Intermediate-Scale Ion Exchange Removal of Technetium from Savannah River Site Tank 44 F Supernate Solution

by

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DISCLAIMER

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SUMMARY

As part of the Hanford River Protection Project waste treatment facility design contracted to BNFL, Inc., a sample of Savannah River Site (SRS) Tank 44 F waste solution was treated for the removal of technetium (as pertechnetate ion). Interest in treating the SRS sample for Tc removal resulted from the similarity between the Tank 44 F supernate composition and Hanford Envelope A supernate solutions. The Tank 44 F sample was available as a by-product of tests already conducted at the Savannah River Technology Center (SRTC) as part of the Alternative Salt Disposition Program for treatment of SRS wastes. Testing of the SRS sample resulted in considerable cost-savings since it was not necessary to ship a sample of Hanford supernate to SRS. The baseline Tc removal technology selected by BNFL is SuperLig® 639 ion exchange resin (a proprietary, elutable, organic material). Besides providing important design information for the waste treatment facility to be constructed at Hanford, this test is the first ion exchange column experiment conducted on SRS waste with SuperLig® 639 resin. The Tank 44 F sample had been previously treated with monosodiumtitanate to remove radioactive strontium, filtered, and passed through a column of crystalline silicotitanate (Ionsiv® IE-911) to remove radioactive cesium as part of the Alternative Salt Disposition Program. Batch contact and column tests were performed on the Sr/Cs-decontaminated Tank 44 F supernate with SuperLig® 639 ion exchange resin to remove technetium. A single 24-hour batch contact with the Tank 44 F sample resulted in approximately 89.4% Tc removal (Tc Kd = 950.1 mL/g), indicating that SuperLig® 639 resin has a high capacity for Tc and that the predominate form of Tc in Tank 44 F waste is pertechnetate (TcO_4^-). Only 45% Tc breakthrough was observed after 579 CV (29.3 L) of Tank 44 supernate had been processed through a 50.6 mL column of SuperLig® 639 resin (resin: 50:50 mixture of batches 981015DHC720011 and 990420DHC720067, column ID: 2.7 cm, feed flow rate: 3.1 CV/hr). The column test was highly successful in demonstrating Tc removal from SRS Tank 44 F supernate. The excellent performance is related to the low concentration of nitrate ion in this sample, which is known to compete with pertechnetate on the resin. The Tc was subsequently eluted from the column with water. The bulk of the Tc was eluted from the column within 12 CV after the start of the elution cycle. However, the [Tc] in the eluate did not decrease to within 1% of the feed [Tc] (the current plant design target) until ~50 CV of eluent had been processed. Further work is needed to develop methods to decrease the eluent volume and the elution duration required for SuperLig® 639 columns.

1.0 INTRODUCTION

The pretreatment process for the Hanford River Protection Project contracted to BNFL, Inc. is to provide decontaminated low activity waste and concentrated eluate streams for vitrification into low and high activity waste glass, respectively. The pretreatment includes precipitation and filtration to remove strontium, transuranics, and entrained solids, and ion exchange processes to remove cesium and technetium. The current plant design utilizes SuperLig® ion exchange resins to remove cesium and technetium (the primary radioactive constituents) from the Hanford low activity waste (LAW). This report describes ion exchange testing to remove technetium from a Savannah River Site Tank 44 F waste solution as part of the BNFL Program. Interest in treating the SRS sample for Tc removal resulted from the similarity between the Tank 44 F supernate composition and Hanford Envelope A waste solutions, and the ready availability of the sample as a by-product of Alternative Salt Disposition Program testing at the SRTC.

The conceptualized process for pretreatment of Hanford LAW utilizes SuperLig® 639 ion exchange resin (a proprietary material) for the removal of Tc-99 (pertechnetate form only). SuperLig® 639 is an elutable, organic resin prepared by attaching a highly-selective ion exchange material to preformed polystyrene beads. The resin removes a salt pair (e.g. $NaTcO_4$ and $NaNO_3$) from acidic or basic solutions. Nitrate anion concentration is inversely related to the adsorption of pertechnetate from the contacting solution. Other anions at concentrations typically present in radioactive waste solutions at Hanford and SRS (e.g. OH^-, Cl^-, F^-, CO_3^{2-}, NO_2^-, SO_4^{2-}) do not significantly affect the adsorption of pertechnetate by SuperLig® 639 resin. Lowering the ionic strength of the solution in contact with the resin reverses the technetium adsorption process. In this way, sodium pertechnetate can be eluted from SuperLig® 639 resin using water or dilute nitric acid solution. SuperLig® 639 resin has not been used previously for technetium removal with SRS supernate. The Tank 44 F sample is a "high hydroxide" supernate, containing a considerably lower nitrate concentration and higher hydroxide concentration (0.5 M NO_3^-, 4.5 M OH^-, 5.4 M Na^+) than previous radioactive samples tested with this resin.

Batch contact tests and intermediate-scale column tests (50.6 mL resin bed, 2.7 cm column ID) were performed on the Tank 44 F solution with SuperLig® 639 resin in the Shielded Cells Facility at SRTC. This data will be used as input to a computer model to determine scale-up parameters for actual plant operation. The computer modeling work will be reported in a future document.

2.0 EXPERIMENTAL

2.1 Materials

Three batches of SuperLig® 639 resin were received from IBC Advanced Technologies, American Fork, Utah. All resin samples were composed of tan, spherical beads and were very similar in appearance. Some physical data reported in an earlier document for the SuperLig® 639 resins is provided in Table 1.[1] A batch contact test was performed with Tank 44 F solution (previously treated to separate cesium and strontium) using batch #981015DHC720011. The Tank 44 F column experiment was conducted using a 50:50 mixture (by as-received weight) of batches 981015DHC720011 and 990420DHC720067.

Table 1. Physical Characteristics of "As-Received" SuperLig® 639 Resins

Batch #	Resin particle density (g/mL)	Bulk dry density (g/mL)	Water content (%)
980624001DC	1.219	0.489	1.4
981015DHC720011	1.147	0.468	1.3
990420DHC720067	not measured	0.479	not measured

The Sr/Cs-decontaminated and filtered Tank 44 F sample composition is given in Table 2. The primary waste composition based on analysis is: 5.4 M Na^+, 0.50 M NO_3^-, 0.48 M NO_2^-, 4.5 M Total OH^-, and 0.2 M AlO_2^-. The [Tc] measured by ICP-MS (mass 99) was 3.09 mg/L. Prior to the technetium ion exchange tests, the Tank 44 F sample was treated with monosodium titanate (MST) by batch contact and dead-end filtration to remove strontium and actinides, and crystalline silicotitanate (Ionsiv® IE-911) in column configuration to remove cesium.[2] The Sr/Cs-decontaminated product was stored in a tank in the High Level Cells Facility at SRTC following the conclusion of these tests. The tank was known to contain small amounts of settled MST. A small sample (~60 mL) of solution was removed from the tank and filtered through a Nalgene® nylon filter unit to be used for the batch contact test. Approximately 35 L of solution was pumped from the tank and filtered using an in-line 0.45 micron Whatman Polycap® 75 TF disposable filter capsule with a polytetrafluoroethylene membrane. The filtered liquid was stored in two polyethylene carboys before being pumped into the SuperLig® 639 ion exchange column. The measured density of the solution was 1.202 g/mL. Sodium hydroxide solutions, 1.0 and 0.1 M, were used for column pretreatment and washing, respectively. These solutions were prepared using ACS certified, high-purity NaOH from Fisher Scientific, Inc.

