc-decontaminated product and the technetium eluate solution are provided in Table 1.

The chemical species present in the decontaminated product were generally as expected, with the exception of calcium, which was considerably lower in the decontaminated product than was observed in the feed. Based on additional tests conducted at SRTC, it is believed that Ca was depleted from the sample during cesium removal testing. Based on the [^{99}Tc] in the original feed (C_o = 3.07 E-05 M) and the final composited product (C_f = 2.28 E-06 M) solutions, the total technetium removal from the AN-103 sample was 92.6%. This corresponds to a ^{99}Tc decontamination factor (DF) of 13.5 for the lead/lag column configuration.

The analysis results in Table 1 indicate that the composited eluate is primarily a dilute sodium salt solution (~0.03 M Na^+, 0.02 M NO_3^-, 9.8 E-05 M ^{99}Tc – presumably as TcO_4^-). Based on very limited information supplied by the resin vendor, it is currently believed that SuperLig® 639 resin is not a traditional ion exchange resin. Instead, the resin extracts pertechnetate as an ion pair, presumably as sodium or potassium pertechnetate. The primary competitors for adsorption are believed to be nitrate salts, which are present in the feed at considerably higher concentrations than the pertechnetate ion.

Figure 1 shows the ^{99}Tc breakthrough profiles (i.e. the ratio of the ^{99}Tc concentration in the effluent (C) to that in the feed (C_o)) observed for the lead and lag columns with the AN-103 sample as a function of the number of BV of feed processed through the columns. 47% ^{99}Tc breakthrough was observed from the lead column after processing 270 BV of feed solution. The lead column effluent ^{99}Tc concentration gradually increased during loading, indicating slow adsorption kinetics relative to the solution residence time in the column. Less than 8% ^{99}Tc breakthrough was observed from the lag column during the loading cycle. However, technetium breakthrough from the lag column was almost immediate, indicating that some channeling of the lag column resin bed occurred. The experiment was stopped at this point due to the unavailability of additional feed solution. The breakthrough data indicates that SuperLig® 639 resin is very selective for technetium removal from AN-103 waste and that it performs adequately to satisfy the RPP-WTP design requirements for lead column breakthrough (100 BV to 50% Tc breakthrough) and overall decontamination.

Significant scatter was observed in the lead column ^{99}Tc breakthrough data for the AN-103 sample (Figure 1). The scatter may be related to wall and channeling effects resulting from the small amount of resin utilized for these tests and the small resin bed diameter (1.1 cm). The average particle diameter of the SuperLig® 639 resin beads was near 0.6 mm. (14) Therefore, the resin bed diameter was ~18 times larger than the particle diameter. Bed diameters that are at least 30 times the resin particle diameter are generally considered sufficient to render wall effects insignificant. (19) However, in order to obtain useful technetium breakthrough profiles, it was necessary to use a small diameter column containing a small total resin volume, due to limited radioactive sample size and high resin capacity.

Another possible cause for the data scatter was the observation that some lead column resin beads began to float soon after the introduction of feed. This observation was not surprising due to fact that the measured particle density of this resin batch (1.219 g/mL) was slightly less than the solution density. (14) In order to avoid floating of the resin beads, the loading cycle was momentarily interrupted and quartz wool and glass beads were added to the lead and lag columns to restrain the tops of the resin beds. The wool and beads remained on the tops of the columns for all subsequent tests. The physical disturbance of the resin bed in the lead column almost certainly contributed to the scatter in the early portion of the breakthrough profile.

The technetium elution profile observed from the lead column after processing the AN-103 sample is shown in Figure 2. Elution was accomplished using de-ionized water at a flow rate of 1 BV/hr. The elution profile exhibited a peak in the [^{99}Tc] after processing 13 BV of eluate that was ~28 times larger than the [^{99}Tc] of the feed. The peak was followed by an initial sharp decrease, however, the profile then decreased gradually resulting in a long elution tail. The design target eluate concentration (1% of the feed [^{99}Tc]) for complete lead column elution was not reached even after processing ~40 BV of eluate (Figure 3). Eluate samples still contained 7% of the feed technetium concentration after processing this eluate volume. Due to the large total volume, the composited eluate was only three times more concentrated in ^{99}Tc than the feed. Based on the calculated total amounts of ^{99}Tc in the feed and the first ~40 BV of the composited eluate collected, 96.5% of the technetium loaded onto the resin was removed during elution. Prior to initiating subsequent column tests with the AN-102 sample, the resin was eluted with additional water until the design target for the eluate was reached. It should be noted that some difficulty was experienced in maintaining a constant flow rate through the resin bed during the elution due to the extremely low flow required (1 BV/hr = 6 mL/hr). This may have contributed to the tailing observed in the elution profile.

The precipitated and filtered AN-102 sample was initially tested for Cs removal using SuperLig® 644 columns. (16) The Cs-decontaminated product was then processed through the SuperLig® 639 columns for Tc removal. Table 2 shows the composition of the decontaminated "product" and the technetium "eluate" solutions for the AN-102 waste sample. The chemical species in the product and eluate solutions were generally as expected, with the exception of uranium. The uranium concentration in the decontaminated product of 0.62 mg/L is only 8% of the feed uranium concentration. This indicates that significant removal of uranium occurred during processing of the AN-102 sample through the SuperLig® 644 and 639 columns. High concentrations of uranium (16.8 mg/L) were also observed in the SuperLig® 644 cesium eluate for this sample, indicating significant uranium uptake with this resin. There is no indication of significant uranium uptake by SuperLig® 639 resin.

Figure 4 shows the technetium breakthrough profile for the AN-102 waste sample. 45% ^{99}Tc breakthrough was observed for the lead column after processing 5 BV of feed and 60% breakthrough occurred after processing 10 BV. The lag column maintained 60-70% ^{99}Tc breakthrough throughout the loading period. Considerable breakthrough of technetium was expected from this sample due to the fact that the technetium in this waste type is known to exist primarily as non-pertechnetate species that do not adsorb to SuperLig® 639 resin. The non-pertechnetate fraction presumably exists as reduced technetium species formed by reduction of pertechnetate ion by the high concentrations of organic species in this sample. The nearly identical breakthrough profiles observed for the lead and lag columns indicate that essentially all of the pertechnetate ion was removed by the lead column.

Figure 5 shows the elution profile for the AN-102 waste sample. The peak in the ^{99}Tc concentration was observed at ~8 BV and was higher than the feed technetium concentration only by a factor of 2.7. The peak concentration was considerably lower than was observed for the AN-103 sample due to the fact that considerably less pertechnetate was loaded onto the column. The elution was continued for ~42 BV and samples were periodically submitted for analysis. The [^{99}Tc] reached <1% of the feed after ~24 BV of eluate had been processed. The smaller volume of eluate required to elute the column was also a consequence of the significantly lower amount of pertechnetate that was loaded onto the column relative to the tests with the other Hanford Site samples. The composited eluate contained 0.06 M Na^+ and 0.04 M NO_3^-. The eluate also contained an order of magnitude higher total organic carbon (TOC) than was observed for the AN-103 column eluate (although the molar concentration of organic compounds in the AN-102 eluate is still ≤0.01 M, depending on the speciation).

