

# **Tank 241-AZ-102 SuperLig<sup>®</sup> 639 Technetium Ion Exchange Eluate Evaporation Study**

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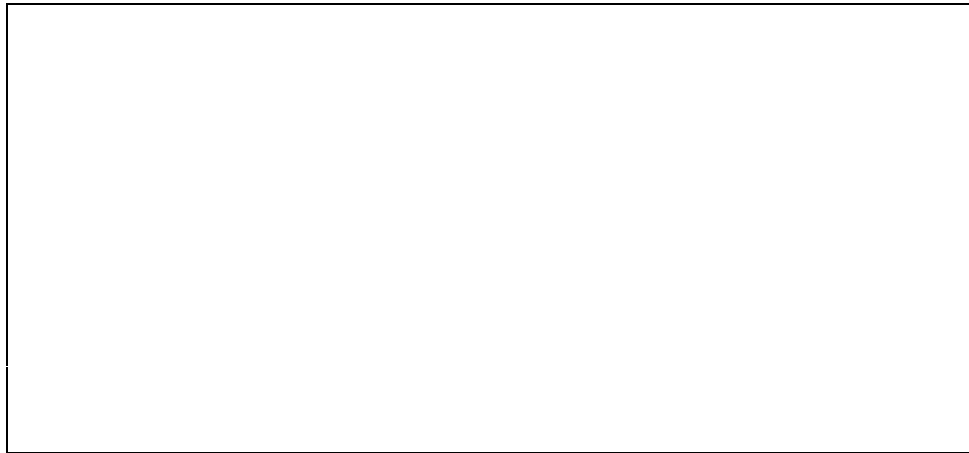
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**TABLE OF CONTENTS**

<b>LIST OF TABLES</b>	<b>iii</b>
<b>LIST OF FIGURES</b>	<b>iii</b>
<b>SUMMARY</b>	<b>iv</b>
<b>1.0 INTRODUCTION</b>	<b>2</b>
<b>2.0 EXPERIMENTAL</b>	<b>4</b>
<b>2.1. Equipment and Materials</b>	<b>4</b>
<b>2.2 Procedures</b>	<b>7</b>
<b>3.0 RESULTS AND DISCUSSION</b>	<b>8</b>
<b>4.0 CONCLUSIONS</b>	<b>11</b>
<b>5.0 ACKNOWLEDGEMENTS</b>	<b>12</b>
<b>6.0 DESIGN CHECK</b>	<b>12</b>
<b>7.0 APPROVALS</b>	<b>12</b>
<b>8.0 REFERENCES</b>	<b>14</b>
<b>9.0 APPENDIX</b>	<b>16</b>
<b>9.1 Attachment 1. Tank 241-AZ-102 SuperLig<sup>®</sup> 639 Ion Exchange Eluate Characterization</b>	<b>16</b>
<b>9.2 Attachment 2. Repeated IC Anion Analysis for the Tc Eluate Sample</b>	<b>17</b>
<b>9.3 Attachment 3. Cs-137 and Tc-99 Analysis Results for Evaporator Concentrate and Condensate Samples Collected During the Experiment</b>	<b>18</b>
<b>9.4 Attachment 4. Tank 241-AZ-102 Tc Eluate Final Evaporator Concentrate Characterization</b>	<b>19</b>
<b>9.5 Attachment 5. Tank 241-AZ-102 Tc Eluate Final Evaporator Condensate Characterization</b>	<b>20</b>

**LIST OF TABLES**

Table 1.	Tc Eluate Evaporation Experimental Data	8
Table 2.	Cs-137 and Tc-99 Data for the Concentrate and Condensate Samples Collected During the Evaporation Experiment	10
Table 3.	Concentration and Decontamination Factors Calculated for the Evaporator Feed and Final Concentrate and Condensate Samples	10

**LIST OF FIGURES**

Figure 1.	Evaporator Design and Approximate Dimensions	5
Figure 2.	Actual Tc Eluate Evaporator Apparatus	6

## SUMMARY

As part of the Hanford River Protection Project (RPP), the Savannah River Technology Center (SRTC) has conducted tests on the pretreatment and vitrification of a radioactive waste sample from Hanford Tank 241-AZ-102. The original, AZ-102 sample which was received at SRTC was characterized and filtered to remove entrained solids.<sup>1</sup> The sample was then passed sequentially through ion exchange columns containing SuperLig<sup>®</sup> 644 and 639 resins for the removal of cesium and technetium ions (Tc removed as pertechnetate,  $\text{TcO}_4^-$ ), respectively.<sup>2</sup> The cesium and technetium absorbed to the resins was then eluted to give separate eluate solutions containing relatively high concentrations of  $\text{Cs}^+$  and  $\text{TcO}_4^-$ . According to the current plant design, the decontaminated Tank 241-AZ-102 sample and the eluate solutions will be subjected to separate evaporation and vitrification processes to give low- and high-activity waste glasses, respectively.