Table 2. Sr/Cs-Decontaminated SRS Tank 44 F Waste Composition

Chemical	Molarity
Na^+	5.40
K^+	5.66E-02
NO_3^-	4.95E-01
NO_2^-	4.76E-01
Total OH^-	4.50
SO_4^{2-}	1.33E-03
PO_4^{3-}	3.12E-03
AlO_2^-	0.2393
F^-	3.38E-04
Cl^-	9.27E-03
$HCOO^-$	2.22 E-3
$C_2O_4^{2-}$	<7.46 E-4

The measured Tc-99 and Cs-137 concentrations were 3.089 mg/L and 1.37 μCi/mL, respectively.

2.2 Equipment and Procedures

2.2.1 Batch Contact Experiments

Duplicate batch contact tests were performed at ambient temperature using an orbital shaker in the High Level Cells Facility at SRTC. Ion exchange resin (0.12 g) and Tank 44 F solution (13.0–13.5 mL) were transferred to a 21 mL polyethylene vial and placed on the shaker. The ratio of solution volume to exchanger mass was ~110. The temperature was measured at the beginning and the end of the experiment (observed range: 25-26 °C). After 24.0 hours, the samples were removed from the shaker. The solution was then filtered through a 0.45 micron Nalgene® nylon filter using vacuum. Visual inspection of the resin after filtration indicated that agitation of the vials during the test did not lead to significant material degradation. Portions (2-4 mL) of the filtrate and similarly-treated samples of the feed solutions (blanks) were analyzed for technetium by the Savannah River Technology Center Analytical Development Section using ICP-MS. Data for the batch contact test is provided in Attachment 1. The Tc distribution coefficient (K_d) and % removal were calculated using the formulas shown in Eqs. 1 and 2, respectively.

$$K_d = [(C_i/C_f) - 1][V/(M*F)] \quad (1)$$

$$\% \text{ removal} = \frac{(100)*(C_i - C_f)}{C_i} \quad (2)$$

C_i = initial [Tc] in feed (mg/L)
C_f = final [Tc] after contact (mg/L)
V = volume of solution used (mL)
M = mass of "as-received" resin (g)
F = resin dry weight correction factor

An F-factor of 98.7% was used to calculate the K_d based on the data reported in Table 1 for batch #981015DHC720011.

2.2.2 Column Experiments

Figure 1 shows the ion exchange column design. A photograph of the actual equipment is shown in Figure 2. Although the BNFL design uses a lead and a lag column, a single ion exchange column was used for treating the Tank 44 F sample, since the primary purpose of this test was to develop the loading profile for the lead column. The ion exchange column was constructed from 2.7 cm ID sodium borosilicate glass tubing. Decals were affixed to the outer wall of the column with 1 mm graduations to measure the resin bed height. The outside of the column was coated with a layer of polyvinylchloride to reduce hazards associated with potentially pressurizing the apparatus. A 3-way, Whitey® 40 Series stainless steel ball valve (#1) was attached to the bottom of the columns. The column head was attached to the column using a Rudivis® ground-glass joint. Two 2-way, stainless steel ball valves (#2 and #3) were attached on opposite sides of the column head to serve as feed ports. The column head also contained a pressure gauge, a pressure relief valve, and a fill reservoir that also served as a vent. The valves were connected to the columns by high-density polyethylene bushings with Viton® O-rings. Swage-lock® fittings were used to connect the valves to low-density polyethylene tubing (11/64" ID) which served as column feed and effluent lines. Stainless steel wire screens (200 mesh) were inserted into the columns to support the ion exchange resin. All solutions were passed through the columns in the downflow direction using Fluid Metering Incorporated QG150 positive displacement pumps with ¼ and $^3/_8$-inch piston sizes. Samples were collected manually at the end of the effluent collection line (see Figure 2) rather than with the manual sample port located at the bottom of the column. The manual sample port was only used to drain the liquid head from the column at specific times during column operation as described in the technical task plan.[3]

A 50.6 mL sample of ion exchange resin was prepared by mixing 11.9889 g of "as-received" SuperLig® 639 resin batch #981015DHC720011 and 12.0010 g of resin batch #990420DHC720067 in a polyethylene bottle. A 50:50 mixture of these resin batches was also used for pilot-scale simulant column tests conducted at SRTC.[4] The resin was soaked overnight in deionized water and transferred into the ion exchange column as a suspension. The measured height of the resin bed in the column just after packing of the resin was 8.75 cm (1 column volume = 50.6 mL, based on 2.7 cm column ID). Quartz wool and glass beads were then added to the top of the resin bed to keep the resin from floating when processing the Tank 44 F sample. A brief simulant experiment was