The filtered AZ-102 sample was initially tested for Cs removal using SuperLig® 644 columns. (17) A portion of the Cs-decontaminated product, which was diluted by ~20% with the SuperLig® 644 column preconditioning solution (0.25 M NaOH) was used for testing with the SuperLig® 639 resin. Therefore, the concentrations of chemical species reported for the "feed" in Table 3 were actually diluted prior to processing the sample through the SuperLig® 639 columns. Exceptions to the above statement include total inorganic (TIC) and organic carbon (TOC) (each of which increased by ~38% in the product relative to the feed). The increase in total organic carbon likely resulted from leaching of organics from the SuperLig® 644 resin.

Figure 6 shows the ^{99}Tc breakthrough profile for the AZ-102 waste sample. Only 10% ^{99}Tc breakthrough was observed for the lead column after processing 170 BV of feed. In contrast to the performance observed with the AN-103 sample, the lag column ^{99}Tc breakthrough remained at ≤0.04% during the entire loading cycle. Total technetium removal from the AZ-102 sample was 99.94% (C_o = 1.57 E-05 M, after correction for sample dilution; C_f = 3.45 E-06 M), which corresponds to an overall decontamination factor (DF) of 1659 for the lead/lag column configuration. The high DF observed for this sample primarily results from the fact that the lead column was only loaded to 10% ^{99}Tc breakthrough.

Figure 7 shows the technetium elution profile from SuperLig® 639 resin after processing the AZ-102 sample. The shape of the curve is similar to the elution profile observed for the AN-103 sample. The peak observed in the [^{99}Tc] after processing 12 BV of eluate was 19 times larger than the feed [^{99}Tc]. The elution was initially terminated after 34 BV of the eluate was processed. Analyses later indicated that the [^{99}Tc] in the last eluate sample was ~8% of the feed [^{99}Tc]. The composited eluate contained ~0.09 M Na^+, 0.05 M OH^-, 0.01 M NO_3^-, and 0.01 M NO_2^-. Some sodium hydroxide solution was presumably carried over from processing the feed and wash solutions through the column. However, hydroxide concentration in the eluate seems high given the large eluate volume and the fact that the feed and wash solutions were each ~0.1 M OH^-.

Savannah River Site sample

As described in the experimental section, the SRS Tank 44F sample was treated for Sr and Cs removal and filtered prior to treatment with SuperLig® 639 resin. The composition of the feed sample prior to technetium removal testing is provided in Table 4. Total technetium removal from the Tank 44F sample based on integration of the breakthrough curve was 85.7% (total ^{99}Tc: feed - 91 mg; effluent - 13 mg), which corresponds to an overall DF of 7.0 for the single column configuration. Figure 8 shows the ^{99}Tc breakthrough observed for the single SuperLig® 639 column with the Tank 44F sample. The resin was very effective at removing pertechnetate ion from this waste sample. Approximately 45% ^{99}Tc breakthrough was observed after processing 579 BV (29.3 L) of Tank 44F sample.

The ^{99}Tc elution profile is shown in Figure 9. A peak was observed in the ^{99}Tc concentration after processing 7 BV of eluate that was 208 times the feed ^{99}Tc concentration. Note that the eluate samples collected for this test were grab samples as opposed to 2-BV eluate fractions (which was the case with the Hanford samples). Therefore the data reveals the instantaneous peak in the [^{99}Tc] as opposed to an averaged concentration over several bed volumes of eluate. The [^{99}Tc] in the eluate did not reach 1% of the feed [^{99}Tc] until 50 BV of eluate had been processed. The composited eluate sample was ~0.01 M Na^+ with a [^{99}Tc] of 3.59 E-04 M.

DISCUSSION

^{99}Tc breakthrough data for the various waste samples reveals significant removal of technetium from all waste samples tested, although the shapes of the breakthrough profiles are indicative of slow adsorption kinetics A summary of the breakthrough performance observed for the various waste samples tested is provided in Table 5. Trends in the performance data provide some insight as to the parameters that effect SuperLig® 639 performance. Comparison of the breakthrough data for the tank 44F sample and the AN-103 sample (which contain comparable sodium and pertechnetate concentrations) reveals significantly different performance for these two samples as indicated by the volumes of feed required to reach approximately 45% ^{99}Tc breakthrough (44F: 580 BV; AN-103: 270 BV). The observation of significantly better performance with the tank 44F sample indicates that the elevated OH^- level and/or the low nitrate concentration in this sample result in significantly enhanced pertechnetate removal. A thorough analysis conducted at SRTC of historical and current data collected with SuperLig® 639 resin using both simulated and actual waste samples indicates that resin performance does correlate to the molar ratio of nitrate to pertechnetate ions. (18)

Intermediate performance was observed for the AZ-102 sample (see Table 5), although this sample contained a significantly lower molar ratio of nitrate-to-pertechnetate ions than all of the samples tested. This indicates that some other liquid phase property, such as ionic strength or pertechnetate ion concentration, impacts column performance. Based on the previously-mentioned historical data review, SuperLig® 639 resin technetium capacity does appear to be a function of solution ionic strength, with higher ionic strength resulting in greater effective capacity. This is consistent with the fact that the columns can be thoroughly eluted with deionized water.

Comparison of the nitrate-to-technetium (presumed to be pertechnetate) molar ratios in the feed and eluate solutions provides a measure of the selectivity of the resin for pertechnetate versus nitrate adsorption. Table 5 provides these ratios for the feed solutions. The calculated nitrate-to-^{99}Tc ratios in the AN-103 and AZ-102 feed solutions were 3.25 E+04 and 1.71 E+03. The nitrate-to-^{99}Tc ratios for the AN-103 and AZ-102 eluate solutions were 225 and 28, respectively, which indicates that the resin is very selective for pertechnetate adsorption from these waste samples.

CONCLUSIONS

Column experiments were performed to demonstrate SuperLig® 639 removal of pertechnetate ion from Hanford and Savannah River Site tank waste supernatants. ^{99}Tc loading and elution profiles were determined for samples of Hanford Site tanks 241-AN-103, 241-AN-102, and 241-AZ-102 and for an SRS sample from tank 44F. The results revealed that SuperLig® 639 is very selective for pertechnetate removal from these Hanford and Savannah River Site waste samples. The performance easily meets the RPP-WTP design criteria for ^{99}Tc decontamination from each Hanford Site waste sample, except for the AN-102 sample. Since the total volume of this waste type is small, blending strategies will likely be utilized to achieve an average mixed product with a ^{99}Tc concentration that satisfies the plant design criteria. Trends noted in the column data obtained for these samples indicate that nitrate-to-pertechnetate ion molar ratios and solution ionic strength may be important parameters impacting resin performance. SuperLig® 639 resin bead density can lead to floating of the resin bed during feed processing. Floating of the resin bed during the plant operation will likely be avoided by fixing the bed in place with screens. Efforts are also underway to increase the resin material density.

Technetium elution from SuperLig® 639 resin was easily accomplished using deionized water at ambient temperature and a flow rate of 1 BV/hr. Although >95% of the ^{99}Tc is eluted from the columns within the first 10-20 BV of eluent, long processing times and excessive eluate volumes are frequently required to reach the design target for complete elution (1% of the feed [^{99}Tc]). Attempts to optimize the elution are currently underway and are primarily focused on eluting the columns at elevated temperatures (up to 65 °C). An alternative strategy might involve stopping the elution after 10-15 BV of solution have been processed, and allowing the small amount of pertechnetate ion remaining on the resin to desorb without generating excess liquid volume.

