

**TECHNETIUM REMOVAL COLUMN FLOW  
TESTING WITH ALKALINE, HIGH SALT,  
RADIOACTIVE TANK WASTE**

David L. Blanchard, Jr.  
Dean E. Kurath  
Gita R. Golcar  
Steven D. Conradson<sup>1</sup>

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## Summary

This report describes two bench-scale column tests conducted to demonstrate the removal of Tc-99 from actual alkaline high salt radioactive waste. The waste used as feed for these tests was obtained from the Hanford double shell tank AW-101, which contains double shell slurry feed (DSSF). The tank sample was diluted to approximately 5 M Na with water, and most of the Cs-137 was removed using crystalline silicotitanates. The tests were conducted with two small columns connected in series, containing 10 mL of either a sorbent, ABEC 5000 (Eichrom Industries, Inc.), or an anion exchanger Reillex™-HPQ (Reilly Industries, Inc.). Both materials are selective for pertechnetate anion ( $\text{TcO}_4^-$ ). The process steps generally followed those expected in a full-scale process and included 1) resin conditioning, 2) loading, 3) caustic wash to remove residual feed and prevent the precipitation of  $\text{Al}(\text{OH})_3$ , and 4) elution. A small amount of Tc-99m tracer was added as ammonium pertechnetate to the feed and a portable GEA counter was used to closely monitor the process. Analyses of the Tc-99 in the waste was performed using ICP-MS with spot checks using radiochemical analysis. Technetium x-ray absorption spectroscopy (XAS) spectra of 6 samples were also collected to determine the prevalence of non-pertechnetate species [e.g. Tc(IV)].

Some of the relevant flow test parameters are given in Table S.1 and outlined below;

- The low decontamination factors (4-6) for the actual Tc-99 indicate that 15-25% of the Tc-99 in the waste is in a non-pertechnetate chemical form. While the decontamination factors are not as great as expected they are approximately equal to the estimated average required decontamination factor of 5.
- The significant decontamination factors based on the Tc-99m tracer data indicate that  $\text{TcO}_4^-$  is effectively removed from the AW-101 feed.
- The 15-25% of the Tc-99 that was not extracted corresponds to a Tc-99 level in the effluent of  $1.65 \times 10^{-2} \text{ Ci/m}^3$  to  $2.75 \times 10^{-2} \text{ Ci/m}^3$ . This is 5.5% to 9.2% of the NRC Class A limit of  $0.3 \text{ Ci/m}^3$ . The concentration in the final waste form would likely be higher.
- The relatively high fraction of non-pertechnetate Tc-99 in the AW-101 waste suggests that this phenomenon may be common in the tank wastes. It was expected that significant fractions of non-pertechnetate Tc-99 would be restricted to tank wastes with a high organic content. The DSSF from AW-101 contains a relatively low amount of organic ( approx. 2.5 g TOC/L in tank).
- As indicated by the  $\lambda_{50}$  values, the effective Tc-99 capacity of the Reillex™-HPQ is greater than that for the ABEC 5000 material. The difference between the  $\lambda_{50}$  values for the Tc-99m tracer data and the actual Tc-99 data is attributed to the non-pertechnetate fraction in the waste.
- Both materials are efficiently eluted, but the ABEC 5000 material is eluted with deionized water which would contribute a relatively small amount of other components to a final waste form.
- Few operational problems were experienced with either material, although a small portion of the Reillex™-HPQ bed on the second column was observed to float in solution and preparation of the ABEC 5000 column was tedious because of the difficulty in removing entrained air from the bed. It is suggested that a larger particle size would alleviate this problem.

- No evidence of fouling or other interactions between the waste and the  $\text{TcO}_4^-$  selective materials was observed.
- XAS spectra confirm the presence of non-pertechnetate Tc in the AW-101 waste feed.
- XAS spectra taken in April 1996 and August 1996 of the same sample of SY-103 waste feed clearly show an increase in the fraction of  $\text{TcO}_4^-$  in the sample. This suggests that the non-pertechnetate Tc in the sample is being oxidized to  $\text{TcO}_4^-$ .

Table S.1. Summary of Flow Test Parameters

	ABEC 5000		Reillex™-HPQ	
	Tc-99m tracer	Actual Tc-99	Tc-99m tracer	Actual Tc-99
Maximum DF	80	4	1100	6
$\lambda_{50}$	60	40	140	130
Eluant	Deionized water		1 M NaOH, 1 M ethylene diamine, 0.005 M $\text{SnCl}_2$	
Eluant Volume (to $C/C_0 = 0.001$ )	5 BV		7 BV	
Elution Rate	4.5 BV/hr		4.5 BV/hr	
Eluant Peak, $C/C_0$	28	17	69	50

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# 1.0 Introduction

## 1.1 Background

The contents of Hanford's 177 underground storage tanks (UST) include a mixture of sludge, salt cake, and alkaline supernatant liquid (Van Vleet, 1993). The insoluble sludge fraction of the waste consists of metal oxides and hydroxides and contains the bulk of the strontium-90 (Sr-90) and the transuranic radionuclides (TRU). The salt cake, generated by extensive evaporation of aqueous solution, consists primarily of dried sodium salts. The supernate consists of concentrated aqueous solutions of sodium nitrate/nitrite salts with smaller quantities of hydroxide, aluminum, potassium, carbonate, sulfate, and phosphate. The bulk of the water soluble radionuclides such as cesium-137 (Cs-137) and technetium-99 (Tc-99) are contained in the salt cake and supernatant fractions.