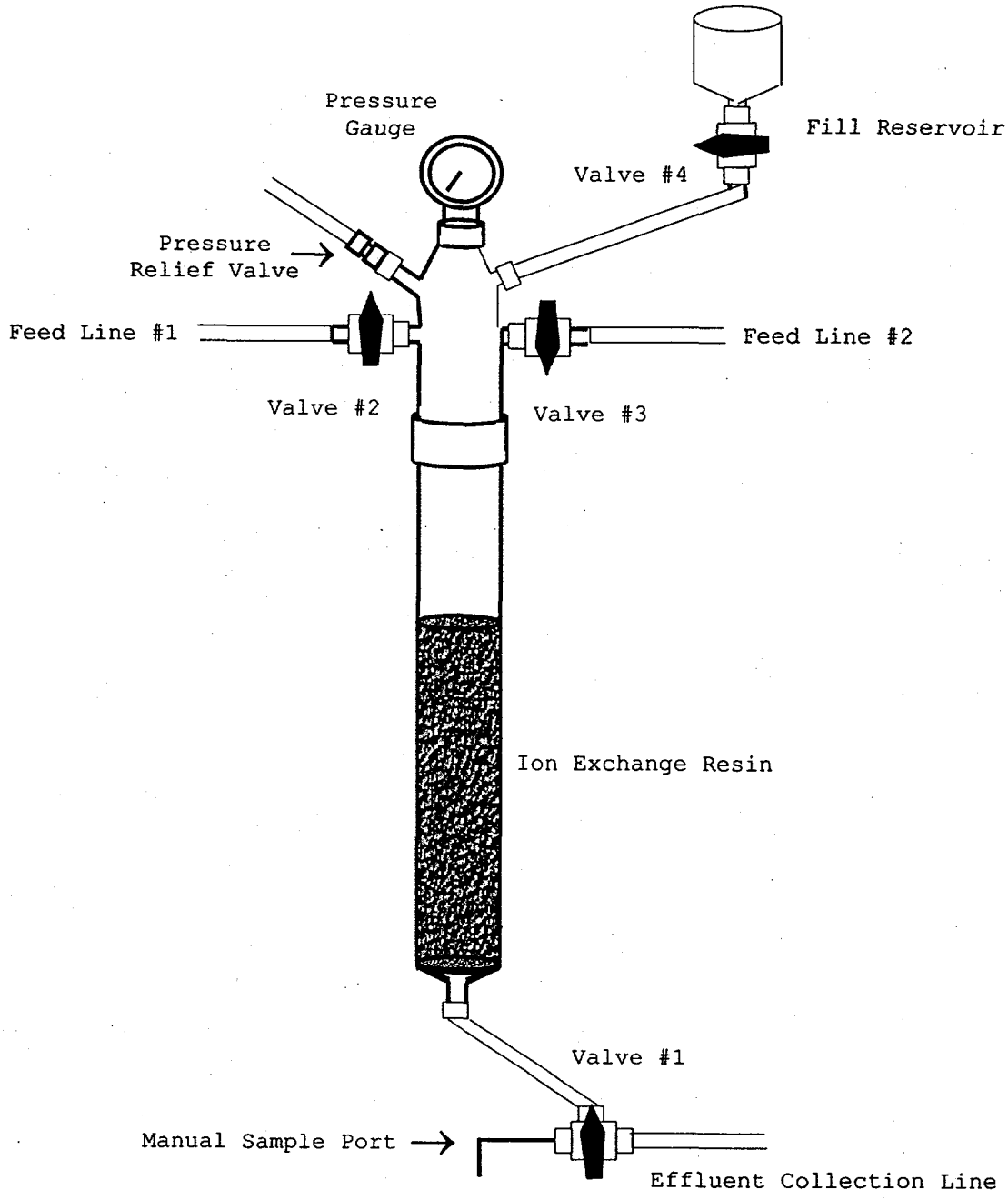

Figure 1. Ion Exchange Column Design

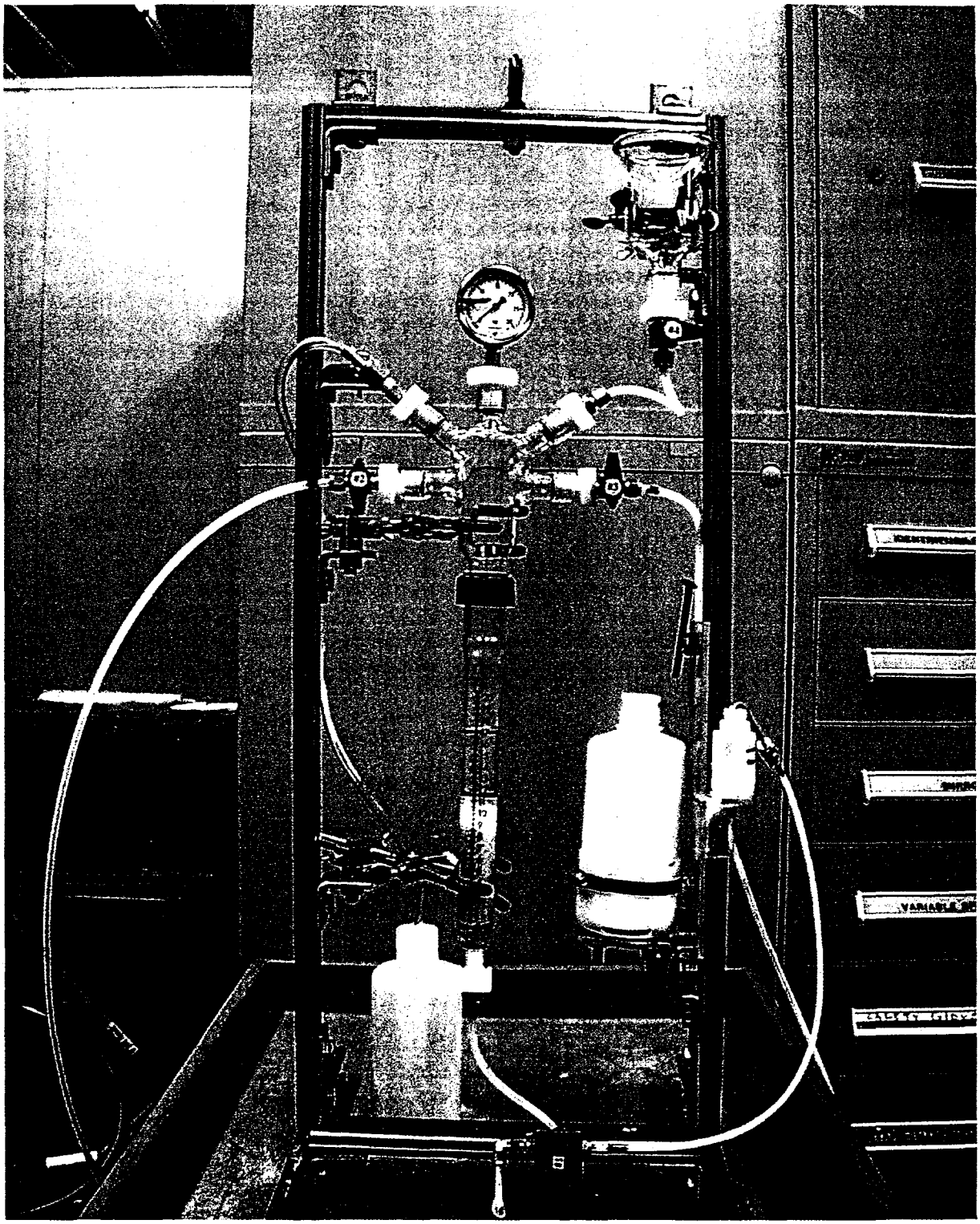

Figure 2. Tank 44 F Technetium Ion Exchange Column Apparatus

performed using a simple Tank 44 F simulant spiked with perrhenate in order to confirm that the column was packed well and would not channel. Approximately 20 CV of simulant was passed through the column. Analysis indicated good column performance with no indication of channeling or early breakthrough of perrhenate. The perrhenate was then thoroughly eluted from the column with water and the column was stored in water for transport to the High Level Cells Facility.