This report describes evaporation testing of the Tc eluate solution derived from ion exchange processing of the Tank 241-AZ-102 sample with SuperLig<sup>®</sup> 639 resin. The primary goals of the testing were to determine the volatility of technetium during evaporation and to confirm Tc eluate evaporation modeling results. Approximately 175 mL (32 ion exchange resin bed volumes) of Tc eluate solution were evaporated in a vacuum evaporator apparatus. The pressure and the temperature of the laboratory evaporator apparatus were selected to mimic the planned operating conditions for the full-scale eluate evaporation system<sup>3</sup> in the RPP waste treatment plant (RPP-WTP). The system was maintained at an absolute vacuum pressure near  $1.09\text{E}+04$  Pa (3.22 in. Hg) during the experiment. The evaporator pot was maintained at  $47.8 \pm 0.3$  °C and the primary and secondary condensers were operated at 40 and 10 °C, respectively. The eluate was concentrated by a factor of 12.2 (based on analysis) to give a final volume of ~15 mL. Very few insoluble solids were found in the concentrate even after cooling to room temperature (measured value: 0.032 wt. %). These results are consistent with preliminary modeling results for the Tank 241-AZ-102 eluate evaporation, which indicated that no solids would be observed in the eluate until evaporation to near dryness. The solution boiling point and system pressure are fairly consistent with the modeling results. The model predicted that an absolute vacuum pressure of  $1.09\text{E}+04$  Pa was required to boil the eluate at 50.0 °C.

Cs-137 concentrations in the original eluate sample and the condensate were used to monitor the level of liquid entrainment to the primary condenser during the evaporation. A large Cs-137 decontamination factor of  $>7.65\text{E}+05$  was observed, indicating that liquid entrainment levels were very low in this system. Analysis of Tc-99 concentrations in the original eluate and the condensate revealed a Tc-99 decontamination factor of  $>1.03\text{E}+06$ , which indicates that no significant volatilization of technetium occurs during eluate evaporation. These results were as expected based on the physical properties of known, caustic-stable Tc species.

These tests were performed following the quality assurance requirements of the Task Technical and Quality Assurance (QA) Plan, BNF-003-98-0301,<sup>4</sup> and were not subject to the QA requirements of the HLW repository program. All of the work scope defined in the Task Technical and QA Plan has been completed and is reported in this document.

## 1.0 INTRODUCTION

Hanford Radioactive Waste materials have been categorized into four envelopes labeled A through D.<sup>5</sup> Envelopes A, B, and C contain primarily solubilized species with less than 2 wt. % entrained solids and are specified as Low-Activity Waste (LAW). Each envelope is defined based on compositional maximums of chemical and radioactive constituents. Envelopes A and B contain low concentrations of organic species and the primary form of technetium is pertechnetate ion ( $\text{TcO}_4^-$ ). Envelope C contains higher levels of organic species and the technetium is primarily present in non-pertechnetate forms. (The presumed non-pertechnetate species are oxo-bridged dimers of the type,  $\text{Tc}_2\text{O}_2\text{L}_2$ , where L = complexing ligands found in the tank waste, such as EDTA, DTPA, etc. The EDTA complex with technetium has been structurally characterized.<sup>6</sup>) Envelope D is sludge solids that may contain residual LAW Envelope A, B, or C supernate and is referred to as High-Level Waste. Envelope D sludge is pretreated to separate soluble components by washing and leaching with sodium hydroxide solutions, followed by cross-flow filtration. The soluble fraction of the Envelope D sludge is mixed with the LAW solutions and processed to separate cesium, technetium, strontium and transuranic elements, as necessary to meet the product specification for low-activity waste glass.

The current waste treatment plant design utilizes SuperLig<sup>®</sup> 644 and 639 ion exchange resins to remove cesium and technetium, respectively, from the Hanford LAW. (Cs and Tc are the primary radioactive constituents in Envelope B supernate.) Cesium is eluted from the SuperLig<sup>®</sup> 644 columns using 0.5 M nitric acid solution at 25 °C and is vacuum evaporated at 50-60 °C to recover and re-use the nitric acid solution and concentrate the cesium eluate solution.<sup>7</sup> Technetium is eluted from the SuperLig<sup>®</sup> 639 columns using water at 50-60 °C and is vacuum evaporated at 50-60 °C to recover and re-use the water and concentrate the technetium eluate solution.<sup>3</sup> After being separately evaporated, the cesium and technetium eluate solutions are combined for interim storage before blending with pretreated HLW sludge for vitrification. The process is designed to produce a decontaminated, low-activity waste stream for vitrification into LAW glass and a concentrated eluate waste stream for blending with pretreated HLW and vitrification into high-activity glass.

Decontamination of a Hanford Envelope B Tank 241-AZ-102 sample was accomplished at the Savannah River Technology Center (SRTC) using ion exchange columns to remove cesium and technetium ions.<sup>2</sup> Elution of the columns was accomplished with 0.5 M  $\text{HNO}_3$  (Cs) and water (Tc). The cesium eluate solution was evaporated and vitrified to yield a high activity waste glass. The technetium eluate (total volume: ~175 mL) was evaporated separately in a smaller evaporation apparatus, with the intent of determining technetium volatility during evaporation and confirming modeling predictions of boiling point and solids formation.

Tc volatility has been reported during evaporation of a 4 M nitric acid ion exchange eluate solution derived from processing of a Savannah River Site radioactive waste sample (total volume of sample evaporated: ~100 mL;  $[\text{Tc-99}]$ : ~15 mg/L).<sup>8</sup> Only mild Tc volatility was reported based on the amount of technetium found in evaporator overheads (~3% of the total Tc), even after evaporation of the sample to near dryness.