## 1.2 Tc-99 Inventory and Removal Requirements

Currently there is a significant amount of Tc-99 in the waste stored in the underground tanks. Estimates of the total inventory range from 1300 kg to 1900 kg (22.2 kCi to 32.5 kCi, Eager, 1995). Most analyses of actual double shell tank waste samples indicate that the highest concentrations of Tc-99 are several hundred  $\mu\text{Ci/L}$  (Van Vleet, 1993; Schmittroth *et al*, 1995). Estimates based on models are in reasonable agreement with these numbers (Shelton, 1994). Technetium-99, with a half life of  $2.12 \times 10^5$  years, is the only Tc isotope found in significant quantities in the waste. Other isotopes of Tc are either not significant fission products, or have short half lives of seconds to minutes (Anders, 1960).

The Tank Waste Remediation System (TWRS) Privatization Request for Proposal (DE-RP-06-96RL13308, abbreviated PRFP) specifies that Tc must be removed from the waste to the extent that the Immobilized Low-Activity Waste (ILAW) have a Tc-99 concentration  $< 0.3 \text{ Ci/m}^3$  (NRC Class A limit) on a volume averaged basis and meet release limits ( $2.8 \times 10^{-14} \text{ s}^{-1}$ ) placed on the ILAW. Most of the supernate in the Phase I tanks could be converted to glass without Tc removal and meet the Class A concentration limit. The latest performance assessment, completed before the PRFP was issued, estimated that an average of 80% of the Tc-99 will have to be removed to meet the release limit<sup>1</sup>. This corresponds to a decontamination factor of 5 and is used in this report as a benchmark for evaluation of process performance.

## 1.3 Need

Historically, much of the work on the removal of Tc-99 from alkaline waste has been directed at the recovery of Tc-99 as pertechnetate ( $\text{TcO}_4^-$ ) product, rather than Tc decontamination of waste (Roberts *et al*, 1962, Beard and Caudill, 1964). Technetium removal from West Valley alkaline supernate simulants by a number of different ion exchangers was investigated in FY 1983 at PNNL (Bray *et al*, 1984). Only charcoal and two organic anion exchange resins removed Tc effectively from the simulants. Technetium removal by ion exchange has also been investigated by several researchers at Los Alamos National Laboratory (LANL). Various ion exchange materials have shown the ability to remove technetium as pertechnetate from various simulated solutions (Marsh *et al*, 1994a; Marsh *et al*, 1994b; Marsh *et al*, 1994c; Marsh *et al*, 1995). Much of the

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<sup>1</sup> From an internal report by C.T. Kincaid and M.D. White, PNNL, 1995.

recent research concerning technetium removal has focused on the Reillex™-HPQ resin (Schroeder *et al*, 1993; Schroeder *et al*, 1994; Schroeder *et al*, 1995a; Schroeder *et al*, 1995b) and ABEC 5000 sorbent (Rogers *et al*, 1996).

In FY-95, samples of cesium decontaminated complexant concentrate (CC) waste from tanks SY-101 and SY-103 were shipped from Hanford to LANL for Tc removal experiments with Reillex™-HPQ. These wastes contain relatively high concentrations of organic complexants (Campbell *et al*, 1993). Ion exchange column experiments on CC simulants and batch contact experiments on the actual CC waste samples were performed at LANL to determine the equilibrium and kinetic parameters for Tc removal using the Reillex™-HPQ material. The results of the batch contacts, radiochemical analyses and Tc-99 NMR analyses indicated that 60-70% of the Tc in the waste samples was not removed via anion exchange and was probably not present as pertechnetate.

During the first half of FY-96, batch contacts were performed at PNNL to test Tc removal from actual Hanford tank waste supernates (Blanchard *et al*, 1996). Supernate samples from tanks SY-101, SY-103 and AN-107 were tested by contacting with Reillex™-HPQ resin and ABEC 5000 sorbent. These are complexant concentrate (CC) wastes, and have high concentrations of organic carbon (14-40 g/L TOC in-tank) due to the presence of organic complexants. Tc removal from these samples was poor (less than 50%), and it was subsequently concluded that they contain a relatively large fraction of non-pertechnetate Tc.