In the High Level Cells, the resin bed was pretreated with 3 column volumes of 1.0 M NaOH over a 1 hour period just prior to beginning the column experiment (Pretreatment Cycle). The NaOH liquid level was adjusted so that the volume of liquid above the resin bed was approximately 50 mL (~1 column volume) before Tank 44 F solution was pumped into the column (see note below). While pumping the Tank 44F solution downflow through the column, samples (10 mL) of effluent were collected approximately every 10 column volumes and the effluent from the column was collected in 1 L bottles in ~20 CV increments (Feed Cycle). After processing all of the Tank 44F solution, the liquid in the column was drained to within approximately 1 cm of the glass beads located on top of the resin bed. Sodium hydroxide solution (0.1 M) was pumped into the column until the volume of liquid above the resin bed was approximately 50 mL. The exit line was opened and 2.5-3.5 column volumes of 0.1 M NaOH was passed through the column in one hour and samples of the effluent were collected every 20 minutes (NaOH Wash Cycle). Wash samples were analyzed for Tc-99 by ICP-MS, Na^+ by ICP-ES, and Free OH^-. The column was eluted with deionized water at a flow rate of 1 column volume per hour. Every 4 hours (4 CV) a sample was collected and the eluate collection bottle was changed (Elution Cycle). Samples were analyzed for technetium by the Savannah River Technology Center Analytical Development Section using ICP-MS. Data from the column experiment is provided in Attachment 2. The cell air temperature during the column experiment ranged from 23-27 °C.

The flow rate was monitored during the column experiments by measuring the time required to collect 5-10 mL samples of effluent. At the conclusion of the experiment, the weight of effluent collected in each 1 L bottle was measured and the volume of the solution was calculated from the density (1.202 g/mL). After correction for the volume of samples collected, the flow rate was calculated from the time of collection for each bottle. The overall flow rate was taken to be the average of the flow rates calculated for each collection bottle. The flow rate calculated for the Feed Cycle was 3.1 CV/hr (superficial velocity: 0.45 cm/min). The minimum and maximum flow rates measured during the Feed Cycle were 2.7 and 3.2 CV/hr (0.39 and 0.46 cm/min), respectively. The flow rate for the elution cycle was calculated by the same method to give an average flow rate of 0.93 CV/hr (0.14 cm/min). The minimum and maximum flow rates measured during the Elution Cycle were 0.88 and 0.99 CV/hr (0.13 and 0.15 cm/min), respectively. The number of column volumes of solution processed at each sampling period during column operation was calculated from the time of collection and the flow rate measured for the corresponding collection bottle.

Note: The column operating procedure was designed to emulate the actual plant operation, where the column is half full of resin and half full of liquid. According to the procedure, the initial feed that was pumped into the ion exchange column during the Feed

Cycle was to be diluted by the 1 CV of 1.0 M NaOH pretreatment solution which remained above the resin bed. Likewise, the eluting solution was allowed to mix with the liquid head left above the resin from the NaOH Wash Cycle. No attempt was made to correct for mixing of solutions in the column head-space when calculating the number of column volumes of feed, wash, or eluate processed. The Feed and Elution cycles were considered to start at the moment that the feed and eluent solutions entered the column head. The NaOH Wash Cycle began at the moment that the valve was opened to the effluent collection line after the liquid head had been reestablished.

3.0 RESULTS AND DISCUSSION

3.1 Batch Contact Experiment

A 24 hr batch contact experiment was conducted with SuperLig® 639 resin batch #981015DHC720011 in order to determine the resin volume needed for the technetium ion exchange column experiment. The average K_d value calculated from duplicate batch contacts was 950.1 mL/g which corresponds to 89.4% technetium removal. The result indicates that at least 89.4% of the Tc in the Tank 44 F sample exists as pertechnetate anion (TcO_4^-) and confirms that SuperLig® 639 resin efficiently removes technetium from Tank 44 F waste during batch contact.

A rough estimate of the 50% Tc breakthrough point in SuperLig® 639 (batch #981015DHC720011) ion exchange columns can be predicted from the K_d and the bulk resin density. The bulk resin density for batch #981015DHC720011 was reported by SRTC to be 0.489 g/mL.[1] The number of column volumes of feed estimated to reach 50% Tc breakthrough (λ) can be calculated using Eq. 3.

$$\lambda = (K_d) \times (\text{bulk resin density}) \qquad (3)$$

The λ value calculated with Eq. 3 is 465 CV. Based on the λ value and the volume of solution to be processed it was decided to use ~50 mL of resin for the column experiments. The 50% Tc breakthrough point would be expected after processing ~23 L of Tank 44 F solution with a 50 mL bed of SuperLig® 639 resin (batch #981015DHC720011).

3.2 Column Experiment

Results from the column experiment performed with the 50.6 mL SuperLig® 639 resin bed and Sr/Cs-decontaminated Tank 44 F solution are shown in Figure 3. A 50:50 mixture (by as-received weight) of resin batches 981015DHC720011 and 990420DHC720067 was used to prepare the column. Based on previous simulant batch contact experiments performed on these SuperLig® 639 resin batches, better column performance was expected than predicted by the λ calculation above.[5] Perrhenate anion (ReO_4^-) K_d values measured for batch #990420DHC720067 at a Re feed concentration of

