Laboratory Report on the Removal of Pertechnetate from Tank 241-AN-105 Simulant using Purolite A530E

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EXECUTIVE SUMMARY

This effort falls under the technetium management initiative and will provide data for those who will make decisions regarding the handling and disposition of technetium. To that end, the objective of this effort is to challenge Purolite®[1] A530E against a double-shell tank simulant from tank 241-AN-105 spiked with pertechnetate (TcO_4^-).

The Purolite® A530E is commercially available and is currently being used at the 200 West Pump and Treat Groundwater Treatment Plant to remove pertechnetate. It has been demonstrated that Purolite® A530E is highly effective in removing TcO_4^- from a water matrix. Purolite® A530E is the commercial product of the Oak Ridge National Laboratory's Biquat™[2] resin. Further work has demonstrated that technetium-loaded A530E achieves a leachability index in Cast Stone of 12.5 (RPP-RPT-39195, *Assessment of Technetium Leachability in Cement-Stabilized Basin 43 Groundwater Brine*).

When the batch contacted with various dilutions of spiked AN-105 simulant, the Purolite® A530E resin demonstrated the following distribution coefficients (K_d):

Distribution Coefficients as a Function of Sodium Molarity.

AN-105 Simulant Sodium Molarity	Distribution Coefficient (K_d)
5	1364
7.5	1195
10	837

Following the batch contact, continuous flow column tests were conducted to determine breakthrough ($C/C_o = 0.5$). The tank 241-AN-105 simulant was adjusted to 6.5 M sodium and spiked to 15.75 mg/L of pertechnetate (ORP-11242, *River Protection Project System Plan*). Two columns in series were used in a lead-lag configuration. The flow rate through the columns was 2 BV/hr.

Breakthrough, $C/C_o = 0.50$, occurred at 284 BV for the lead column, and $C/C_o = 0.98$ occurred at 342 BV, when the experiment was halted. The guard column reached a $C/C_o = 0.01$ and maintained that value throughout the experiment. The column runs were halted when the pertechnetate spike simulant was depleted.

There was no visible degradation of the resin during the flow of approximately 171 hr.

The Purolite® A530E resin is a viable candidate for treating tank supernate in the 5.5 to 6.5 M sodium range for the removal of the pertechnetate ion.

[1] Purolite is a registered trademark of Brotech Corporation, Bala Cynwyd, Pennsylvania.
[2] Biquat is a trademark of UT-Battelle LLC, Oak Ridge, Tennessee.

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Abbreviations

AN-105	tank 241-AN-105
C/C_o	column effluent concentration/column influent concentration
DST	double-shell tank
ICP-MS	inductively coupled plasma-mass spectrometer
K_d	distribution coefficient
LAW	low-activity waste
ρ	density

Units

BV	bed volume
cm	centimeter
g	gram
hr	hour
L	liter
µm	micrometer
M	molar
MeV	million electron volts
mg	milligrams

1 INTRODUCTION

This report documents the laboratory testing and analyses as directed under the test plan, LAB-PLN-11-00010, *Evaluation of Technetium Ion Exchange Material against Hanford Double Shell Tank Supernate Simulate with Pertechnetate.*

Technetium (Tc-99) is a major fission product from nuclear reactors, and because it has few applications outside of scientific research, most of the technetium will ultimately be disposed of as nuclear waste. The radioactive decay of Tc-99 to ruthenium 99 (Ru-99) produces a low energy β^- particle (0.1 MeV max). However, due to its fairly long half-life ($t_{1/2}$ = 2.13E05 years), Tc-99 is a major source of radiation in low-level waste (UCRL-JRNL-212334, *Current Status of the Thermodynamic Data for Technetium and its Compounds and Aqueous Species*).

Technetium forms the soluble oxy anion, TcO_4^- under aerobic conditions. This anion is very mobile in groundwater and poses a health risk (*ANL, Radiological and Chemical Fact Sheets to Support Health Risk Analyses for Contaminated Areas*).