A double shell slurry feed (DSSF) composite supernate was also tested by contacting with Reillex™-HPQ and ABEC 5000. Both sorbents removed more than 90% of the Tc in the samples and subsequent flow tests using a DSSF feed were recommended. Those tests are the main subject of this report.

## 1.4 Objectives and Scope

The work described in this report involves the decontamination of liter quantities of actual Hanford tank waste. The testing involved using a small (10 ml beds) dual column system with the columns connected in series so that the effluent from the first column was fed to the second column. Two materials were tested: Reillex™-HPQ, an anion exchange material, and ABEC 5000, a sorbent. The feed was cesium decontaminated double shell slurry feed from tank AW-101 with a sodium concentration of about 5 M.

The objectives of the bench-scale flow testing for Tc removal were:

- Demonstrate Tc-99 decontamination factors;
- Determine the loading and elution efficiency of these materials;
- Assess the potential impact of exchanger fouling/poisoning;
- Investigate waste/exchanger chemistry;
- Assess the level of non-pertechnetate Tc.

## 1.5 Approach

An event diagram is shown in Figure 1.1 as an aid to understanding the test approach. The first action taken was to perform batch contacts to assess the effectiveness of the ABEC 5000 and the Reillex™-HPQ materials. The waste used in the batch contacts was an archived sample of DSSF (70% AW-101, 20% AP-106, 10% AP-102; Brown *et al.*, 1996). The results of these contacts indicated that as much as 96% of the Tc could be removed, so flow testing with this waste type was pursued. Several liters of waste were obtained and the cesium was removed using crystalline silicotitanates (CST's) at the 222-S laboratory operated by the Westinghouse Hanford Company. Removal of the Cs-137 allowed the experiments to be conducted in a fume hood instead of a remotely operated system in a hot cell.

The flow tests were conducted with two small columns in series to maximize the observed DF while still allowing a substantial breakthrough on the first column. The column size was chosen to be small enough to provide a  $C/C_0$  of 70% with the feed available but large enough to provide credible column data. The columns were at least 30 particle diameters wide in order to minimize the effects of channeling.

Monitoring of the Tc removal performance was done using 3 methods;

- 1) A small amount of Tc-99m (6 hr half life, 142.7 keV gamma) tracer was added as ammonium pertechnetate. A portable GEA counter was set up in the laboratory next to the columns and allowed the breakthrough of the Tc to be monitored closely and the length of the experiment to be optimized (end point of  $C/C_0 = 0.7$ ). The addition of the tracer as pertechnetate also allowed a performance baseline for pertechnetate removal to be developed simultaneously with the removal of the Tc initially present in the waste. Isotopic redistribution of the tracer was probably not significant since the tracer was added immediately prior to the experiment.
- 2) The bulk of the analyses for Tc were conducted using Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS). This has been found to be an accurate and relatively inexpensive method that is not sensitive to the oxidation state of the Tc or to the waste matrix. This method could be impacted by other isotopes with an  $m/z$  of 99. Fortunately, other elements with an  $m/z$  of 99 are either not significant fission products and are not known to have been added to the tank waste (i.e. Ru-99), or have very short half lives (i.e. Mo-99;  $t_{1/2}=67$  hrs, Nb-99,  $t_{1/2}=2.4$  m).
- 3) A limited number of samples were analyzed using a standard radiochemical method as a check on the ICP-MS method. This method determines the Tc-99 concentration by beta counting after separation of the Tc-99 from the waste matrix.

In addition, 5 samples were analyzed by x-ray absorption spectroscopy (XAS) to determine the oxidation state of the Tc present in the waste, and to determine if the fraction of pertechnetate observed in actual samples changes with time outside tank conditions.