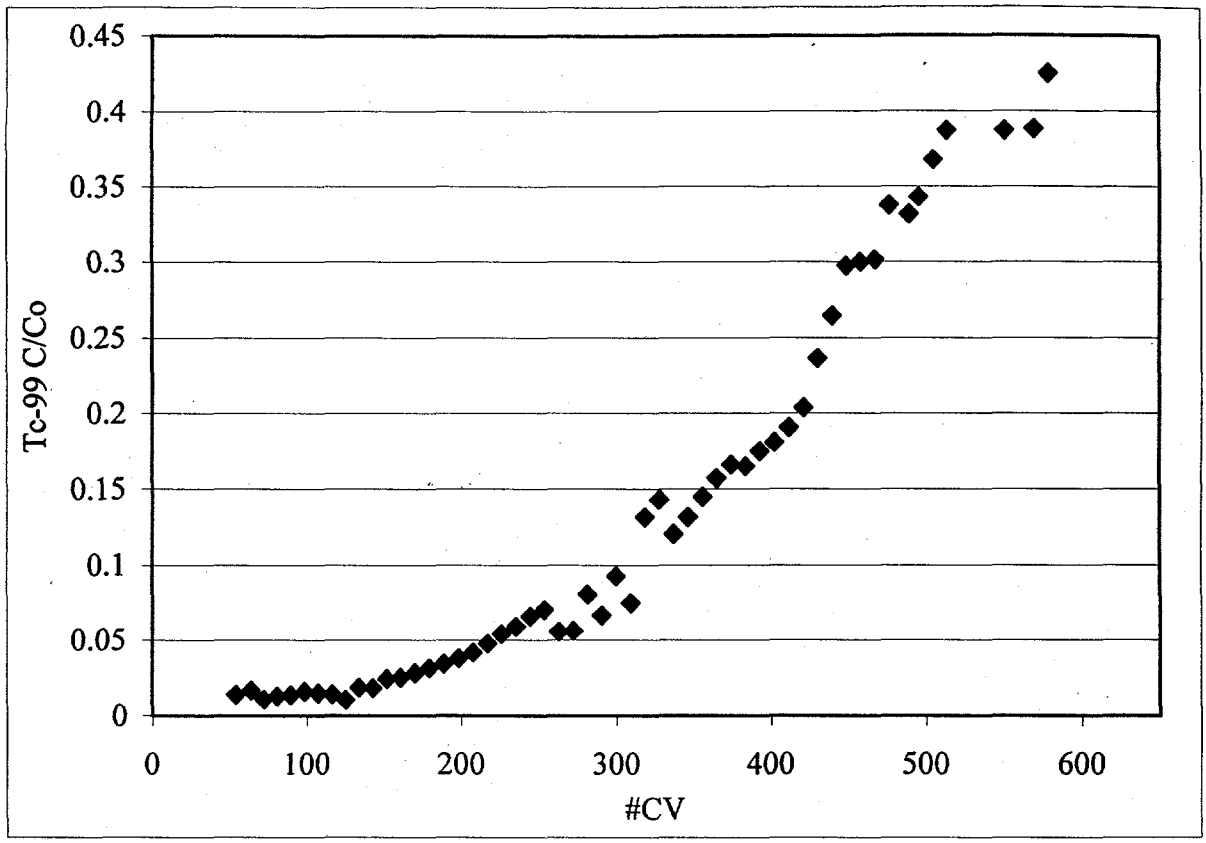

Figure 3. SuperLig® 639 Column Technetium Breakthrough Profile with SRS Tank 44 F Solution (resin batches: 981015DHC720011 and 990420DHC720067, flow rate: 3 CV/hr, T = 23-27 °C.)

3.8 E-5 M (Hanford Env. A simulant) were 31% higher than those observed for batch #981015DHC720011 at a similar initial Re concentration. (The [Tc] in the Sr/Cs-decontaminated Tank 44 F waste was 3.1 E-5 M.) At a feed flow rate near 3 CV/hr, ~45% Tc breakthrough was observed after 579 CV (29.3 L) of Tank 44 F solution had been processed. This result is consistent with the 50% Tc breakthrough that would be expected after increasing the calculated λ value above by 15.6% (λ_{corr} = (465) x (1.156) = 538 CV) due to the higher measured capacity of SuperLig® 639 batch #990420DHC720067. (**Note**: An additional 8 CV of Tank 44 F solution was processed prior to stopping the Feed Cycle, but no additional samples were collected for analysis. The total volume of Tank 44 F solution processed was 29.7 L or 587 CV.) The lower than expected Tc-99 C/Co values observed at 260-320 CV and 550-570 CV cannot be explained based on any processing anomalies. Integration of the Tc breakthrough curve in Figure 3 indicates that approximately 78 mg of Tc were adsorbed onto the resin during the Feed Cycle out of a total of 91 mg of Tc in the feed solution. This corresponds to a decontamination factor of 7.1 for the single column. **Note:** The sample appears to contain very little material with an atomic mass of 99 that cannot be removed by the resin. The first effluent sample, which was collected after 54 CV of solution were processed, contains 0.0436 mg/L of a mass 99 element, which is 1.4 % of the initial concentration. Theoretically, this could be pertechnetate, a non-pertechnetate form of technetium, or Ru-99.

Following the Feed Cycle, the liquid head was drained from the column and then reestablished with 1 CV of 0.1 M NaOH. The column was washed with 3 CV of 0.1 M NaOH over a 1 hour period. The effluent during the Wash Cycle was collected in approximately 1 CV increments and analyzed for Tc-99, Na^+ and Free OH^-. Analysis results are shown in Table 3. The results reveal that Tc begins to elute from the column during the NaOH wash. The [Tc] in the first CV of wash solution collected (1.8 mg/L Tc-99) is comparable to the last effluent samples analyzed during the Feed Cycle (~1.3 mg/L Tc-99). The [Tc] in the second and third wash fractions gradually increased to 2.8 mg/L, which approaches the feed Tc concentration (3.1 mg/L). However, the total amount of Tc-99 removed from the column during the 0.1M NaOH feed displacement was only ~0.35 mg or 0.45% of the total Tc-99 estimated to be loaded onto the resin. As expected, the Na^+ and free OH^- concentrations decrease in successive wash fractions to 0.34 and 0.21 M, respectively. These values approach the initial concentrations of these species in the 0.1 M NaOH wash solution.

Table 3. Characterization of SuperLig® 639 Column Post-Feed 0.1 M NaOH Wash Solutions

CV	Tc-99 (mg/L)	Na^+ (M)	Free OH^- (M)	Tc99 (mg)	Tc99 Loss
1	1.774	5.06	3.68	0.09	0.12%
2	2.365	2.26	1.53	0.12	0.15%
3	2.755	0.339	0.211	0.139	0.18%

Figures 4 and 5 show the Tc elution profile resulting from elution of the column with deionized water at a flow rate of 1 CV/hr. Analysis indicated that the Tc concentration in the eluate peaked after 4-7 CV of eluate had been collected. The actual peak in the Tc concentration is uncertain since eluate samples were only collected at ~4 CV intervals. The pertechnetate elution peak is consistent with perrhenate elution profiles observed with simulated Hanford Envelope A solutions and SuperLig® 639 resin (Re eluate peak concentrations: 2-5 CV).[5] The majority of the Tc eluted from the column in the first 12 CV of eluate and then the [Tc] gradually decreased. The Tc concentration in the eluate did not reach the plant design criteria of 1% of the feed until approximately 50 CV of eluate had been processed. The column was stored in deionized water at the conclusion of the elution.