It has been demonstrated that Purolite® A530E is highly effective in removing TcO_4^- from a water matrix (RPP-RPT-23199, *The Removal of Technetium-99 from the Effluent Treatment Facility Basin 44 Waste Using Purolite A-530E, Reillex HPQ, and Sybron IONAC SR-7 Ion Exchange Resins*). Purolite® A530E is the commercial product of the Oak Ridge National Laboratory's Biquat™ resin (Gu, B. et. al, *Development of Novel Bifunctional Anion-Exchange Resins with Improved Selectivity for Pertechnetate Sorption from Contaminated Groundwater*). Further work has demonstrated that technetium-loaded A530E achieves a leachability index in Cast Stone of 12.5 (ANSI/ASN-16.1-2003, *Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-term Test Procedure*) as reported in RPP-RPT-39195, *Assessment of Technetium Leachability in Cement-Stabilized Basin 43 Groundwater Brine.*

This effort falls under the technetium management initiative and will provide data for those who will make decisions on the handling and disposition of technetium. To that end, the objective of this effort was to challenge Purolite® A530E against a double-shell tank (DST) simulant (tank 241-AN-105 or AN-105) spiked with pertechnetate (TcO_4^-) to determine breakthrough of the lead column.

Unless otherwise noted, all testing was conducted at ambient temperature and pressure conditions.

2 MATERIALS AND METHODS

2.1 SIMULANT

Envelope A (*Statement of Work* [DE-AC27-01RV14136, M147]), which is also known as Double-Shell Slurry Feed or Double-Shell Slurry, was chosen because it is an alkaline ([OH^-] >1 M), high sodium (>8 M) supernate. The envelope contains ^{137}Cs and ^{99}Tc at concentrations that require removal prior to low-activity waste (LAW) vitrification. The removal of Sr/TRU is not required for this waste. The AN-105 supernate recipe reported in WSRC-TR-2000-00338, *Hanford Waste Simulants Created to Support the Research and Development on the River Protection Project – Waste Treatment Plant,* was formulated and spiked with 15 mg/L of ^{99}Tc. Table 1 shows the simulant recipe.

Table 1. Tank 241-AN-105 Double-Shell Tank Simulant Chemical Makeup (1 L Batch).

Reagent	Formula	g/L
Boric Acid	H_3BO_3	0.292
Cadmium Nitrate	$Cd(NO_3)_2 \bullet 4H_2O$	0.009
Calcium Nitrate	$Ca(NO_3)_2 \bullet 4H_2O$	0.236
Cesium Nitrate	$CsNO_3$	0.024
Lead Nitrate	$Pb(NO_3)_2$	0.085
Magnesium Nitrate	$Mg(NO_3)_2 \bullet 6H_2O$	0.057
Potassium Nitrate	KNO_3	19.221
Silver Nitrate	$AgNO_3$	0.026
Zinc Nitrate	$An(NO_3)_2 \bullet 6H_2O$	0.046
Sodium Chloride	NaCl	14.984
Sodium Fluoride	NaF	0.420
Sodium Chromate	Na_2CrO_4	4.205
Sodium Sulfate	Na_2SO_4	1.140
Potassium Molybdate	K_2MoO_4	0.204
Aluminum Trihydroxide	Al(OH)3	114.77
Sodium Hydroxide	NaOH	196.68
Selenium Dioxide	SeO_2	0.001
Sodium meta-Silicate	$Na_2SiO_3 \bullet 9H_2O$	2.135
Sodium Phosphate	$Na_3PO_4 \bullet 12H_2O$	2.281
Sodium Carbonate	Na_2CO_3	22.149
Sodium Nitrate	$NaNO_3$	209.70
Sodium Nitrite	$NaNO_2$	166.48
Water	H_2O	669.37

The challenge simulant was prepared without the organic fraction. This allowed unobstructed observation of the resin and resin bed, as the simulant is quite transparent. During the experiment, the resin did not show any degradation. The distribution coefficient (K_d) for the simulant with organic fraction at 7.5 molar sodium is 3021, while the K_d for the simulant without the organic fraction at 7.5 molar sodium is 2998. It was felt that the K_ds were close enough to justify a simulant without an organic fraction to allow visualization of the resin to occur.