An additional 12% of the total Tc was lost to the container walls. The volatile Tc species in acidic solution is presumed to be pertechnic acid,  $\text{HTcO}_4$ .<sup>9</sup>

The current design plan for the Hanford River Protection Project (RPP) utilizes water for the elution of technetium from SuperLig<sup>®</sup> 639 ion exchange columns.<sup>10</sup> The resulting technetium eluate solution is slightly caustic due to mixing of the eluate with the 0.1 M NaOH solution that is utilized to displace residual feed from the ion exchange columns prior to elution. In caustic solutions, technetium volatility is expected to decrease relative to acidic solutions due to the low volatility of alkali metal pertechnetates and the known caustic-stability of pertechnetate ion.<sup>11</sup> Any Tc volatility during eluate evaporation would almost certainly be attributed to some reduced and/or complexed Tc species. One possible mechanism for producing these Tc species could be interaction of pertechnetate ion with the ion exchange resin. Currently, there is no evidence that such species are produced by contact with the resin. In addition, no known volatile Tc species have been identified with significant stability and solubility in caustic solutions. It was, however, decided to conduct a small-scale experiment to confirm that no volatile Tc species exist which might reach evaporator overheads.

## 2.0 EXPERIMENTAL

### 2.1 Equipment and Materials

Glassblowers at SRTC prepared the evaporation apparatus. Figure 1 shows the evaporator design and approximate dimensions. A photograph of the actual apparatus (taken prior to small modifications noted in the figure caption) is shown in Figure 2. The apparatus was primarily prepared from borosilicate glass tubing and included a small evaporator pot and two condensers (primary and secondary) arranged in sequence. The inner diameter and approximate volume of each of these vessels is given in Figure 1. The graduations on each collection vessel were calibrated with water prior to starting the experiment. A sampling port was attached to the side of the evaporator pot. The liquid in the evaporator pot was continuously stirred throughout the experiment. Although the RPP-WTP evaporator does not include mixing of the technetium eluate in the evaporator vessel, the laboratory experiment included mixing to promote uniform heat transfer. The top to the evaporator pot, which included a vacuum gauge and a Cole-Palmer thermocouple, was attached using a Duran<sup>®</sup> reaction flange clamp. The thermocouple probe extended down to within ~1 in. of the bottom of the vessel. A stainless steel wire mesh demister, supplied by Koch-Otto York<sup>™</sup>, which was approximately 3 in. in length was inserted into the tubing exiting the evaporator pot in order to limit liquid entrainment during operation. The evaporator pot was heated with a hot plate to promote boiling and the evaporator pot and the tubing leading to the primary condenser were insulated to minimize heat loss and aid the evaporation.

The condensate collection pots were attached to the primary and secondary condensers using Rudavis ground glass joints. A second thermocouple was attached to the primary condenser and the probe was positioned inside the condenser coil. The probe extended through approximately half the length of the coil but did not touch the glassware at any point. A second sampling port was located on the primary condenser collection pot. The primary condenser collection pot was stirred with a magnetic stir bar throughout the experiment. A vacuum line was attached to the secondary condenser pot and a VacuuBrand GMBH+CO MZ2C diaphragm pump was utilized to apply vacuum to the system. A bleed-in valve was used to adjust the vacuum pressure to the target value (1.09E+04 Pa absolute).

Teflon<sup>®</sup> bushings were used for all glass-metal connections. Similar bushings were used to attach Tygon<sup>®</sup> tubing to the condensers in order to pump heating and cooling water through the coils and the outer jackets of the condensers. A NesLab Coolflow DC-25 Dual Temperature recirculator was used to control the temperature of the condensers. The vacuum gauge and both thermocouples were calibrated prior to use. The sample ports were prepared from Whitey stainless steel ball valves. Swagelok fittings containing Supelco Thermogreen LB-2 rubber septa (diameter: 11 mm, thickness: 11/16 in.) were attached to the valves. Sampling was accomplished with 5 or 10 mL plastic syringes and stainless steel needles obtained from Fisher Scientific.

The Tank 241-AZ-102 Tc ion exchange eluate solution was obtained from ion exchange column experiments reported elsewhere.<sup>2</sup> Of the total of 34.4 resin bed volumes of