After the completion of the column experiment, the first 37.3 CV of Tc eluate were combined in a single polyethylene carboy and the solution was allowed to mix for several days. The remaining ~15 CV of eluate contained an estimated 0.1 mg of Tc based on integrating the elution data presented in Figure 5. Since this amount of Tc is not significant, little error was introduced by analyzing only the first 37.3 CV of eluate. Attachment 3 shows the analysis results for the composited eluate. Based on ICP-MS analysis, the eluate (total volume: ~1.83 L; Note: The total eluate volume is less than 37.3 CV due to the volume of samples collected.) contained ~41.6 mg/L Tc which corresponds to a total of 76 mg Tc (97.5% of the total Tc adsorbed on the resin during the Feed Cycle). There is moderate agreement (~15%) between the ICP-MS and ICP-ES

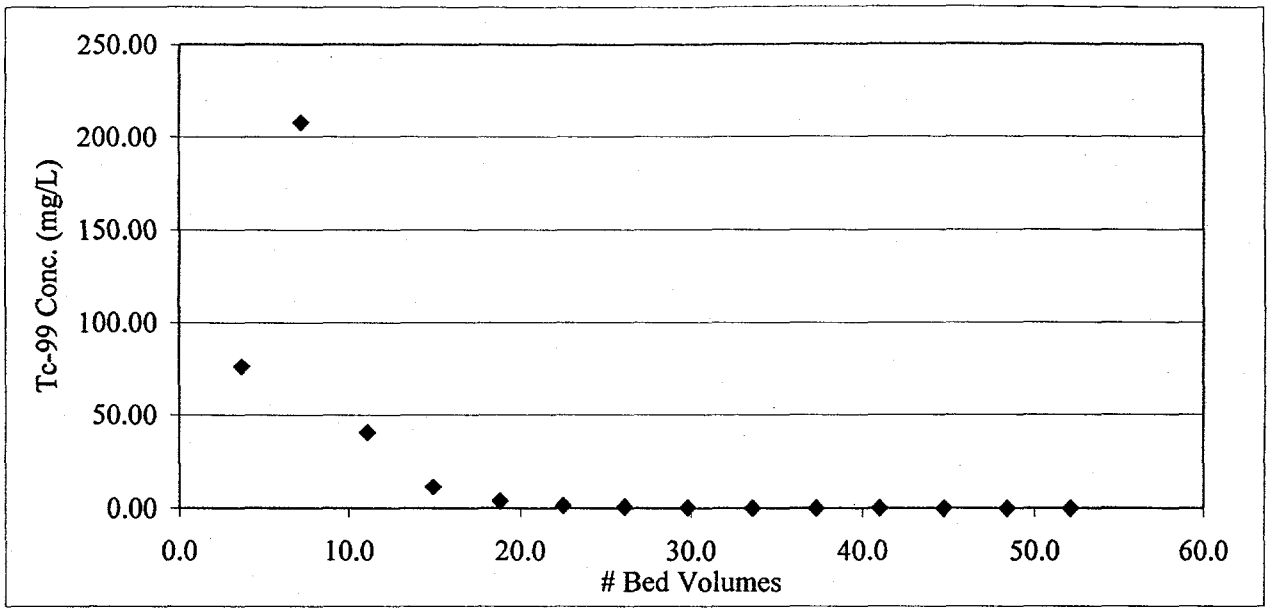

Figure 4. SuperLig® 639 Column Technetium Elution Profile with SRS Tank 44 F Solution (resin batches: 981015DHC720011 and 990420DHC720067, eluent: water, flow rate: 1 CV/hr, T = 23-27 °C.)

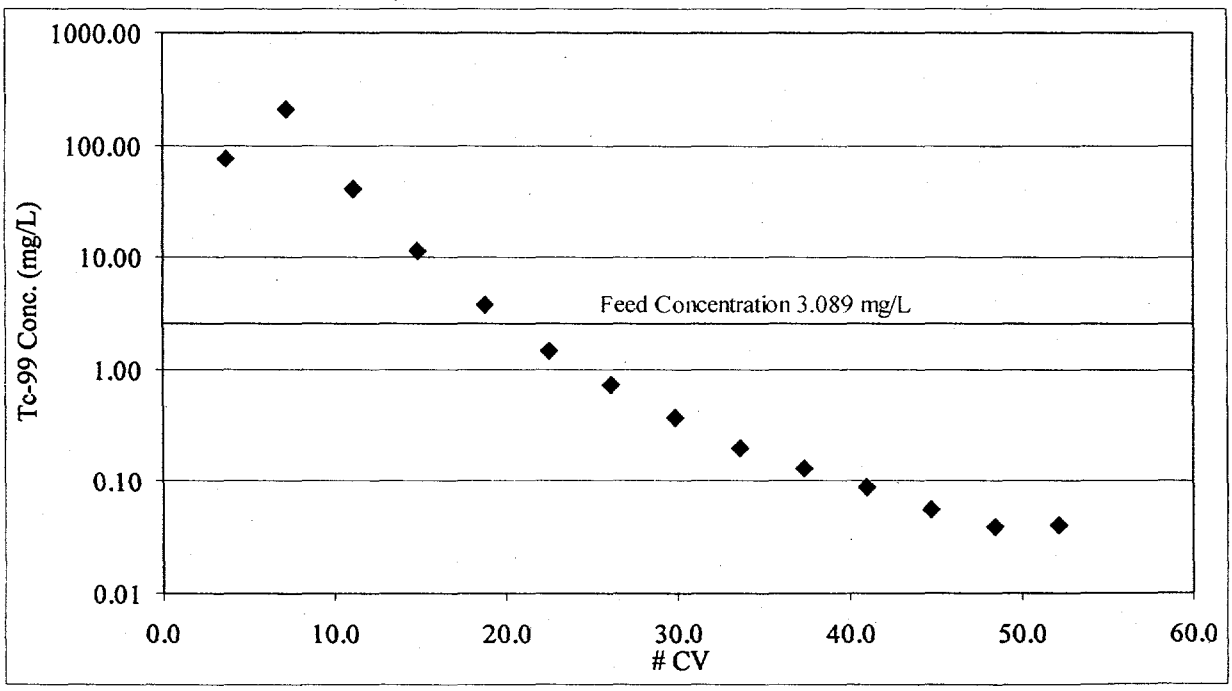

Figure 5. SuperLig® 639 Column Technetium Elution Profile with SRS Tank 44 F Solution Semi-Log Plot (resin batches: 981015DHC720011 and 990420DHC720067, eluent: water, flow rate: 1 CV/hr, T = 23-27 °C.)

analyses of the Tc in the eluate (41.6 vs. 35.5 mg/L, respectively). Use of ICP-ES for Tc analysis has been developed at SRTC for this program. In general, consistent analysis results were observed between duplicate samples for all analysis techniques. However, chloride ion concentration in the eluate varied considerably between the two analysis techniques used. Ion chromatography (IC) analysis indicated that chloride levels were <500 mg/L. In contrast, ion selective electrode (ISE) analysis indicated that the chloride concentration was near 1150 mg/L (2101 mg Cl^-), which corresponds to ~22% of the total chloride in the feed. No chloride analysis was conducted on the column effluent. These observations indicate that chloride anion may be concentrated by the technetium ion exchange resin, but the analysis techniques in these complex mixtures are variable. Alternatively, the "as-received" SuperLig® 639 resin may have contained residual chloride ion which leached off during the water elution. High chloride ion concentration in SuperLig® 639 technetium eluates has been reported previously for ion exchange column experiments performed on Hanford waste supernates.[6] It is also noted that silicon is concentrated by the resin. This may be attributable to high Si concentrations in the feed due to leaching from Ionsiv® IE-911. Alternatively, the Si concentration may have been high in the original Tank 44F sample, prior to treatment with Ionsiv® IE-911.