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REFERENCES

1. S. F. Marsha, Z. V. Svitra, and S. M. Browen, LA-12654, Los Alamos National Laboratory Report, 1994.

2. S. F. Marsha, Z. V. Svitra, and S. M. Browen, LA-12862, Los Alamos National Laboratory Report, 1995.

3. S. F. Marsha, Z. V. Svitra, and S. M. Browen, LA-13000, Los Alamos National Laboratory Report, 1995.

4. N. C Schroeder, K. D. Abney, M. Attrep, Jr., S. Radzinski, J. Brewer, K. R. Ashley, J. Ball, F. Stanmore, N. LaFebre, T. Pinkerton, and R. Turner, LA-UR-93-4092, Los Alamos National Laboratory Report, November, 1993.

5. N. C Schroeder, K. D. Abney, M. Attrep, Jr., S. Radzinski, J. Brewer, K. R. Ashley, J. Ball, F. Stanmore, N. LaFebre, T. Pinkerton, and R. Turner, LA-UR-94-62, Los Alamos National Laboratory Report, January, 1994.

6. D. L. Blanchard, G. N. Brown, S. D. Conradson, S. K. Fadeff, G. R. Golcar, N. J. Hess, G. S. Klinger, and D. Kurath, *PNL-11386 (UC-2030)*, Pacific Northwest National Laboratory Report, May 1996.

7. D. J. McCabe, SRTC-BNFL-014, Rev. 0, Savannah River Technology Center, December 5, 1997.

8. N. M. Hassan, D. J. McCabe, SRTC-BNFL-017, Rev. 0, Savannah River Technology Center, August 15, 1997.

9. N. M. Hassan, D. J. McCabe, SRTC-BNFL-018, Rev. 0, Savannah River Technology Center, October 24, 1997.

10. N. M. Hassan, D. J. McCabe, SRTC-BNFL-019, Rev. 0, Savannah River Technology Center, October 24, 1997.

11. N. M. Hassan, D. J. McCabe, SRTC-BNFL-021, Rev. 0, Savannah River Technology Center, November 13, 1997.

12. N. M. Hassan, D. J. McCabe, SRTC-BNFL-027, Rev. 0, Savannah River Technology Center, January 19, 1998.

13. D. D. Walker, WSRC-TR-99-00308, Rev.0, Savannah River Technology Center,.

14. N. M. Hassan, W. D. King, D. J. McCabe, BNF-003-98-0051, Rev. 0, Savannah River Technology Center,.

15. N. M. Hassan, D. J. McCabe, W. D. King, BNF-003-98-0146, Rev. 1, Savannah River Technology Center, April 12, 2000.

16. N. M. Hassan, D. J. McCabe, W. D. King, M. L. Crowder, SRTC-BNFL-021, Rev. 0, Savannah River Technology Center, March 29, 2000.

17. N. M. Hassan, D. J. McCabe, W. D. King, SRT-RPP-2000-00036, Rev. 0, Savannah River Technology Center, January, 2001.

18. C. E. Schwartz, J. M. Smith, Industrial and Engineering Chemistry, Vol. 45, No. 6, 1209-1218.

19. L. L. Hamm, F. G. Smith, D. J. McCabe, WSRC-TR-2000-00011, Rev. 0, Savannah River Technology Center, August 2000.

Table 1. Compositions of the feed, decontaminated product, and technetium eluate solutions for the AN-103 sample

	Feed[a] (M)	**Product[b] (M)**	**Eluate[c] (M)**
Na^+	4.99 E+00	5.00 E+00	3.20 E-02
K^+	1.17 E-01	1.09 E-01	1.85 E-03
Al	8.40 E-01	8.30 E-01	2.52 E-03
Ca	2.00 E-03	5.05 E-05	2.00 E-05
Cr	1.40 E-03	1.38 E-03	< 1.33 E-05
Si	3.40 E-03	5.41 E-03	< 1.87 E-04
NO_3^-	9.98 E-01	1.39 E+00	2.22 E-02
NO_2^-	8.66 E-01	8.75 E-01	2.57 E-03
SO_4^{2-}	9.00 E-03	< 1.00 E-02	< 7.25 E-04
PO_4^{3-}	5.90 E-03	< 1.10 E-02	< 1.46 E-03
Cl^-	8.50 E-02	7.69 E-02	< 4.96 E-04
OH^- (free)	1.87 E+00	----	----
^{99}Tc	3.07 E-05	2.28 E-06	9.83 E-05
U (mg/L)	4.08 E+00	----	< 1.39 E-01
TIC (mg/L)	3.68 E+03	2.31 E+03	6.39 E+01
TOC (mg/L)	5.68 E+02	1.45 E+03	5.82 E+01

[a] Analysis data for the AN-103 sample after dilution and dead-end filtration but before cesium and technetium column testing.

[b] Analysis data for the cesium- and technetium-decontaminated AN-103 sample.

[c] Analysis data for the composited technetium eluate solution obtained after processing the AN-103 sample.

Table 2. Compositions of the feed, decontaminated product, and technetium eluate solutions for the AN-102 sample

	Feed[a] (M)	**Product[b] (M)**	**Eluate[c] (M)**
Na^+	5.98 E+00	5.22 E+00	6.00 E-02
K^+	2.92 E-02	2.33 E-02	2.35 E-04
Al	2.72 E-01	2.44 E-01	9.93 E-03
Ca	5.14 E-03	5.05 E-03	1.64 E-03
Cr	1.69 E-03	1.31 E-03	1.79 E-04
P	4.27 E-02	2.63 E-02	< 3.07 E-04
Si	2.68 E-03	2.13 E-03	3.51 E-03
NO_3^-	1.89 E+00	6.5 E-01	3.61 E-02
NO_2^-	8.32 E-01	1.47 E-01	< 4.67 E-02
SO_4^{2-}	6.20 E-02	3.65 E-04	< 1.11 E-02
PO_4^{3-}	< 1.26 E-02	< 1.04 E-03	< 2.26 E-02
Cl^-	4.35 E-02	8.01 E-03	< 1.21 E-02
OH^- (free)	1.69 E+00	8.30 E-01	----
^{99}Tc	4.60 E-05	2.55 E-05	1.96 E-05
U (mg/L)	7.80 E+00	6.21 E-01	< 2.24 E-01
TIC (mg/L)	1.09 E+04	6.62 E+03	2.15 E+01
TOC (mg/L)	4.66 E+04	2.87 E+04	4.70 E+02

[a] Analysis data for the AN-102 sample after Sr/TRU precipitation and cross-flow filtration but before cesium and technetium column testing.

[b] Analysis data for the cesium- and technetium-decontaminated AN-102 sample.

[c] Analysis data for the composited technetium eluate solution obtained after processing the AN-102 sample.