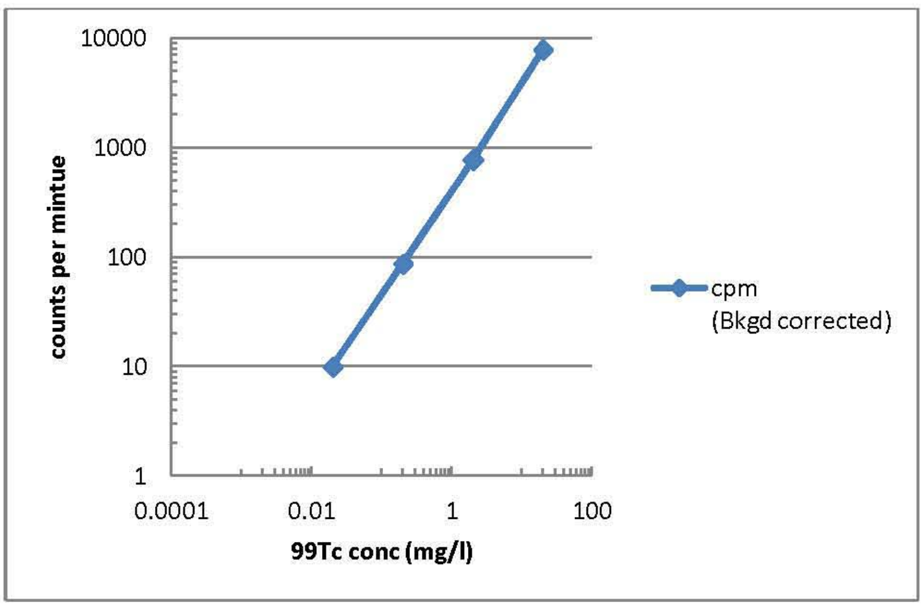
2.2 PERTECHNETATE

Pertechnetate was obtained from the Oak Ridge High Flux Isotope Reactor as ammonium pertechnetate. The material was solubilized and appropriate dilutions were carried out and confirmed using a Perkin Elmer Elan DRC-e model inductively coupled plasma-mass spectrometer (ICP-MS).

For the column tests, a standard curve was generated using a Ludlum Model 2929 dual scaler (Sweetwater, TX), Figure 1. The standard curve was generated by comparing the 5 min averaged and background-corrected counts to the analyses obtained using the ICP. The matrix for the standard curve was the 6.5 M Na matrix used for the Purolite® A530E ion exchange resin challenge.

For the resin test, a sample of 200 uL of column effluent at progressive BVs was pipetted onto smear pads (Hi-Q Environmental Products Company, part number FP1441-20), allowed to dry, and subjected to 5 min counts, twice for each sample. The average of the two 5 min counts was background corrected and compared to the standard curve in Figure 1 to determine the concentration of pertechnetate in the column effluent.

Figure 1. Calibration Curve with Ludlum Model 2929 Dual Scaler.



2.3 DISTRIBUTION COEFFICIENT DETERMINATION

Batch contact tests, using the above simulant spiked with pertechnetate, were conducted to determine distribution coefficients for Purolite® A530E. The phase ratio was 100:1 (for example 20 mL of simulant:0.2 g of dry basis sorbent), placed on a shaker for 24 hr.

The K_d was determined using Equation 1 (Harland, *Ion Exchange Theory and Practice*):

$$K_A^B = [C_B]_r [C_A]_s / [C_A]_r [C_B]_s \quad (1)$$

Where:

K_A^B = Distribution coefficient
$[C_B]_r$ = molar concentration of ion B in the resin
$[C_A]_s$ = molar concentration of ion A in the bulk solution
$[C_A]_r$ = molar concentration of ion A in the resin
$[C_B]_s$ = molar concentration of ion B in the bulk solution

2.4 PUROLITE® A530E ION EXCHANGE RESIN

The Purolite® A530E resin specifications (*Purolite® A530E Strong Base Anion Macroporous Ion Exchange Resin*, "Purolite," Product Data Sheet,) are presented in Table 2.

Table 2. Purolite® A530E Product Data.