# Tc Removal Event Diagram

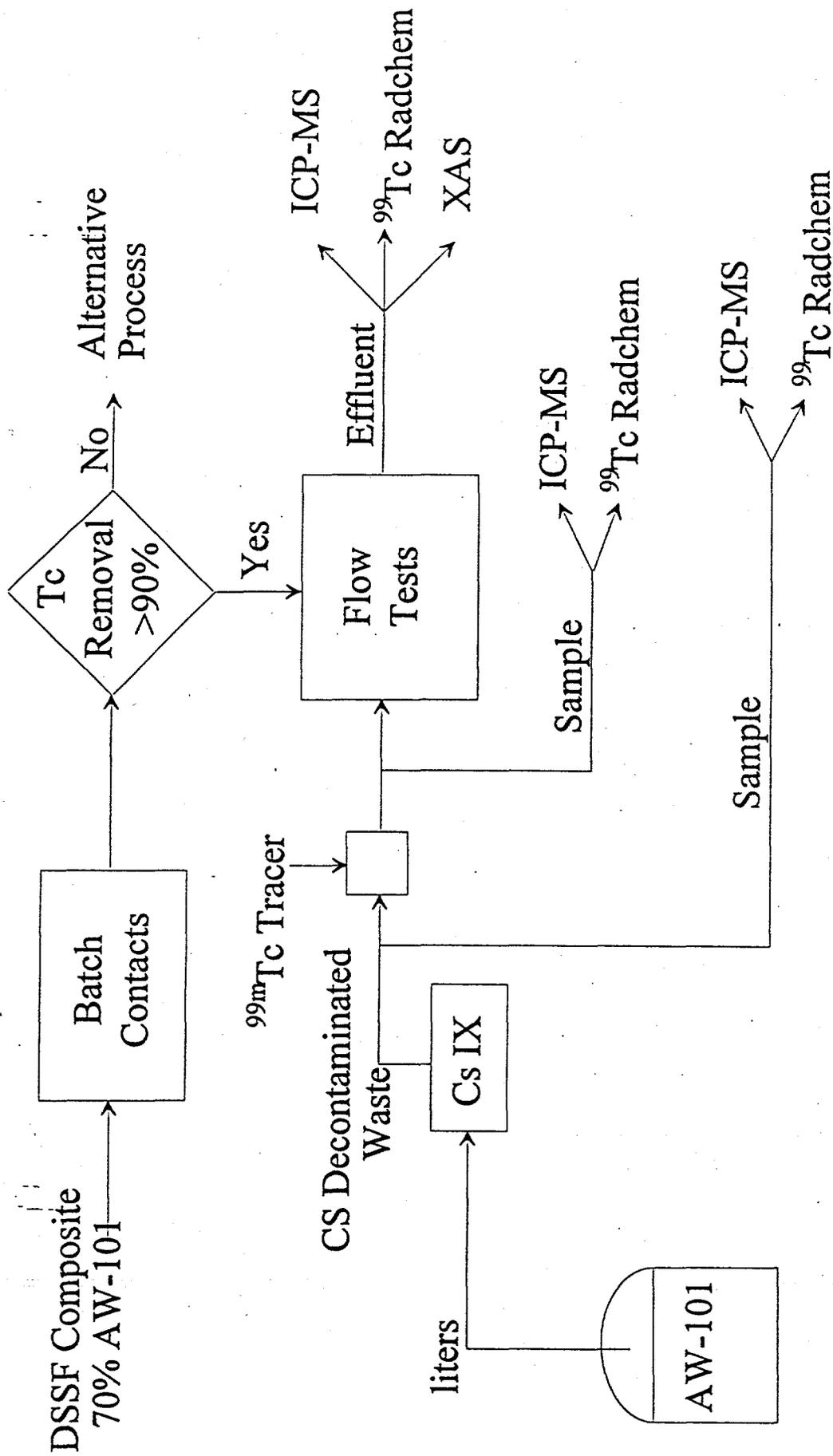


Figure 1.1. Tc Removal Event Diagram

## 2.0 Experimental

Reillex™-HPQ (Reilly Industries), an anion exchange resin, and ABEC 5000 (Eichrom Industries), a sorbent, were chosen for these tests because of their high selectivity for pertechnetate. Approximately 3 liters of cesium decontaminated supernate from tank AW-101 was used in the tests. It was passed downflow through two 10 ml beds in series, and eluted in the same direction. Technetium breakthrough and elution were followed during the tests with a Tc-99m tracer. Samples were subsequently analyzed for Tc-99 to determine the loading and elution behavior of the Tc-99 in the actual waste.

### 2.1 Sorbent Description and Preparation

ABEC 5000 is a polyethylene glycol based solid sorbent. The use of polyethylene glycol aqueous biphasic systems for metal ion extraction has been reviewed (Rogers et al, 1993; Rogers et al, 1995a), and the extraction of pertechnetate from high salt systems has been studied (Rogers and Zhang, 1996; Rogers et al, 1995b; Rogers et al, 1995c). The modification of this liquid/liquid extraction technology for use as a solid sorbent, and the use of the solid sorbent for pertechnetate uptake, has been described (Rogers et al, 1996). ABEC 5000 was shown in batch contact tests to effectively remove Tc from an actual Hanford tank waste DSSF composite, as discussed in Sec. 1.3. Therefore it was chosen for demonstrating Tc removal from AW-101 supernate (a DSSF waste).

The ABEC 5000 sorbent was provided by Eichrom Industries Inc. as a damp granular material. Approximately 10 ml of the ABEC 5000 was transferred to each ion exchange column and washed with 20 column volumes (BV) of deionized water in the downflow direction. A significant amount of trapped air bubbles and floating sorbent were observed, presumably due to attachment of air bubbles to the small (approximately 50 micron) sorbent beads. A significant effort (hours) was required to produce a well packed bed, and included column agitation (by hand), repetitive and alternating up- and down-flow cycles, pressurization of the column to approximately 80 psi, and eventually removal of a small amount of sorbent (2 mL) that remained floating. It has been reported that sonication of the column results in a well packed bed<sup>1</sup>. The size of the columns and the presence of an outer safety jacket on the columns made sonication with a bath ineffective. A narrow sonic probe inserted in the column may be useful for this purpose, but was not available. Sonication of ABEC 5000 in a beaker prior to transfer resulted in greater air entrainment, and a more difficult transfer of the material into the column. After the beds were well packed, they were washed with 6.0 BV of simulated DSSF solution.