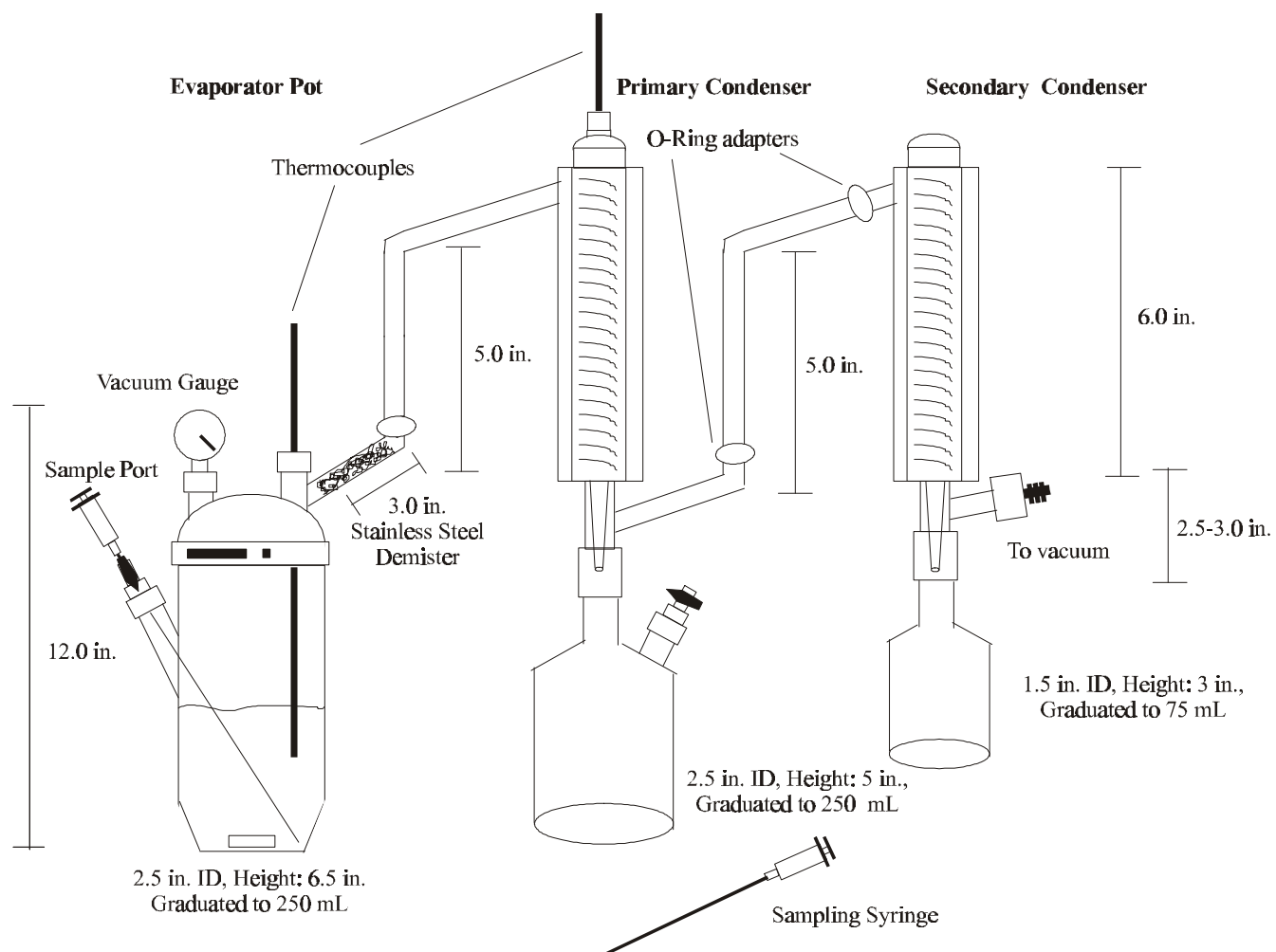


Figure 1. Evaporator Design and Approximate Dimensions (Note: The inner diameter of the glass tubing used to connect the evaporator pot and the condensers was 1.5 cm.)



Figure 2. Actual Tc Eluate Evaporator Apparatus (Note: Prior to use, the connection between the evaporator pot and the primary condenser was modified. The Vigreux column and upper O-ring connector were removed as indicated in Figure 1.

solution utilized for column elution, ~92 % (32 bed volumes) was used for the evaporation. The remainder of the sample was used for analysis.

## 2.2 Procedures

Liquid entrainment levels were checked prior to conducting the test on the actual material by evaporating 200 mL of a 3.3 M NaNO<sub>3</sub> solution. The Na<sup>+</sup> decontamination factor (DF) calculated from analysis of the feed and condensate solution was 1.5E+05. The entire apparatus was then rinsed with deionized water and allowed to dry. Just prior to conducting the evaporation experiment with the actual material, the apparatus was assembled and leak-checked at an initial vacuum pressure of 1.16E+04 Pa absolute (3.42 in. Hg absolute). Based on a total system volume of 1200 mL, the leak rate was calculated to be 6.7 vol. %/hr (1.34 mL/min), which compares favorably with commercial vacuum evaporation systems (typical leak rate: 20 vol. %/hr).<sup>12</sup>

The actual pretreated Tank 241-AZ-102 sample was then transferred to the evaporator pot and duplicate analysis samples were collected with syringes prior to starting the experiment. During the evaporation, the primary and secondary condensers were operated at 40 and 10 °C, respectively. The system vacuum was maintained at 1.09E+04 Pa absolute based on preliminary modeling results<sup>13</sup> which indicated that this pressure would result in a solution boiling point of 50 °C. The Tc eluate modeling results will be reported in a separate document.<sup>14</sup> These experimental parameters were determined based on the current plant design parameters for the Tc eluate evaporation.<sup>3</sup>

Samples were collected during the evaporation by opening the sampling valve and inserting a needle through the septum and into the solution. Sufficient liquid volume could not be collected with the syringes without briefly reducing the system vacuum pressure. The entire sampling operation typically required 2-3 minutes per sample. Very little change was observed in the vacuum pressure after inserting the needles through the septa, which indicated that a sufficient seal formed around the needle to maintain the vacuum. Samples of the concentrated eluate were collected from the evaporator pot during the evaporation at ~1 hr intervals (total number of samples: 3). Samples were collected from the primary condenser collection pot during the evaporation at approximately the same time that samples were collected from the evaporator pot. Duplicate samples of the final concentrate and condensate were collected after the completion of the evaporation. The temperature in the evaporator pot increased during sampling due to the decreased vacuum pressure. However, the temperature rise never exceeded 5 °C and the temperature decreased to the original value each time after sampling was complete. Sample analysis results are shown in Attachments 1-5. All values reported have been corrected for sample dilution and dilution factors are provided. Feed and concentrate samples were 1-3 mL in volume and were diluted with 9-14 mL of deionized water prior to analysis (dilution factor range: 6-13). Condensate sample volumes were 5-10 mL and samples were submitted for analysis without dilution. The Analytical Development Section (ADS) at SRTC conducted all analyses.