Basic Features	
Application	Perchlorate and Pertechnetate Removal
Polymer Structure	Macroporous polystyrene crosslinked with divinylbenzene
Appearance	Spherical Beads
Functional Group	Quaternary Ammonium
Ionic Form as Shipped	Chloride
Product Information	
Total Capacity, Chloride Form	0.6 eq/L
Moisture Retention, Chloride Form	50-57%
Mean Diameter	725 ± 125 μm
Uniformity Coefficient	1.7
Specific Gravity	1.4
Temperature Limits, Chloride Form	100 °C
pH limits, Stability	0 – 14

Before use, the resin was washed with distilled water in an upflow configuration to remove fines. The washing was stopped when the water overflowing the column contained no visible discoloration from fines, etc.

2.5 ION EXCHANGE COLUMNS

The ion exchange columns were Kontes®[3] Flex-Column®[4] glass columns with a diameter of 1.5 cm and a length of 20 cm. A flow adapter was fitted to the column to ensure uniform delivery of spiked simulant to the resin bed in a downward flow configuration.

The resin was backwashed to remove the fines by expanding the bed volume with a sufficient velocity of water to maintain the expanded bed while the fines washed out. The resin was slurried into the ion exchange columns to attain 1 BV at 11 mL resin. The resin was then classified by placing the pump in an upflow configuration and allowing the bed to expand to approximately two times its depth. The pump was turned off and the valve closed, allowing the resin to settle and produce a classified bed.

The resin did exhibit buoyancy at the sodium molarity of 6.5. The flow adapter enabled the bed to adhere to a constrained geometry during the experiment.

The simulant was delivered using a Masterflex®[5] peristaltic pump, calibrated to deliver 22 ml/hr (2 BV/hr). Particulates in the simulant feedstock container were filtered in line using a glass wool filter.

3 RESULTS

3.1 DISTRIBUTION COEFFICIENTS

Table 3 shows the K_d as a function of sodium molarity. The K_ds were determined at 10 and diluted to 7.5 M and 5 M sodium concentrations.

Table 3. Distribution Coefficients for Tank 241-AN-105.

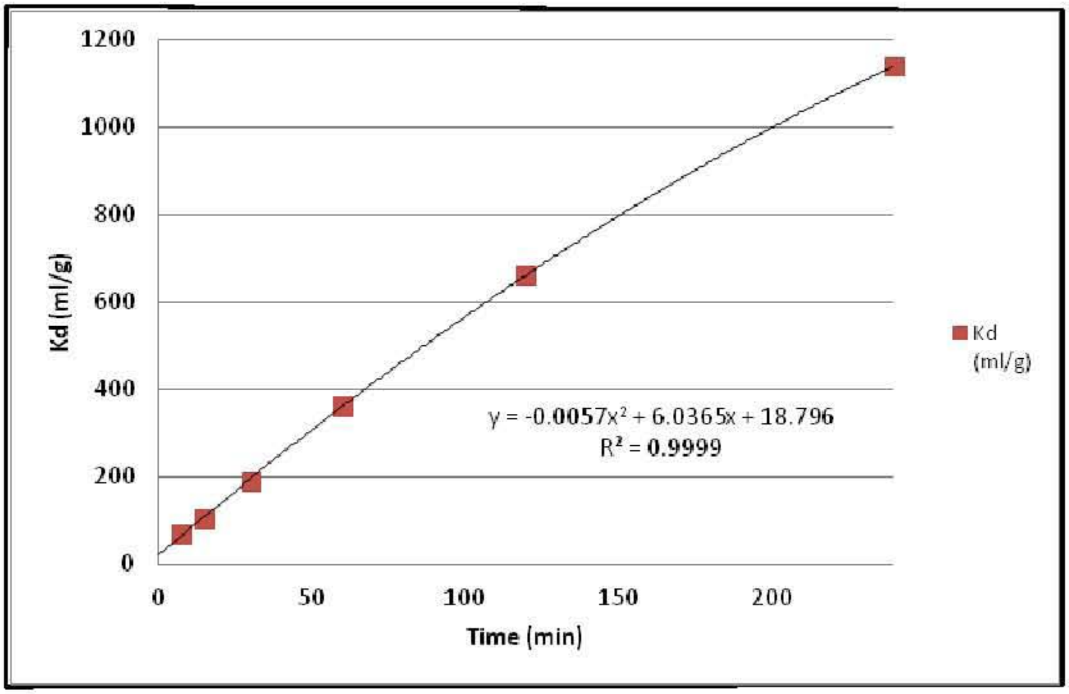
AN-105 [Na]	Distribution Coefficient (K_d) mL/g
5	2300
7.5	1987
10	984