The Reillex™-HPQ organic anion exchange resin is a co-polymer of divinylbenzene and 4-vinylpyridine that is subsequently methylated at the pyridine nitrogen. The methylation provides a strong base anionic site found to be highly selective for pertechnetate. The resin is macroporous and highly stable to radiolysis; its preparation and performance have been reported (Schroeder *et al*, 1993, Schroeder *et al*, 1994, Schroeder *et al*, 1995a). Reillex™-HPQ was reported by Schroeder *et al* (1995b) to effectively remove pertechnetate from simulated DSSF and double shell slurry (DSS), and was shown to remove greater than 90% of the Tc from a DSSF supernate sample (Blanchard *et al*, 1996)

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<sup>1</sup>Professor Robin D. Rogers, University of Alabama Department of Chemistry. Private communication.

The Reillex™-HPQ, provided by Reilly Industries, was received in the chloride form. It was granular with a particle size distribution ranging from 295 - 595 micron. Before use in the flow tests, the resin was contacted with 20.0 BV of 1.0 M nitric acid to convert the resin from the chloride form to the nitrate form. The discharged effluent was monitored for the presence of chloride ion with a silver nitrate solution. The resin was washed with 20 BV of deionized water and dried under low vacuum for 24 hours. Approximately 10 ml of the dried nitrate form resin was then added to each ion exchange column. The columns were flushed in the downflow direction with approximately 10 BV of deionized water, followed by 6 BV of simulated DSSF solution at 9.0 BV/hr.

When the materials were weighed and transferred to the columns, a small portion of each was set aside, weighed and dried for 48 hours at 60°C. The F factors, the mass of the dried sample divided by the mass of the initial sample, were determined (Table 2.1). The F factor is used to evaluate material performance on a standard dry-weight basis. The bed densities (in DSSF simulant) and the dry densities of the materials were also determined (Table 2.1).

**Table 2.1.** F-Factors and Densities for ABEC 5000 and Reillex™-HPQ

TcO <sub>4</sub> <sup>-</sup> Selective Material	F- Factor	Dry Density (g/ml)	Wet Density (g/ml)
ABEC 5000	0.331 (48 hrs)	0.666	0.894
Reillex™-HPQ	0.921 (48 hrs)	0.585	0.538

## 2.2 Selection of Column Size

A key decision in the design of an ion exchange cycle is the cycle time and the corresponding column size to obtain a meaningful and complete breakthrough curve. In these experiments the column bed volume was limited by the amount of actual AW-101 supernate available (maximum of 9.0 L). The column diameter required was estimated to be 30 times bigger than the resin particle diameter to avoid wall effects for accurate scale-up data. The Reillex™-HPQ resin diameter (dried nitrate form) varied from 110 microns to over 640 microns, but 81% was in the range from 260 microns to 450 microns, so a column diameter of 1.0 cm was considered adequate. To allow direct comparison of the materials, the same column configuration was used for the ABEC 5000 sorbent test, although the average resin diameter was much smaller (approximately 50 microns).

The choice of column bed volume, 10 mL, was based on batch distribution data collected previously (Blanchard *et al*, 1996), simulant studies (Schroeder *et al*, 1995b) and the volume of waste feed available. The  $\lambda$  values determined by Blanchard *et al* (1996) for DSSF waste feed indicated that 70% breakthrough on a Reillex™-HPQ column would be reached between 100 BV and 250 BV, and on an ABEC 5000 column between 20 BV and 40 BV. A total feed volume of at least 5 L was expected to be available, so 10 mL bed volumes was a conservative choice. The same bed volume was used for the two sorbents so the results could be directly compared.

## 2.3 Equipment Description, Assembly, and Testing

The test apparatus consisted of: polyethylene feed and effluent storage bottles; a valveless, reciprocating, positive displacement piston pump; a low internal volume pressure gauge; two chromatography columns in series; a three way ball valve (316 stainless steel) located between the columns for sampling; and 1/8" and 1/16" O.D. PTFE tubing. Tubing connectors were made of nylon or PTFE. The column assemblies were composed of heavy wall glass columns (1.0 cm I.D. X 30 cm long) mounted inside a clear acrylic jacket for safety and temperature control. (The temperature of the columns during the tests was left at ambient, approximately 21°C.) Effluent samples were collected at the ball valve in 20 mL glass scintillation vials. A photograph of the test apparatus is shown in Figure 2.1. A schematic of the test system is presented in Figure 2.2.