Wt. % solids and total solids measurements were conducted on the final concentrate sample at the conclusion of the experiment in the following manner. Total solids content

Table 1. Tc Eluate Evaporation Experimental Data

Time (min)	P (Pa absolute)	T1 (°C)	V1 (mL)	T2 (°C)	V2 (mL)	V3 (mL)	Comments
0	1.12E+04	47.9	175	38.4	0	0	condensation in primary condenser
60	1.12E+04	47.9	---	39.8	---	0	
105	1.09E+04	47.9	100	40.9	70	0	collected first sample
130	1.09E+04	47.8	---	42.0	---	0	brief period of rapid condensation
165	1.09E+04	47.8	60	44.5	107	0	collected second sample
190	1.09E+04	47.8	---	43.0	---	0	
210	1.06E+04	47.1	30	42.0	140	0	collected third sample
235	1.12E+04	48.1	15	40.2	155	0	turned off heater
Average	1.09E+04	47.8		41.4			
Range	+/-7E+02	+/-0.3		+/-6.1			

T1 = evaporator pot temperature; V1 = liquid volume in evaporator pot; T2 = primary condenser temperature as measured by the condenser thermocouple; V2 = liquid volume in the primary condenser collection pot; V3 = liquid volume in the secondary condenser collection pot (Note: 1.09 E+04 Pa absolute vacuum pressure corresponds to 3.22 in. Hg absolute and 26.7 in. Hg gauge.)

was determined by pipeting the liquid concentrate sample onto a quartz filter pad which had been pressed into a glass beaker and weighed. Volatile components were evaporated by heating the beaker to 115 °C. After allowing the beaker to cool, the residue was weighed. This cycle was repeated until a constant weight was obtained in two successive measurements. Insoluble solids were measured similarly, except that the sample was filtered and the filtrate was washed with DI water prior to cyclic drying to constant weight.

These tests were performed following the quality assurance requirements of the Task Technical and Quality Assurance (QA) Plan, BNF-003-98-0301,<sup>4</sup> and were not subject to the QA requirements of the HLW repository program. All of the work scope defined in the Task Technical and QA Plan has been completed and is reported in this document.

### 3.0 RESULTS AND DISCUSSION

Analysis results for the Tc eluate solution are provided in Attachments 1 and 2. The results are generally consistent with earlier reported results. In order to obtain better detection limits for the IC anion results, additional duplicate samples of the Tc eluate were submitted for analysis without dilution (Attachment 2). Based on analysis, the primary composition of the eluate solution was 0.09 M Na<sup>+</sup>, 0.002 M K<sup>+</sup>, 0.01 M NO<sub>3</sub><sup>-</sup>, 0.01 M NO<sub>2</sub><sup>-</sup>, and 0.006 M SO<sub>4</sub><sup>2-</sup>. The major radioactive constituents were Cs-137 (0.285 µCi/mL) and Tc-99 (34.9 mg/L). (Note: Cesium levels in the Tc eluate were higher than expected due to incomplete removal of Cs during ion exchange treatment with SuperLig<sup>®</sup> 644 resin. Consequently, the feed to the Tc ion exchange columns contained Cs and residual amounts of cesium were present in the Tc eluate, presumably due to incomplete feed displacement during post-feed column washing prior to elution.) The sample also contained ~16 mg/L Cr, which imparted a light yellow color to the solution. Based on

the results in Attachment 2, the  $\text{Cl}^-$  concentration is 0.01 M. However, earlier analysis results (Table 1 of Ref. 2) indicated lower chloride levels and  $\text{Cl}^-$  analyses on this sample type have often been inconsistent. Therefore, the chloride analysis for the Tc eluate samples is suspect and should not be used without additional validation.

Pressure, temperature, volume and sampling data for the experiment are provided in Table 1. The average system pressure during the experiment was  $1.09\text{E}+04$  Pa absolute (3.22 in. Hg absolute) and the pressure varied by only  $\pm 7\text{E}+02$  Pa ( $\pm 0.2$  in. Hg). The average evaporator pot temperature was  $47.8^\circ\text{C}$  and the temperature varied by only  $\pm 0.3^\circ\text{C}$  during normal operation. As discussed earlier, during sampling the evaporator pot temperature did rise slightly due to the decreased vacuum pressure. (Note: The evaporator pot temperatures (T1) in Table 1 represent steady-state conditions. The slight temperature increases that occurred during sampling are not represented in this data.) The average primary condenser temperature (T2) was  $41.4^\circ\text{C}$  and the temperature varied by  $\pm 6.1^\circ\text{C}$  based on the primary condenser thermocouple readouts. The recirculator temperature readout was stable at  $40^\circ\text{C}$  throughout the experiment, while the thermocouple readout (T2) varied depending upon the condensation rate. The volumes of solution reported for the evaporator pot during the experiment were approximate since the solution was actively boiling while readings were taken. All condensate volumes (V2) were corrected for the volume of samples collected. The sum of the evaporator pot volume and the condensate volume in Table 1 at each measurement time is typically near 170 mL, which accounts for  $>95\%$  of the total sample volume. No liquid was observed in the secondary condenser collection pot throughout the experiment. The eluate boiling point does not appear to have changed as a result of increasing solution molality during the experiment as is indicated by the essentially constant evaporator pot temperature.