Figure 2 shows the distribution coefficients exhibited by the A530E resin over time when challenged with AN-105 simulant at 6.5 M sodium. Sampling intervals for the time-based K_d testing were 7.5, 15, 30, 60, 120, and 240 minutes. The regression equation for the response curve is:

$$y \text{ estimate} = -0.0057x2 + 6.0365x + 18.796 \qquad (2)$$

[3] Kontes is a registered trademark of the Kontes Glass Company, Vineland, New Jersey.
[4] Flex-Column is a registered trademark of the Kontes Glass Company, Vineland, New Jersey.
[5] Masterflex is a registered trademark of the Cole-Parmer Instrument Company, Vernon Hills, Illinois.

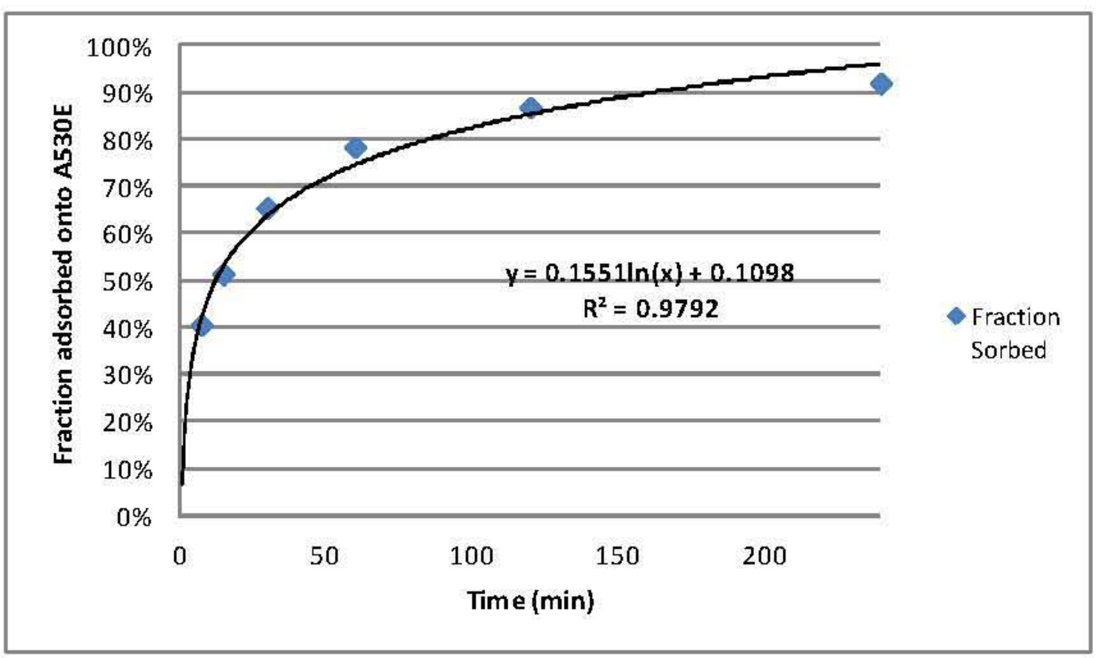
Figure 2. Distribution Coefficients versus Contact Time.



A sorption curve was obtained by sampling at time intervals of 7.5, 15, 30, 60, 120, and 240 min (Figure 3). The response equation is:

$$y \text{ estimate} = 0.1551\ln(x) + 0.1098 \qquad (3)$$

Figure 3. Pertechnetate Sorbed onto A530E from AN-105 Simulant at 6.5 M Sodium.



The lambda value, which is obtained by Equation 4, is an estimation of the bed volumes to breakthrough (C/C_o = 0.5) and is a function of the distribution coefficient and resin density (BNF-003-98-0219, *Small-Scale Ion Exchange Removal of Cesium and Technetium from Hanford Tank 241-AN-102).*

$$\lambda = (K_d)(\rho) = \text{BV to breakthrough (unit less)} \quad (4)$$

Using this parameter, the associated BVs to breakthrough were calculated as shown in Table 4.