Table 3. Compositions of the feed, decontaminated product, and technetium eluate solutions for the AZ-102 sample

	Feed[a] (M)	**Product[b] (M)**	**Eluate[c] (M)**
Na^+	2.65 E+00	1.79 E+00	8.96 E-02
K^+	8.10 E-02	6.60 E-02	2.02 E-03
Al	2.79 E-02	1.49 E-02	1.57 E-03
Ca	2.70 E-03	1.42 E-05	4.77 E-05
Cr	1.48 E-02	1.03 E-02	2.98 E-04
Si	----	3.56 E-03	2.32 E-04
NO_3^-	2.73 E-01	2.15 E-01	1.12 E-02
NO_2^-	8.32 E-01	5.67 E-01	1.26 E-02
SO_4^{2-}	1.72 E-01	1.39 E-01	6.21 E-03
PO_4^{3-}	< 3.00 E-03	< 2.58 E-03	< 1.05 E-03
Cl^-	7.00 E-03	5.13 E-03	9.69 E-03
OH^- (free)	1.09 E-01	----	5.20 E-02
^{99}Tc	1.57 E-05	3.45 E-06	3.98 E-04
U (mg/L)	----	1.68 E+01	< 2.24 E-01
TIC (mg/L)	6.14 E+03	8.62 E+03	1.85 E+02
TOC (mg/L)	6.04 E+03	8.34 E+03	1.52 E+02

[a] Analysis data for the AZ-102 sample after dead-end filtration but before cesium and technetium column testing.
[b] Analysis data for the cesium- and technetium-decontaminated AZ-102 sample.
[c] Analysis data for the composited technetium eluate solution obtained after processing the AZ-102 sample.

Table 4. Compositions of the feed and technetium eluate solutions for the tank 44F sample

	Feed[a] (M)	**Eluate[b] (M)**
Na^+	5.40 E+00	1.04 E-02
K^+	5.66 E-02	2.08 E-04
Al	2.39 E-01	<4.45 E-04
Ca	---	<1.25 E-05
Cr	---	<6.73 E-05
Si	---	6.39 E-03
NO_3^-	4.95 E-01	<1.61 E-03
NO_2^-	4.76 E-01	<2.17 E-03
SO_4^{2-}	1.33 E-03	<5.20 E-03
PO_4^{3-}	3.12 E-03	<5.26 E-03
Cl^-	9.27 E-03	<1.14 E-02
OH^- (free)	4.50 E+00	---
^{99}Tc	3.13 E-05	3.59 E-04
TIC (mg/L)	---	82.8
TOC (mg/L)	---	567.3

[a] Analysis data for the 44F sample after strontium- and cesium-decontamination and in-line filtration but before technetium column testing.

[b] Analysis data for the composited technetium eluate solution obtained after processing the 44F sample.

Table 5. Summary of feed characteristics and SuperLig® 639 column performance data

Sample	Na^+ (M)	^{99}Tc (M)	$[NO_3^-]/[^{99}Tc]$ Molar Ratio	10% ^{99}Tc Breakthrough (BV)[a]	45% ^{99}Tc Breakthrough (BV)[a]	^{99}Tc DF[b]	% ^{99}Tc Removal[b]
AN-103	4.99	3.07 E-05	3.25 E+04	50	270	14	93
AN-102[c]	6.00	4.60 E-05	4.11 E+04	<5	5	1.8	55
AZ-102	2.25[d]	1.58 E-04	1.71 E+03[d]	170	NA	1659	100
44F	5.40	3.13 E-05	1.58 E+04	300	580	7[e]	86[e]

[a] These ^{99}Tc breakthrough points were chosen for comparison because the AZ-102 sample was only processed to 10% lead column breakthrough, while the three remaining samples were processed to ~45% breakthrough.

[b] Decontamination factors and % removals for the lead/lag column configuration unless otherwise indicated.

[c] Approximately 65% of the ^{99}Tc in the AN-102 sample is believed to exist as nonextractable forms of technetium. Correction of the data considering only the pertechnetate ion and disregarding contribution from the remaining unidentified technetium species yields the following: $[TcO_4^-]$ ~1.6 E-05 M, $[NO_3^-]/[TcO_4^-]$: 1.2 E+05. Based on these values, the maximum % TcO_4^- breakthrough from the lead column is considered to be <10% and the % TcO_4^- removal is believed to be >90% after processing ~60 BV.

[d] Based on measured values for these species after sample dilution with 0.25 M NaOH during cesium column testing.

[e] Decontamination factor and % removal calculated for the single column used for testing.

LIST OF FIGURES

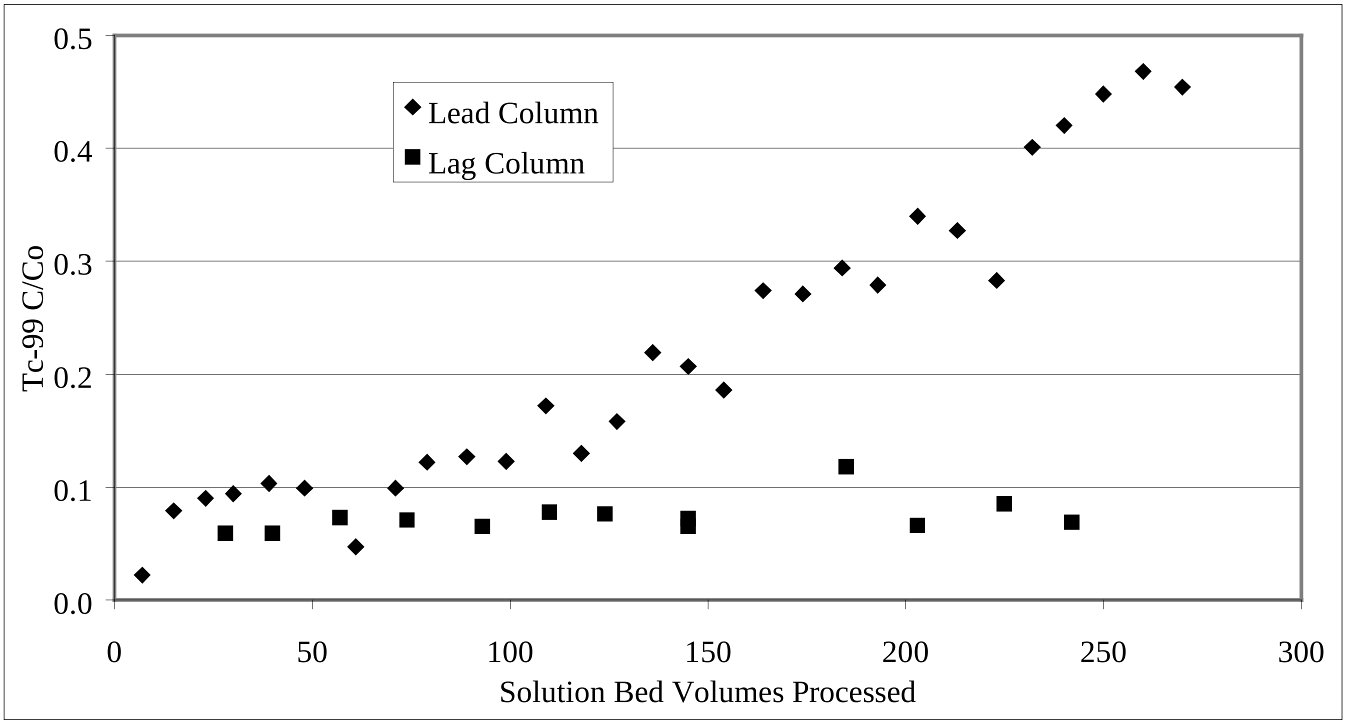

Figure 1. ^{99}Tc Breakthrough Profiles for the AN-103 waste sample. (Column ID: 1.1 cm, Resin Bed: 6 mL, Flow Rate: 3 BV/hr (0.32 cm/min), T = 25 ±2 ºC)