Attachment 3 shows the analysis results for the evaporator concentrate and condensate samples during the experiment. Attachments 4 and 5 provide the characterization data for the final evaporator concentrate and condensate samples, respectively. As shown in Table 2, concentration factors (CF) calculated from the Cs (gamma) and Tc (ICP-MS) analyses are generally consistent throughout the experiment. The average final concentration factor was 12.2. The final concentrate sample was reported to contain 0.032 wt. % insoluble solids, which approaches the minimum detection limit (0.022 wt. %). The measured total solids content of 5.49 wt. % approaches the calculated value of 6.48 wt. % (based on total mg/L of individual species analyzed). The original sample contained  $49.9\text{ }\mu\text{Ci}$  total Cs and 6.11 mg total Tc (based on an initial volume of 175 mL). The final concentrate (15 mL) contained  $49.1\text{ }\mu\text{Ci}$  Cs (98% recovery) and 6.68 mg Tc (109% recovery). No Cs-137 or Tc-99 was detected by either analysis technique in any of the condensate samples. Decontamination factors (DF) calculated for Cs and Tc are consistent and indicate that the overall decontamination factor may be  $>1\text{E}+06$ . Lower detection limits and higher initial concentrations resulted in higher calculated decontamination factors for the Tc-99 than were calculated for Cs-137 (although both are “greater than” values). A higher Cs-137 DF was calculated for the final condensate sample than for condensate samples 1-3 because more sample was available for analysis, which resulted in a lower detection limit for this sample. The condensate was slightly acidic (pH: 4.3, Attachment 5), presumably as a result of absorption of atmospheric carbon dioxide.

Table 2. Cs-137 and Tc-99 Data for the Concentrate and Condensate Samples Collected During the Evaporation Experiment

Sample ID	Time (min.)	App. Vol. (mL)	Cs-137 ( $\mu\text{Ci/mL}$ )	Tc-99 (mg/L)	Cs-137 CF	Tc-99 CF
Feed	0	175	0.285	3.49E+01	1.0	1.0
Concentrate #1	105	100	0.456	5.91E+01	1.6	1.7
Concentrate #2	165	60	0.717	6.11E+01	2.5	1.8
Concentrate #3	210	30	2.318	2.86E+02	8.1	8.2
Concentrate Final	235	15	3.275	4.45E+02	11.5	12.8
Sample ID	Time (min.)	Vol. (mL)	Cs-137 ( $\mu\text{Ci/mL}$ )	Tc-99 (mg/L)	Cs-137 DF	Tc-99 DF
Condensate #1	105	70	<1.96E-06	<2.8E-05	>1.45E+05	>1.25E+06
Condensate #2	165	107	<2.09E-06	<3.40E-05	>1.36E+05	>1.03E+06
Condensate #3	210	140	<2.12E-06	<3.40E-05	>1.34E+05	>1.03E+06
Condensate Final	235	155	<3.77E-07	<3.40E-05	>7.56E+05	>1.03E+06

CF = concentration factor; DF = decontamination factor

Table 3. Concentration and Decontamination Factors Calculated for the Evaporator Feed and Final Concentrate and Condensate Samples

Analyte	Feed (mg/L)	Concentrate <sup>1</sup> (mg/L)	Condensate <sup>1</sup> (mg/L)	CF <sup>2</sup>	DF <sup>2</sup>
Cs-137 ( $\mu\text{Ci/mL}$ )	0.285	3.275	<3.77E-07	11.5	>7.56E+05
Tc-99 (ICP-MS)	34.91	445.34	<3.40E-05	12.8	>1.03E+06
Tc-99 ( $\mu\text{Ci/mL}$ ) <sup>3</sup>	0.599 <sup>4</sup>	---	<3.59E-07	---	>1.67E+06
Na (AA)	1964.57	---	2.80	---	701.6
K (AA)	80.25	873.30	0.03	10.9	2432
<b>ICP-ES</b>					
Al	43.63	449.73	0.022 <sup>5</sup>	10.3	1983
B	7.51	83.00	0.192	11.0	39
Cr	15.47	169.45	<0.007	11.0	>2.42E+04
Mo	5.05	60.69	<0.006	12.0	>841
Na	2265.39	25624.91	2.9475	11.3	768
P	4.93	59.91	<0.028	12.2	>176
Si	7.18	38.75	0.182	5.4	39
Tc	38.05	406.87	0.009 <sup>5</sup>	10.7	4227

- 1) Evaporator concentrate and condensate samples (primary condenser) at conclusion of test
- 2) CF = concentration factor; DF = decontamination factor
- 3) Measured by beta analysis after removal of Cs-137
- 4) Calculated from ICP-MS data
- 5) Minimum Detection Limit: Al, 0.016 mg/L; Tc, 0.007 mg/L (Note: The Minimum Detection Limit (MDL) was determined from 10 replicates on a matrix-matched blank. The standard deviation ( $\sigma$ ) for these results was calculated and the MDL was reported as  $5\sigma$ .)