The equipment was completely assembled on the bench, and leak tested with DI water. The columns were then packed with ABEC 5000 or Reillex™-HPQ and prepared as described in Sec. 2.1. The systems were then partially disassembled and reassembled in a radiological "Contamination Area" fume hood. Sufficient DSSF simulant was run through the columns to ensure the integrity of all seals and to remove voids and bubbles prior to running the tests.

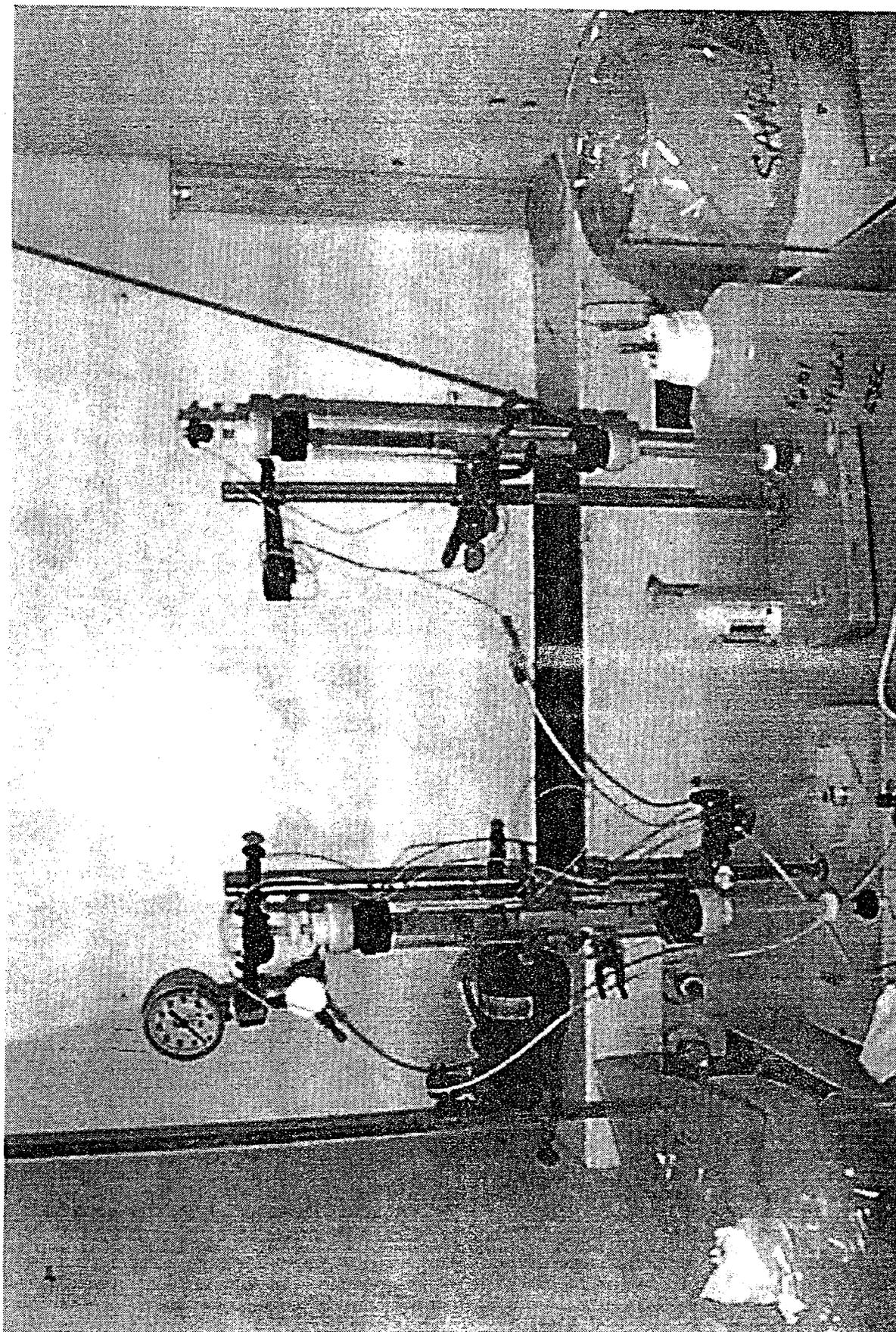


Figure 2.1. Photograph of the Test System

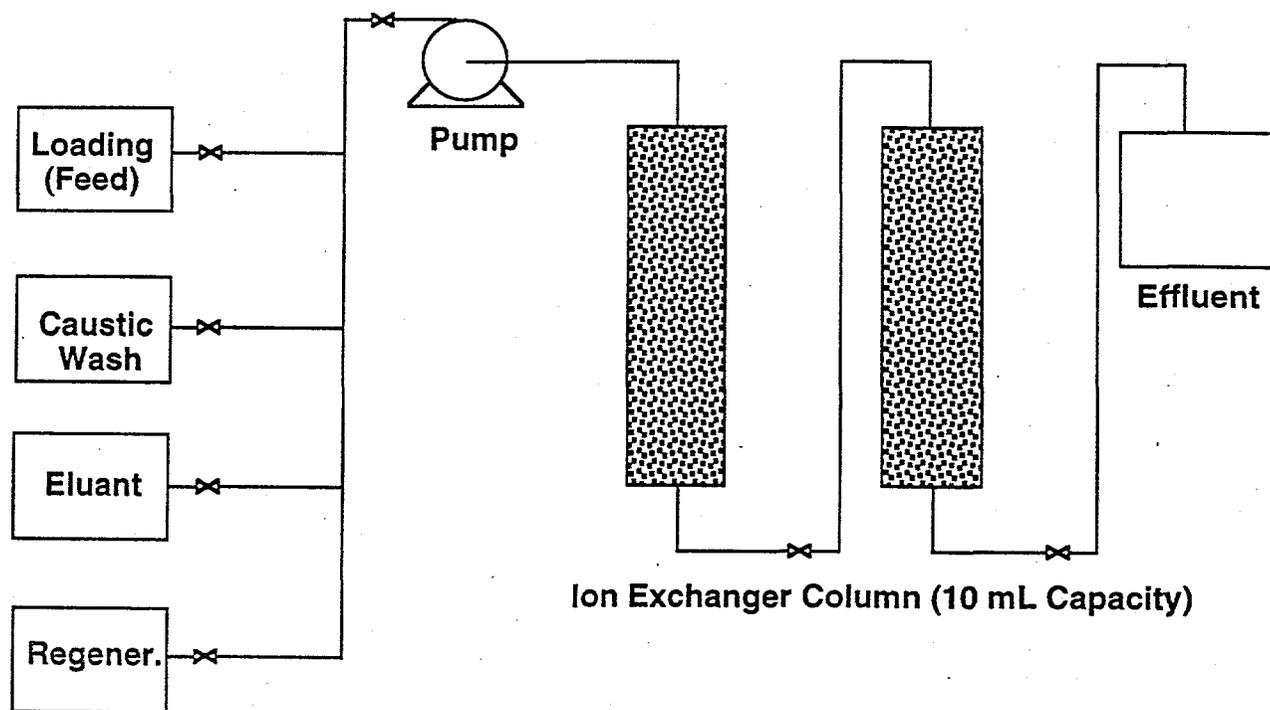


Figure 2.2. Schematic of the Test System

## 2.4 Feed Preparation

The supernate was removed from tank AW-101 in May, 1996, and diluted to approximately 5 M Na with water. The waste was cesium decontaminated with crystalline silicotitanate (CST) at the WHC 222-S laboratory. Details of the feed preparation and tests may be found in Hendrickson *et al* (1996). Approximately 6.5 liters of the diluted, filtered, Cs decontaminated AW-101 supernate was received at PNNLs 325 Building in seven 1 liter bottles. The low dose rate resulting from Cs decontamination allowed the Tc removal experiments to be conducted in a radiological "Contamination Area" fume hood. Preparation of the feed received from the Cs decontamination demonstration was minimal, and consisted of mixing the bottles of feed and adding a Tc-99m tracer to follow breakthrough progress. (Additional Cs decontamination was performed, as described below, on about 1.5 L of the feed to reduce the high dose rate from this material.)