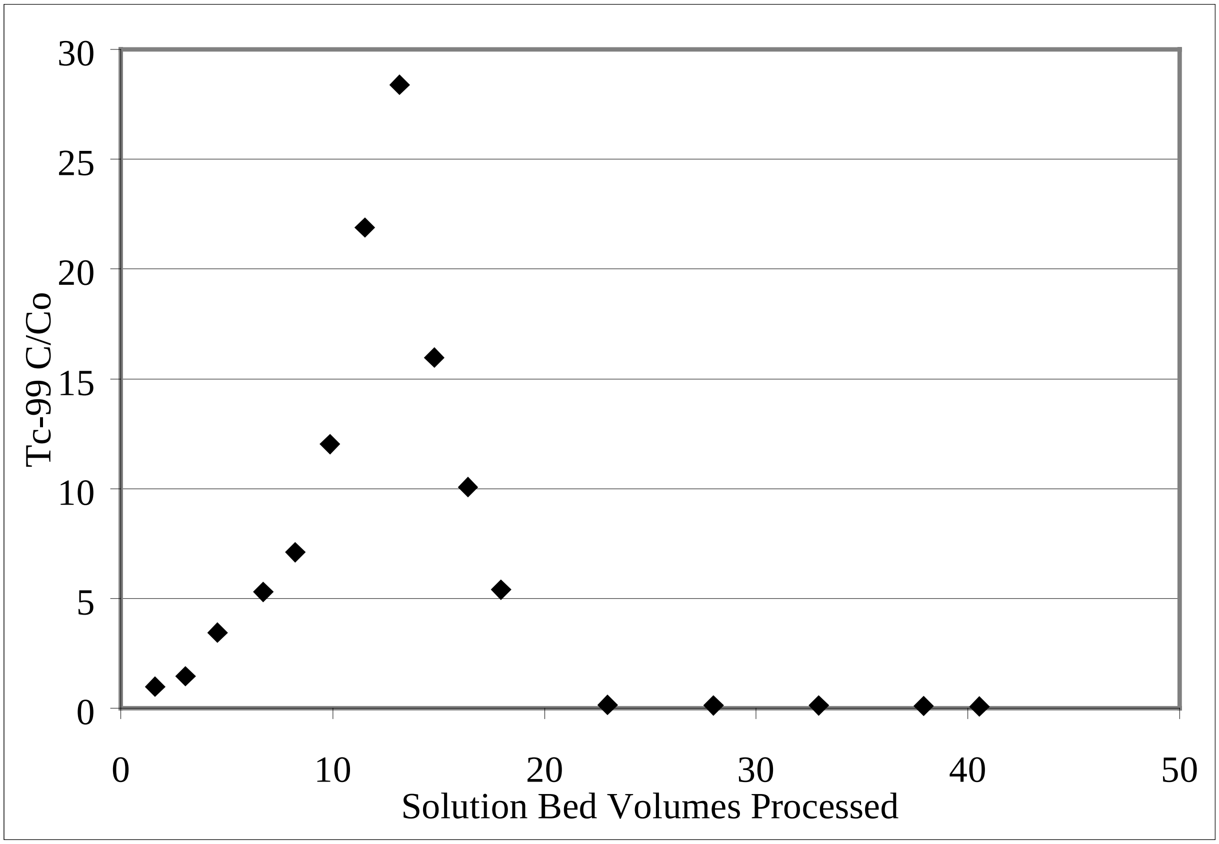

Figure 2. ^{99}Tc Water Elution Profile for the AN-103 waste sample. (Column ID: 1.1 cm, Resin Bed: 6 mL, Flow Rate: 1 BV/hr (0.11 cm/min), T = 25 ±2 ºC)

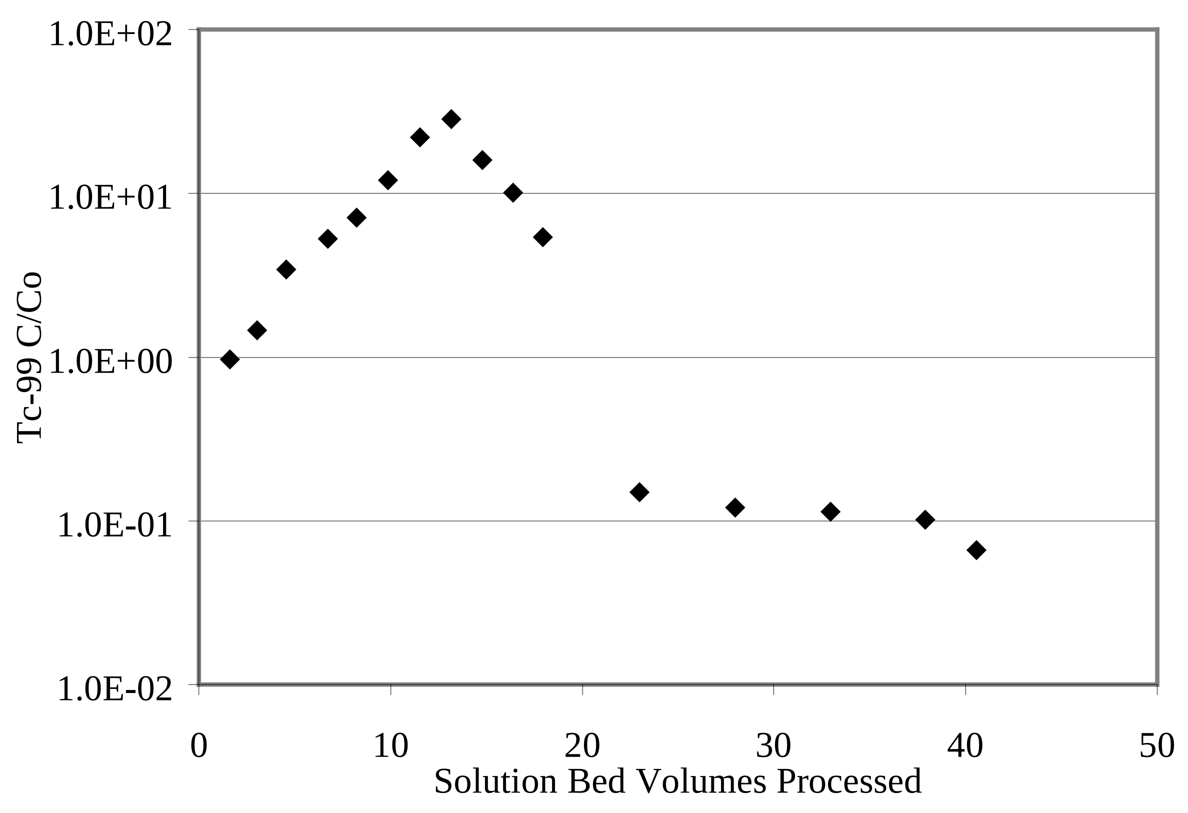

Figure 3. ^{99}Tc Water Elution Profile for the AN-103 waste sample – Semi-log Plot.
(Column ID: 1.1 cm, Resin Bed: 6 mL, Flow Rate: 1 BV/hr (0.11 cm/min), T = 25 ±2 ºC)