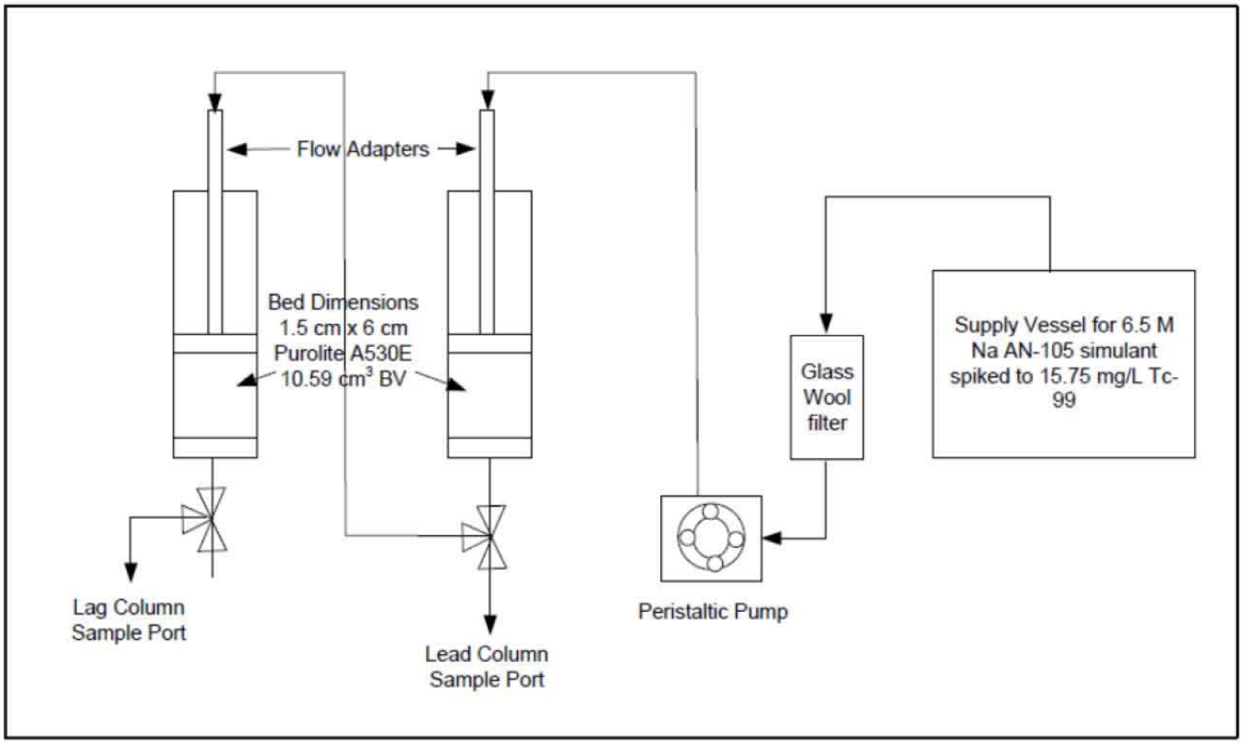
Table 4. Lambda Calculated Bed Volumes to Breakthrough (C/C_o = 0.5).

Distribution Coefficient (K_d) mL/g [Na]	Resin Density ρ	Lambda Calculated BV to C/C_o = 0.5
2300 [5]	1.4	3220
1987 [7.5]	1.4	2781
984 [10]	1.4	1377