Table 3 shows calculated CF and DF values for a number of analytes in the final concentrate and condensate samples. Tc-99 concentrations in the condensate samples were analyzed by beta scintillation counting as well as ICP-MS in order to confirm the technetium DF. No Tc-99 was observed in the condensate by beta counting and the calculated DF is consistent with that calculated from the ICP-MS data ( $>1\text{E}+06$ ). Selected AA and ICP-ES concentrate and condensate analysis results (for analytes that were present in the original eluate at concentrations  $\geq 4$  mg/L) are also shown in Table 3. Calculated CF values were generally consistent with the average value determined from the Cs and Tc data (12.2). The calculated CF for Si of 5.4 is one notable exception. Si analysis results by ICP-ES with this sample type are often inconsistent. Calculated DF values varied widely ranging from 39 to  $>2.42\text{E}+04$ , indicating that the ICP-ES data is not highly reliable at such low analyte concentrations. Surprisingly, both AA and ICP-ES Na analysis indicated that the sodium concentration in the condensate was 2.9 mg/L, which corresponds to an average sodium DF of 735. The potassium DF of 2432 is also much lower than expected. These results are inconsistent with the Cs and Tc data and indicate that the condensate sample may have been contaminated prior to analysis. Repeated analyses conducted with freshly-prepared samples gave similar results. The source of the suspected contamination is not known,

#### 4.0 CONCLUSIONS

The Cs and Tc decontamination factors obtained for the Tank 241-AZ-102 Tc ion exchange eluate evaporation indicate very proficient sample concentration by the evaporator and imply that volatile Tc species will not reach overheads during evaporation. These results were as expected based on the physical properties of known, caustic-stable Tc species. The results were also generally consistent with preliminary modeling results. The eluate boiling point observed during the evaporation at  $1.09\text{E}+04$  Pa absolute was within  $2.5$  °C of the temperature predicted by the model. In addition, the final concentrate contained only 0.032 wt. % insoluble solids after concentration by a factor of 12.2, as predicted by the technetium eluate model.

Separate evaporation testing of cesium- and pertechnetate-decontaminated Envelope C Tank 241-AN-102 samples which contained significant amounts of non-pertechnetate forms of Tc, also showed no Tc volatility.<sup>15, 16</sup> This indicates that Tc volatility is not an issue during evaporation of caustic solutions containing pertechnetate or non-pertechnetate forms of Tc which are present in the Hanford waste tanks.

## 5.0 ACKNOWLEDGEMENTS

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## 6.0 DESIGN CHECK

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Mark Crowder, Actinide Technology Section

## 7.0 APPROVALS

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### Task Plan

King, W. D. Task Technical and Quality Assurance Plan for the Envelope B (Tank 241-AZ-102) SuperLig<sup>®</sup> 639 Tc Eluate Evaporation, BNF-003-98-0301, Rev. 0.



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## 9.0 APPENDIX

### 9.1 Attachment 1. Tank 241-AZ-102 SuperLig<sup>®</sup> 639 Ion Exchange Eluate Characterization (Tc Eluate Evaporator Feed)

ADS#		300148835		300148837		Average
Dilution Factor		10.8		8.4		
Cs-137 (μCi/mL)		0.285		0.285		0.285
Tc-99 (mg/L)		35.28		34.54		34.91
ADS#		300148848		300148849		Average
Dilution Factor		9.4		10.3		
Free OH- (M)		0.052		0.051		0.052
AA (mg/L)						
Na		2064.16		1864.98		1964.57
K		78.58		81.92		80.25
IC Anion (mg/L)						
Fluoride (mg/L)	<	187	<	206	<	197
Formate	<	935	<	1029	<	980
Chloride	<	187	<	206	<	197
Nitrite		477	<	1029	<	753
Nitrate		374	<	1029	<	702
Phosphate	<	935	<	1029	<	982
Sulfate		252		515		383
Oxalate	<	935	<	1029	<	982
ICP-ES (mg/L)						
Al		43.805		43.455		43.630
B		7.433		7.594		7.514
Ba	<	0.187	<	0.206	<	0.196
Ca		0.916		1.513		1.214
Cd	<	0.281	<	0.309	<	0.295
Co	<	0.468	<	0.515	<	0.491
Cr		15.549		15.384		15.466
Cu	<	0.281	<	0.309	<	0.295
Fe	<	0.187	<	0.206	<	0.196
La	<	1.029	<	1.132	<	1.080
Li		0.196	<	0.206	<	0.201
Mg	<	0.094	<	0.103	<	0.098
Mn	<	0.094	<	0.103	<	0.098
Mo		4.722		5.371		5.047
Na		2275.902		2254.868		2265.385
Ni		0.795	<	0.720	<	0.758
P		5.320		4.538		4.929
Pb		3.516		3.025		3.270
Si		6.938		7.419		7.178
Sn	<	1.403	<	1.544	<	1.473
Sr		0.122	<	0.103	<	0.112
Tc		37.924		38.176		38.050
Ti		0.215	<	0.206	<	0.210
V		0.374	<	0.309	<	0.341
Zn	<	0.281	<	0.309	<	0.295
Zr	<	0.374	<	0.412	<	0.393