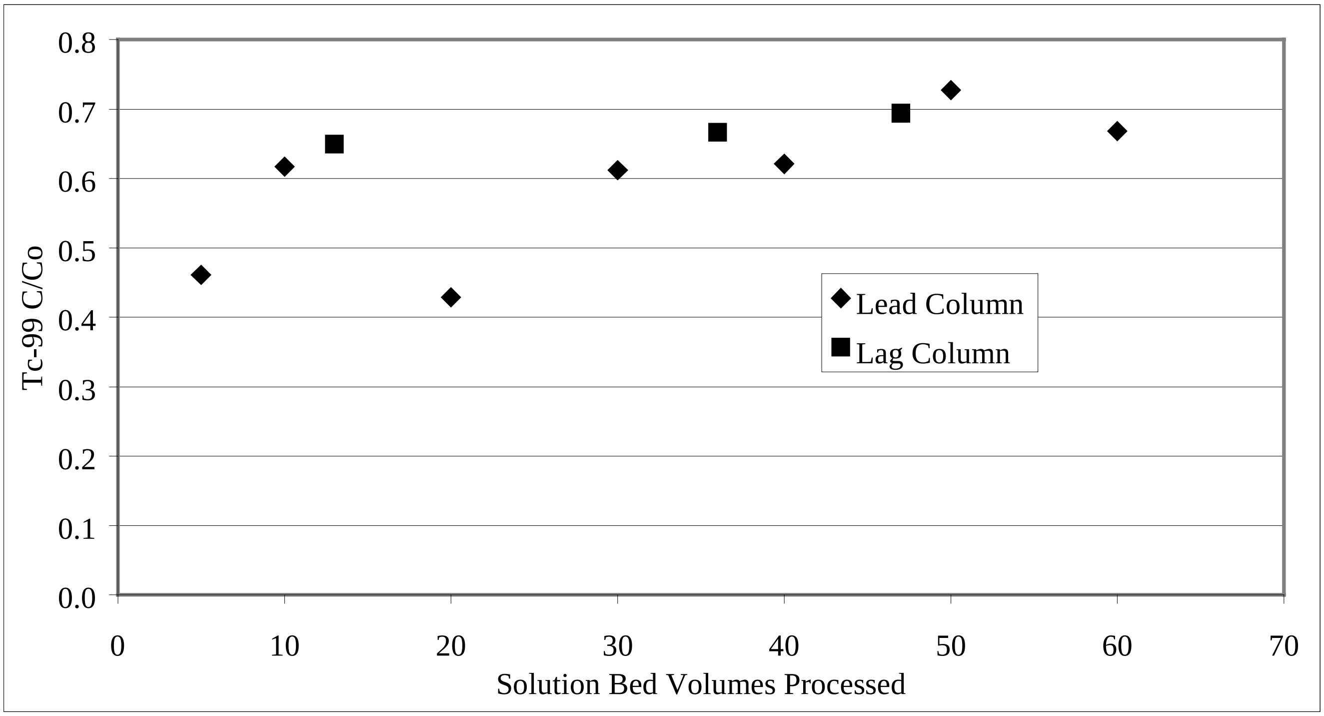

Figure 4. ^{99}Tc Breakthrough Profiles for the AN-102 waste sample. (Column ID: 1.1 cm, Resin Bed: 6 mL, Flow Rate: 3 BV/hr (0.32 cm/min), T = 25 ±2 ºC)

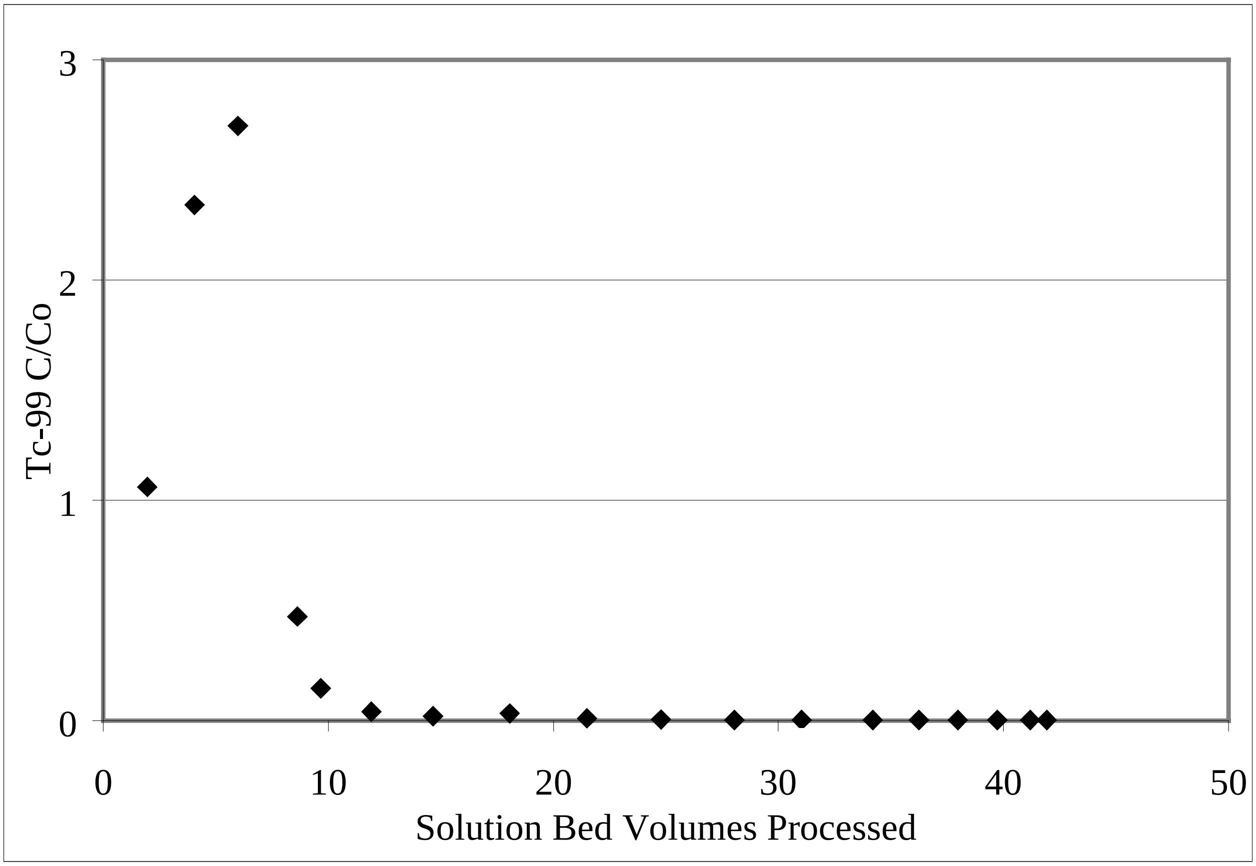

Figure 5. ^{99}Tc Water Elution Profile for the AN-102 waste sample. (Column ID: 1.1 cm, Resin Bed: 6 mL, Flow Rate: 1 BV/hr (0.11 cm/min), T = 25 ±2 ºC)