After analysis of the eluate samples confirmed that the column had been fully eluted, the water storage solution was drained from the column and the resin was partially dried by purging the system with compressed air. The column head was removed and resin samples were collected from the top of the bed. Duplicate samples of resin particles were submitted for analysis along with two samples of "as-received" resin. All resin samples were dissolved by acid digestion and analyzed by ICP-ES. Analysis results are shown in Attachment 4. In general, the analysis results for the resin used in the Tank 44 F column experiment were similar to the results for the "as-received" resin. The sodium weight % was higher by a factor of ~5.5 for the resin used in the column experiment relative to the "as-received resin". The lead content reported for the "as-received" resin is higher than expected, but the value reported (~0.1 wt. %) is very near the minimum detection limit. ICP-ES results reported for additional samples of "as-received" resin which were digested and analyzed at a lower dilution factor, indicated that the lead content was less than 0.0050 wt. % (Attachment 4). Similar results were observed for several other metals. These observations are corroborated by analyses of "as-received" resin at Pacific Northwest National Laboratory.[7] It is concluded that the high values reported for these metals were an artifact of the large dilution of the sample and are not accurate. Most importantly, no measurable amounts of Tc were found in the resin samples from the column experiment.

4.0 CONCLUSIONS

Batch contact and column tests completed on the Sr/Cs-decontaminated SRS Tank 44 F supernate confirmed that SuperLig® 639 resin efficiently removes technetium from this solution. The observed column performance far exceeds the current plant design criteria, which requires a minimum of 100 CV of feed to be processed prior to elution and regeneration. (The current BNFL design criteria utilizes two columns in a lead/lag

configuration and required column regeneration at 50% Tc breakthrough from the lead column.) However, synthesis of the resin should be modified to increase the density to avoid floating the resin bed while processing these dense feed solutions. Additional research is also needed to identify the manufacturing variables that affect resin capacity and develop methods for its optimization. The column was effectively eluted with water at a flow rate of 1 CV/hr. Further work is needed to evaluate methods for reducing column elution duration and volume. These may include heating the water used for elution (as recommended by IBC personnel), slowing the elution flow rate after the first several column volumes, or periodically stopping the flow during the elution to allow the resin to continue to desorb technetium without generating more eluate volume.

5.0 DESIGN CHECK

M. C. Thompson 7/29/00
M. C. Thompson Date

6.0 QUALITY ASSURANCE

McCabe, D. J. *Intermediate Scale Radioactive Ion Exchange Task Technical and Quality Assurance Plan (U)*, BNF-003-98-0165, Rev. 0.

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8.0 APPENDIX

8.1 Attachment 1. SuperLig® 639 Batch Contact Data

SuperLig® 639 K_d Measurements		
ICP-MS Analysis		
Resin Batch #981015DHC720011		
Sample #	SRS-1	SRS-1-D
ADS #	300132736	300132737
Solution Mass (g)	15.94	16.22
Resin Mass (g)	0.1217	0.1201
Solution Volume (mL)	13.28	13.52
Initial Tc Conc. (mg/L)	3.09	3.09
Final Tc Conc. (mg/L)	0.3274	0.32567
Kd (mL/g)	**932.8**	**967.5**
solution volume/exchanger mass	109.15	112.55
Shake Time (hrs)	**24.0**	
Temperature (C)	27-28	
Average Kd (mL/g)	**950.1**	
% Tc removal	89.4	89.5
average % Tc removal	89.4	
Feed		
Sample	SRS-1-FD	
ADS #	300132738	
Tc-99 mg/L	3.09	

8.2 Attachment 2. SuperLig® 639 Column Data

Feed Cycle (ICP-MS Analysis)
Co = 3.1 mg/L Tc-99

ADS #	3-134403	3-134404	3-134405	3-134406	3-134407	3-134408	3-134409	3-134410	3-134411	3-134412
mg/L (Tc-99)	0.04361	0.05267	0.03390	0.04042	0.04317	0.04986	0.04669	0.04453	0.03351	0.05785
#CV	54.0	63.8	72.0	80.7	89.7	98.6	107.4	116.3	125.1	134.0
C/Co (Tc-99)	0.014	0.017	0.011	0.013	0.014	0.016	0.015	0.014	0.011	0.019
ADS #	3-134413	3-134414	3-134415	3-134416	3-134417	3-134418	3-134419	3-134420	3-134421	3-134422
mg/L (Tc-99)	0.05718	0.07576	0.07890	0.08757	0.09757	0.10645	0.11754	0.12948	0.14815	0.16787
#CV	142.8	151.9	161.0	170.2	179.4	188.8	198.3	207.5	216.7	225.9
C/Co (Tc-99)	0.018	0.024	0.025	0.028	0.031	0.034	0.038	0.042	0.048	0.054
ADS #	3-134423	3-134424	3-134425	3-134426	3-134427	3-134428	3-134429	3-134430	3-134431	3-134432
mg/L (Tc-99)	0.18317	0.20364	0.21771	0.17298	0.17450	0.24934	0.20615	0.28745	0.23195	0.40778
#CV	235.1	244.2	253.3	262.7	272.1	281.2	290.4	299.8	309.1	318.4
C/Co (Tc-99)	0.059	0.066	0.070	0.056	0.056	0.080	0.067	0.093	0.075	0.132
ADS #	3-134433	3-134434	3-134435	3-134436	3-134437	3-134438	3-134439	3-134440	3-134441	3-134442
mg/L (Tc-99)	0.44362	0.37310	0.40770	0.44875	0.48767	0.51517	0.51168	0.54334	0.56153	0.59163
#CV	327.7	336.9	346.1	355.5	365.0	374.3	383.6	392.9	402.1	411.6
C/Co (Tc-99)	0.143	0.120	0.132	0.145	0.157	0.166	0.165	0.175	0.181	0.191
ADS #	3-134443	3-134444	3-134445	3-134446	3-134447	3-134448	3-134449	3-134450	3-134451	3-134452
mg/L (Tc-99)	0.63235	0.73237	0.81977	0.92183	0.93025	0.93441	1.04700	1.02883	1.06327	1.14033
#CV	421.2	430.5	439.8	448.8	457.9	467.2	476.5	489.4	495.4	504.8
C/Co (Tc-99)	0.204	0.236	0.264	0.297	0.300	0.301	0.338	0.332	0.343	0.368
ADS #	3-134453	3-134734	3-134736	3-134737						
mg/L (Tc-99)	1.20036	1.20036	1.20408	1.31804						
#CV	513.9	550.8	569.7	578.8						
C/Co (Tc-99)	0.387	0.387	0.388	0.425						