## 9.2 Attachment 2. Repeated IC Anion Analysis for the Tc Eluate Sample

ADS#		300148106		300148109		Average
Dilution Factor		NA		NA		
Fluoride (mg/L)	<	20	<	20	<	20
Formate	<	100	<	100	<	100
Chloride		342		346		344
Nitrite		578		581		580
Nitrate		695		696		696
Phosphate	<	100	<	100	<	100
Sulfate		597		596		597
Oxalate		212		216		214

9.3 Attachment 3. Cs-137 and Tc-99 Analysis Results for Evaporator Concentrate and Condensate Samples Collected During the Experiment

	ADS#	Dilution Factor	Cs-137 ( $\mu\text{Ci}/\text{mL}$ )	Tc-99 ( $\text{mg}/\text{L}$ )
Concentrate #1	300148839	10.2	0.456	59.066
Concentrate #2	300148838	6.7	0.717	61.142
Concentrate #3	300148840	12.4	1.794	286.498
Condensate #1	300148843	NA	<1.96E-6	<2.80E-05
Condensate #2	300148844	NA	<2.09E-6	<3.40E-05
Condensate #3	300148845	NA	<2.12E-6	<3.40E-05

9.4 Attachment 4. Tank 241-AZ-102 Tc Eluate Final Evaporator Concentrate  
Characterization

**Concentrate**

<b>ADS#</b>	<b>300148841</b>	<b>300148842</b>	<b>Average</b>
Dilution Factor	9.6	9.8	
Cs-137 (μCi/mL)	3.265	3.286	3.275
Tc-99 (mg/L)	436.87	453.81	445.34

<b>ADS#</b>	<b>300148850</b>	<b>300148851</b>	<b>Average</b>
Dilution Factor	6.3	7.0	
AA (mg/L)			
K	871.75	874.86	873.30
<b>ICP-ES (mg/L)</b>			
Al	459.156	440.297	449.727
B	83.823	82.184	83.004
Ba	0.157	0.160	0.159
Ca	1.544	1.723	1.634
Cd	0.389	0.349	0.369
Co	0.421	0.356	0.388
Cr	171.287	167.612	169.450
Cu	0.741	0.774	0.758
Fe	1.086	1.081	1.084
La	< 0.690	0.851	< 0.771
Li	< 0.126	< 0.140	< 0.133
Mg	0.182	0.202	0.192
Mn	0.320	0.314	0.317
Mo	60.812	60.559	60.685
Na	25909.441	25340.376	25624.908
Ni	1.839	1.758	1.799
P	61.270	58.543	59.906
Pb	4.683	4.409	4.546
Si	38.830	38.668	38.749
Sn	5.078	5.399	5.239
Sr	0.245	0.223	0.234
Tc	409.041	404.692	406.866
Ti	0.245	0.223	0.234
V	0.458	0.356	0.407
Zn	0.778	1.081	0.930
Zr	0.264	0.314	0.289

<b>ADS#</b>	<b>300150695</b>
Dilution Factor	NA
Wt. % Insoluble Solids	0.032
Total Wt. % Solids	5.49
Specific gravity (g/mL)	1.0546

## 9.5 Attachment 5. Tank 241-AZ-102 Tc Eluate Final Evaporator Condensate

## Characterization

ADS#		300148846		300148847		Average
Dilution Factor		NA		NA		
Cs-137 (μCi /mL)	<	3.42E-07	<	4.11E-07	<	3.77E-07
Tc-99 (mg/L)	<	3.40E-05	<	3.40E-05	<	3.40E-05
Tc-99 (μCi/mL)	<	1.66E-07	<	2.76E-07	<	3.59E-07
ADS#		300148852		300148853		Average
Dilution Factor		1.0		1.0		
pH		4.331		4.232		4.282
AA (mg/L)						
Na		3.230		2.376		2.803
K		0.025		0.042		0.033
IC Anion (mg/L)						
Fluoride (mg/L)	<	20	<	20	<	20
Formate	<	100	<	100	<	100
Chloride	<	20	<	20	<	20
Nitrite	<	100	<	100	<	100
Nitrate	<	100	<	100	<	100
Phosphate	<	100	<	100	<	100
Sulfate		50		50		50
Oxalate	<	100	<	100	<	100
ICP-ES (mg/L)						
Al		0.019		0.025		0.022
B		0.192		0.192		0.192
Ba	<	0.002		0.003	<	0.0025
Ca	<	0.001	<	0.001	<	0.001
Cd	<	0.003	<	0.003	<	0.003
Co	<	0.005	<	0.005	<	0.005
Cr	<	0.007	<	0.007	<	0.007
Cu	<	0.003	<	0.003	<	0.003
Fe		0.003		0.004		0.0035
La	<	0.011	<	0.011	<	0.011
Li	<	0.002		0.003	<	0.0025
Mg		0.004		0.004		0.004
Mn	<	0.001	<	0.001	<	0.001
Mo	<	0.006	<	0.006	<	0.006
Na		2.936		2.959		2.9475
Ni	<	0.007	<	0.007	<	0.007
P		0.03	<	0.026	<	0.028
Pb	<	0.028	<	0.028	<	0.028
Si		0.181		0.182		0.1815
Sn	<	0.015	<	0.015	<	0.015
Sr	<	0.001	<	0.001	<	0.001
Tc		0.008		0.01		0.009
Ti	<	0.002		0.003	<	0.0025
V	<	0.003		0.004	<	0.0035
Zn	<	0.003	<	0.003	<	0.003
Zr		0.007		0.016		0.0115