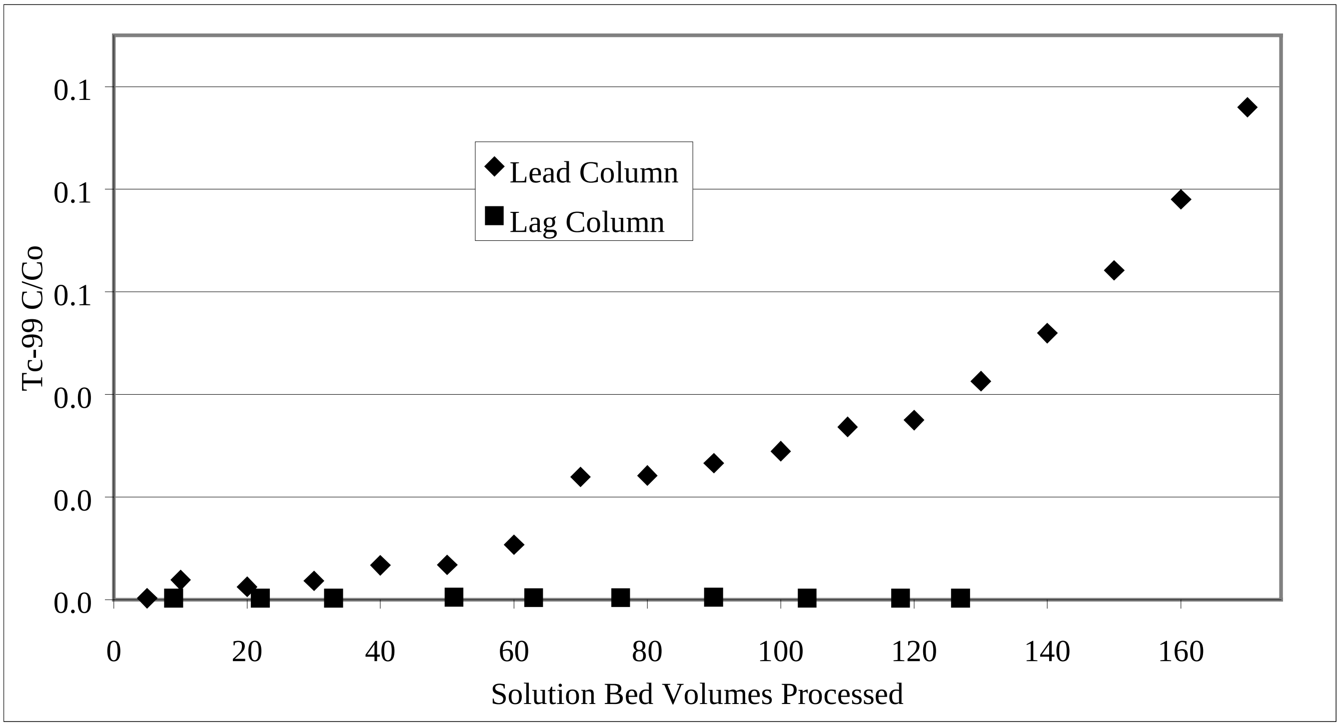

Figure 6. ^{99}Tc Breakthrough Profiles for the AZ-102 waste sample. (Column ID: 1.1 cm, Resin Bed: 6 mL, Flow Rate: 3 BV/hr (0.32 cm/min), T = 25 ±2 ºC)

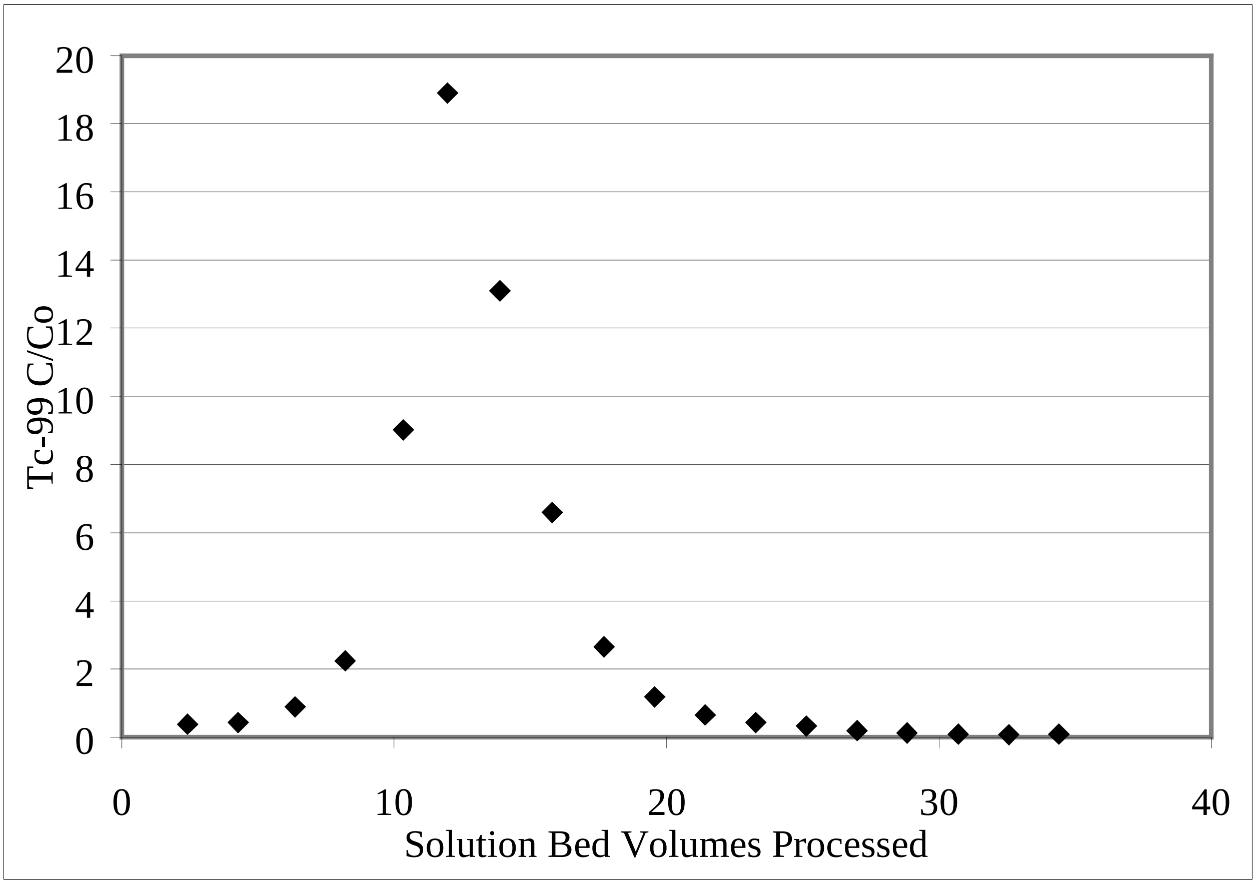

Figure 7. ^{99}Tc Water Elution Profile for the AZ-102 waste sample. (Column ID: 1.1 cm, Resin Bed: 6 mL, Flow Rate: 1 BV/hr (0.11 cm/min), T = 25 ±2 ºC)