For the ABEC 5000 tests the contents of the first five 1 liter bottles were combined and mixed to ensure a homogeneous feed. The last two bottles containing approximately 1.5 L of feed were not included because they exhibited a 5X to 10X greater Cs-137 activity (as measured by contact dose rates) than the first 5 bottles. (This is consistent with the presence of more Cs in effluent collected at later times, due to Cs breakthrough, during the Cs decontamination demonstration.) Immediately prior to the experiment, Tc-99m, a gamma emitting isotope with a 6.01 hour half life, was added as ammonium pertechnetate to follow breakthrough progress and to provide an indication of the behavior of pertechnetate in the actual waste feed. The concentration of Tc-99m was approximately 0.5 micro Ci/L in the feed. Complete decay of the Tc-99m to Tc-99 resulted in the addition of  $1 \times 10^{-10}$  g/L Tc-99. The total concentration of Tc-99 in the feed was found to be  $4.2 \times 10^{-3}$  g/L, so the contribution from the decayed tracer is negligible.

For the Reillex<sup>TM</sup>-HPQ tests, all feed remaining from the ABEC 5000 test was combined with the feed in bottles 6 and 7, after the later was Cs decontaminated by contacting with an excess of CST for approximately 72 hours. Immediately prior to the experiment, fresh Tc-99m tracer was added as ammonium pertechnetate to the ~ 5.5 L of feed to give a Tc-99m concentration of approximately 1.5 micro Ci/L. Contribution of Tc-99 from the tracer is again negligible. The feed compositions for both the Cs decontamination test (described in Hendrickson *et al*, 1996) and the Tc removal tests are shown in Tables 2.2 - 2.4.