Elution Cycle (ICP-MS Analysis)
Co = 3.1 mg/L Tc-99

ADS #	3-134460	3-134461	3-134462	3-134463	3-134464	3-134465	3-134466	3-134467	3-134468	3-134469
mg/L (Tc-99)	686.6590	661.3620	40.6290	11.5350	3.8281	1.4623	0.7472	0.3796	0.1978	0.1333
C/Co (Tc-99)	221.503	213.343	13.106	3.721	1.235	0.475	0.243	0.123	0.064	0.043
# CV	3.7	7.2	11.1	14.9	18.8	22.5	26.1	29.8	33.6	37.3
ADS #	3-134470	3-134471	3-134472	3-134473						
mg/L (Tc-99)	0.0895	0.0570	0.0398	0.0403						
C/Co (Tc-99)	0.029	0.018	0.013	0.013						
# CV	41	44.7	48.4	52.1						

8.3 Attachment 3. Characterization of the Composited Tc Eluate

ICP-ES Analysis

ADS #	300140393	300140394
	mg/L	mg/L
Al	<12	<12
B	7.50	6.80
Ba	<1	<1
Ca	<0.5	<0.5
Cd	<1.5	<1.5
Co	<2.5	<2.5
Cr	<3.5	<3.5
Cu	<1.5	<1.5
Fe	<1.5	<1.5
La	<5.5	<5.5
Li	<1	<1
Mg	<0.5	<0.5
Mn	<0.5	<0.5
Mo	<3	<3
Na	283.00	213.40
Ni	<3.5	<3.5
P	<13	<13
Pb	<14	<14
Si	180.75	178.50
Sn	<7.5	<7.5
Sr	<0.5	<0.5
Sc	<8.5	<8.5
Tc	36.10	34.85
Ti	<1	<1
V	<1.5	<1.5
Zn	2.05	1.55
Zr	2.30	<2

RadChem

ADS #	300140397	300140398
Cs-137 (uCi/mL)	0.0145	0.01628
Pu-239/240 (uCi/mL)	5.65E-04	3.22E-04
Pu-238 (uCi/mL)	3.31E-04	2.41E-04
Am-241 (uCi/mL)	2.15E-03	1.52E-03
Cm-244 (uCi/mL)	6.78E-04	1.28E-03
Sr-90 (uCi/mL)	3.40E-03	3.29E-03

Attachment 3. Cont.

IC Anion

ADS #	300140395	300140396
F^- (mg/L)	<100	<100
Cl^- (mg/L)	<500	<500
NO_3^- (mg/L)	<100	<100
NO_2- (mg/L)	<500	<500
PO_4^{3-} (mg/L)	<500	<500
SO_4^{2-} (mg/L)	<500	<500
$C_2O_4^-$ (mg/L)	<250	<250
$HCOO^-$ (mg/L)	<500	<500

ISE

ADS #	300140395	300140396
F- (mg/L)	<500	<500
Cl- (mg/L)	1200	1100

ICP-MS

ADS #	300140393	300140394
mass 99 (mg/L)	41.958	41.275
mass 238 (mg/L)	0.086	0.054

TIC/TOC

ADS #	300140395	300140396
TIC (mg/L)	85.5	80
TOC (mg/L)	699.5	435
Total Carbon (mg/L)	785	515

AA

ADS#	300140395	300140396
Na (mg/L)	201.495	259.065
K (mg/L)	8.775	7.525

Note: Identical samples were used for ADS #300140393 through #300140398. ICP-MS analysis indicated no masses other than 238 in the range 230-247 amu.

8.4 Attachment 4. SuperLig® 639 Resin Analysis Data

ICP-ES Data

Sample	As-received	As-received	Tank 44 F Col.	Tank 44 F Col.	As-received*
ADS #	300137375	300137374	300137373	300137372	300131500-300131503
	wt. %	wt. %	wt. %	wt. %	wt. %
Al	[0.0961]	[0.1009]	[0.0286]	<0.0522	0.0036
B	<0.0129	<0.137	<0.004	<0.0109	0.0107
Ba	[0.0053]	<0.0055	<0.0016	<0.0043	<0.0002
Ca	0.2396	0.248	0.0739	0.1947	0.0060
Cd	<0.0077	<0.0082	<0.0031	<0.0065	<0.0002
Co	[0.0138]	[0.0184]	[0.0042]	<0.0109	<0.0005
Cr	<0.018	<0.0191	<0.0056	<0.0152	0.0014
Cu	[0.0095]	[0.0088]	[0.0028]	<0.0065	0.0030
Fe	0.0183	0.0213	0.0153	0.0481	0.0102
La	<0.0283	<0.0301	<0.0087	<0.0239	NA
Li	<0.0051	<0.0055	<0.0016	<0.0043	<0.0070
Mg	0.0140	0.0148	0.0037	0.0089	<0.0013
Mn	<0.0026	<0.0027	<0.0008	<0.0022	<0.0002
Mo	<0.0154	<0.0164	<0.0048	<0.013	<0.0004
Na	0.3017	0.3515	1.6927	1.8889	<0.0775
Ni	[0.0291]	[0.028]	[0.0108]	<0.0152	0.0113
P	<0.0669	<0.071	<0.0206	<0.0565	<0.0950
Pb	[0.1031]	[0.1104]	[0.0225]	<0.0609	<0.0050
Si	0.1047	[0.085]	[0.0254]	[0.0358]	<0.0060
Sn	<0.0386	<0.041	<0.0119	<0.0326	<0.0040
Sr	<0.0026	<0.0027	<0.0008	<0.0022	<0.0005
Tc	<0.018	<0.0191	<0.0056	<0.0153	NA
Ti	[0.0081]	[0.0096]	[0.003]	<0.0043	<0.0149
V	0.0153	[0.0163]	[0.0046]	<0.0065	<0.0012
Zn	0.0174	0.0204	0.0065	0.0113	<0.0011
Zr	[0.0144]	[0.017]	[0.0054]	<0.0087	<0.0015

Note: Dissolution of the resins was accomplished using a high-pressure, sealed vessel (Parr bomb) and concentrated nitric acid. 0.1 g of SuperLig® 639 resin was added to the vessel with 3 ml of concentrated (16 M) HNO_3. The temperature was raised to 150° C and maintained for 1.5 hours. Then the vessel was cooled and the sample was diluted with water to a final volume of 250 mL and analyzed by ICP-ES. Results in brackets were less than 2 times the minimum detection limit and are considered suspect.

*The "as-received" resin was reanalyzed at a dilution factor of 100:1. The average of four analyses, which were conducted on two original samples are reported.