3.2 COLUMN EXPERIMENT

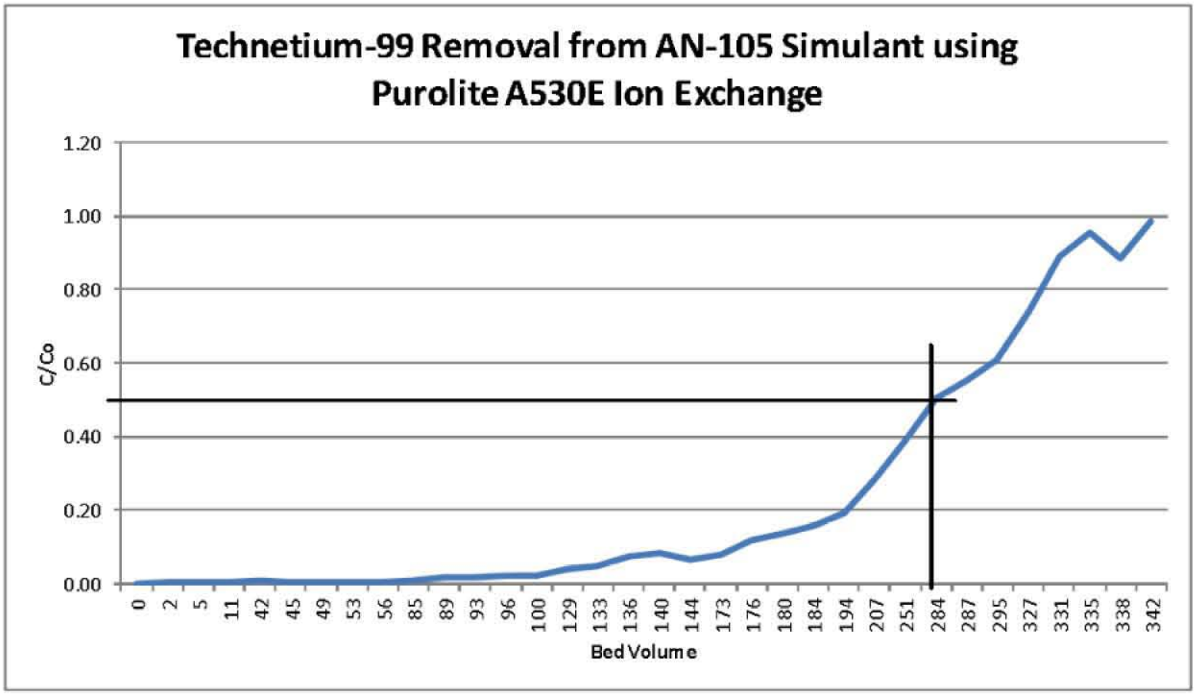
The columns, pump, filter, and sampling points were configured as depicted in Figure 4.

Figure 4. Column Test Configuration.



Samples were taken over a 188 hr run time. The lead column was at a C/C_0 of 0.98 when the run was halted due to the exhaustion of pertechnetate-spiked AN-105 simulant. Figure 3 shows the breakthrough curve, with $C/C_0 = 0.5$ at 284 BV at 156 hr.

Figure 5. Breakthrough Curve for the Lead Column.



The test was terminated at 342 BV due to the exhaustion of the AN-105 technetium-spiked simulant and the exhaustion of the supply of pertechnetate.

The lag column never achieved a C/C_0 of more than 0.01 during the test.

Appendix A contains the matrix of bed volumes and C/C_0 that apply to the breakthrough curve.

4 DISCUSSION

The Purolite® A530E was successful in removing pertechnetate from a supernate simulant for tank 241-AN-105 at 6.5 M sodium. The resin should be considered as a candidate in the technetium management effort. Over the course of the run, no visual degradation of the resin was apparent.

There is a definite matrix influence on the resin performance as evidenced by the distribution coefficient as a function of sodium molarity. As evidenced by the breakthrough at 284 BV versus the calculated λ, Table 4, it is evident that a matrix effect overrides this simplified approach to calculated breakthrough.

If the Purolite® A530E is to be used with undiluted tank supernate or with dissolved tank solids, further testing needs to be carried out, such as:

- Column configurations
- Leaching of sorbed pertechnetate from resin under environmental conditions
- Effects of long term exposure at sodium and pH levels of interest
- Sequestration of spent resin into Cast Stone as a final waste form

It is recommended that testing using Hanford double-shell tank waste be carried out in a hot cell environment.

5 REFERENCES

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APPENDIX A

Table A-1. Lead Column Response, C/C_o versus Bed Volumes

BV	C/Co
0	0.00
2	0.01
5	0.00
11	0.00
42	0.01
45	0.00
49	0.00
53	0.00
56	0.01
85	0.01
89	0.02
93	0.02
96	0.02
100	0.02
129	0.04
133	0.05
136	0.07
140	0.08
144	0.06
173	0.08
176	0.12
180	0.14
184	0.16
194	0.19
207	0.28
251	0.39
284	0.50
287	0.55
295	0.61
327	0.74
331	0.89
335	0.95
338	0.89
342	0.98

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