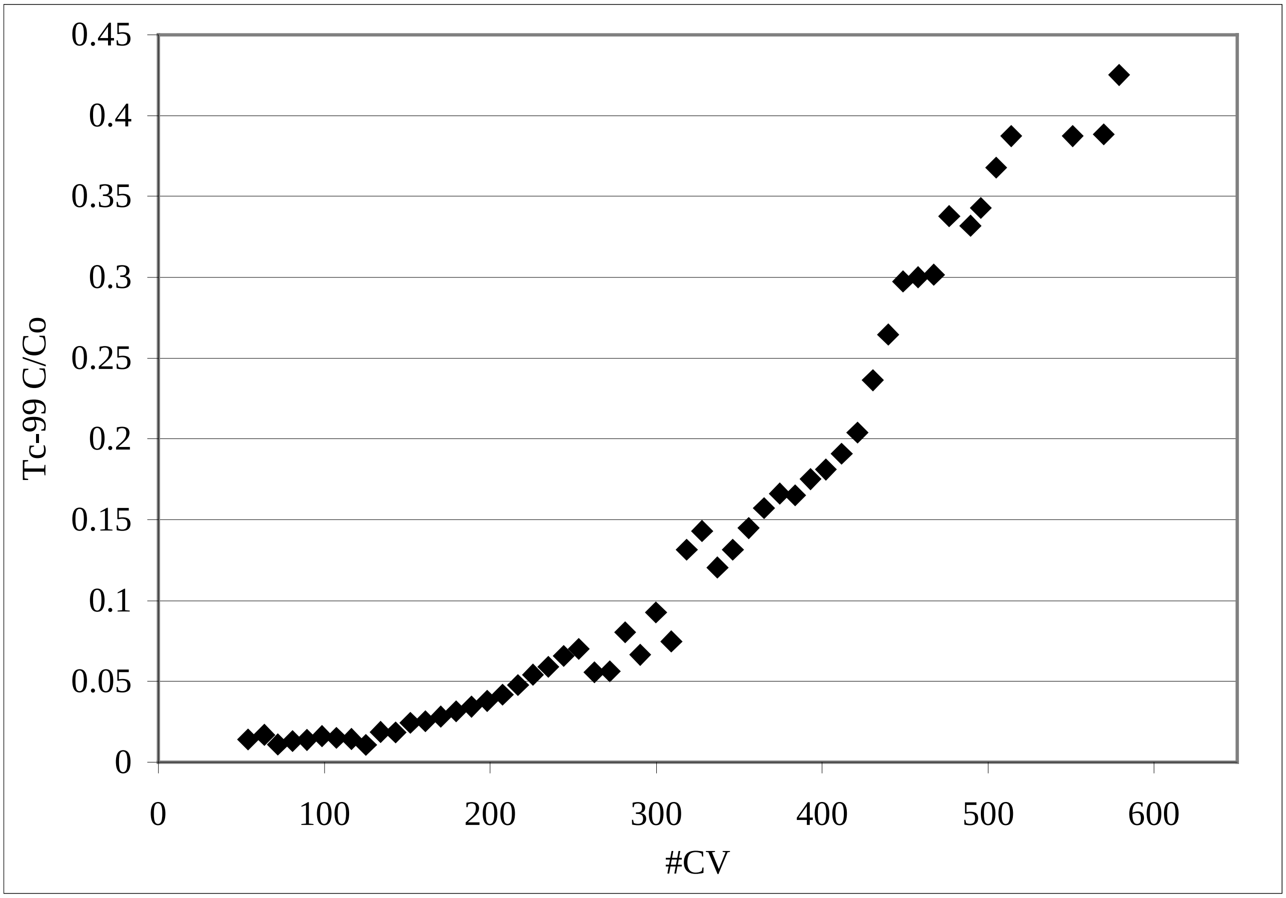

Figure 8. ^{99}Tc Breakthrough Profile for the 44F waste sample. (Column ID: 2.69 cm, Resin Bed: 50.6 mL, Flow Rate: 3 BV/hr (0.45 cm/min), T = 25 ±2 ºC)

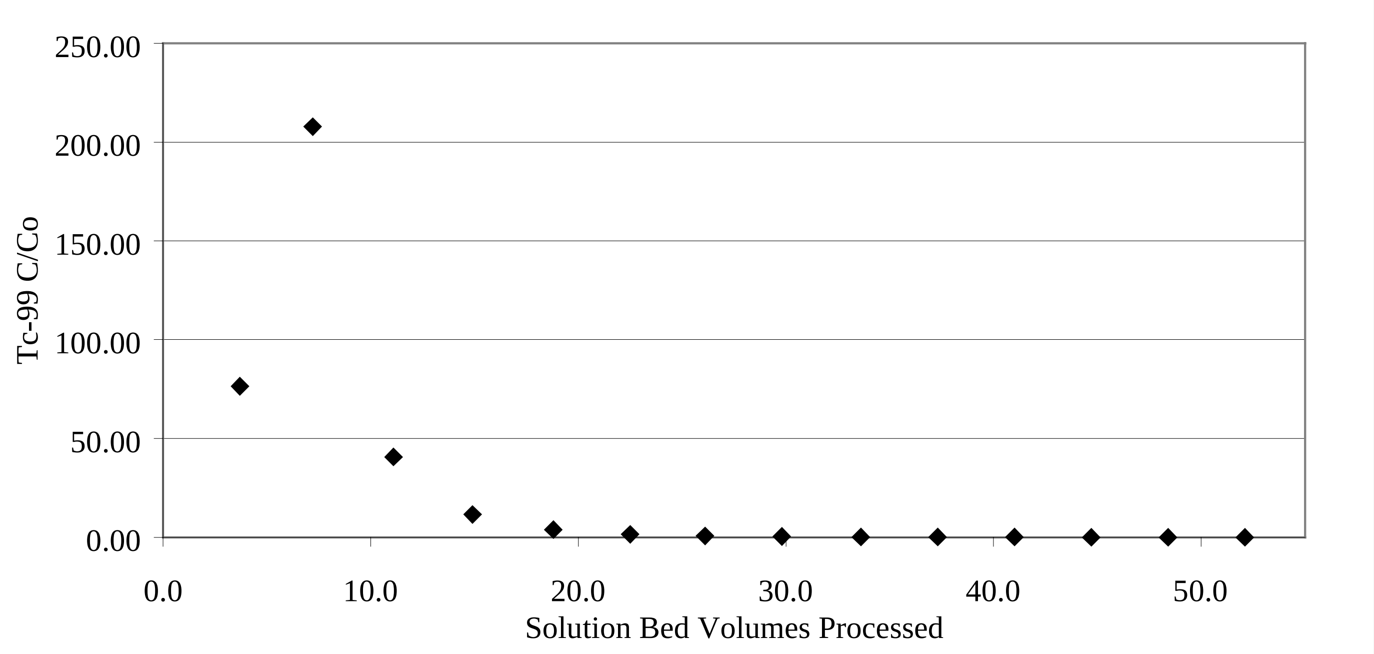

Figure 9. ^{99}Tc Water Elution Profile for the 44F waste sample. (Column ID: 2.69 cm, Resin Bed: 50.6 mL, Flow Rate: 3 BV/hr (0.45 cm/min), T = 25 ±2 ºC)