**Table 2.2.** Concentrations of Nonradioactive Cations in AW-101 Feed

Cation	Units	<sup>137</sup> Cs Column Flow Feed	<sup>99</sup> Tc Column Flow Feed
Ag	<u>M</u>	8.30 E-05	8.44 E-05
Al	<u>M</u>	5.75 E-01	5.56 E-01
As	<u>M</u>	5.35 E-04	5.35 E-04
B	<u>M</u>	2.35 E-03	2.09 E-03
Ba	<u>M</u>	1.46 E-04	1.46 E-04
Bi	<u>M</u>	1.92 E-04	1.92 E-04
Cr	<u>M</u>	1.09 E-03	9.70 E-04
K	<u>M</u>	4.95 E-01	4.73 E-01
Li	<u>M</u>	6.43 E-04	6.06 E-04
Mg	<u>M</u>	1.65 E-03	1.65 E-03
Mn	<u>M</u>	8.25 E-05	7.30 E-05
Mo	<u>M</u>	3.28 E-04	3.14 E-04
Na	<u>M</u>	5.52 E+00	5.50 E+00
Ni	<u>M</u>	1.37 E-04	1.46 E-04
P	<u>M</u>	4.89 E-03	4.17 E-03
S	<u>M</u>	6.76 E-03	6.23 E-03
Sb	<u>M</u>	1.98 E-04	1.98 E-04
Si	<u>M</u>	4.07 E-03	3.22 E-03
Ti	<u>M</u>	8.37 E-05	8.37 E-05
Zn	<u>M</u>	1.55 E-04	1.61 E-04
Zr	<u>M</u>	8.35 E-05	1.11 E-04

**Table 2.3. Concentrations of Nonradioactive Anions in AW-101 Feed**

Anion	Units	<sup>137</sup> Cs Column Flow Feed	<sup>99</sup> Tc Column Flow Feed
Br <sup>-</sup>	<u>M</u>	3.34 E-03	NA
Cl <sup>-</sup>	<u>M</u>	8.18 E-02	NA
F <sup>-</sup>	<u>M</u>	3.34 E-02	NA
NO <sub>2</sub> <sup>-</sup>	<u>M</u>	1.13 E+00	NA
NO <sub>3</sub> <sup>-</sup>	<u>M</u>	1.40 E+00	NA
OH <sup>-</sup>	<u>M</u>	2.69 E+00	NA
Ox	<u>M</u>	3.90 E-03	NA
PO <sub>4</sub> <sup>3-</sup>	<u>M</u>	5.53 E-03	NA
SO <sub>4</sub> <sup>2-</sup>	<u>M</u>	3.28 E-03	NA
TIC	<u>M</u>	1.15 E-01	NA
TOC	<u>M</u>	6.16 E-01	NA

NA - Not available at the time of issuance of this report.

**Table 2.4. Concentrations of Radionuclides in AW-101 Feed**

Component	Units	Tank Sample	Cs Decontaminated - WHC
Cs-137	Ci/L	2.14 E-01	2.23 E-04
Co-60	Ci/L	6.07E-06	2.18 E-06
Eu-154	Ci/L	4.32 E-05	1.32 E-06
Eu-155	Ci/L	2.29 E-04	1.47 E-06
Am-241	Ci/L	5.28 E-04	2.21 E-06
Am-243	Ci/L	NA	5.43 E-02
Cm-243/244 --	Ci/L	3.45 E-08	NA
Pu-236	Ci/L	NA	5028 E-02
Pu-238	Ci/L	3.97 E-08	NA
Pu-239/240	Ci/L	4.05E-06	1.63 E-07

NA - Not available at the time of issuance of this report.

## 2.5 Process Steps

Both sorbents were conditioned with DSSF simulant before loading as described in Section 2.1. This reduces bed volume changes that may occur when actual feed is introduced if the bed is not in a solution similar to the feed. Technetium was loaded onto the sorbents directly from the alkaline waste, and 5 mL samples were collected from the first and second columns at various intervals. Breakthrough was followed by monitoring the activity of Tc-99m in the samples with a portable gamma energy analysis instrument located on the bench adjacent to the fume hood. After approximately 70% breakthrough of the Tc-99m was observed, the columns were washed with an NaOH solution (2 M for ABEC 5000, 1 M for Reillex™-HPQ) to remove residual feed. The hydroxide was used to prevent precipitation of aluminum hydroxides and oxides, and in the case of ABEC 5000, to ensure that Tc remained on the sorbent during the wash. Technetium was eluted from the ABEC 5000 beds with distilled de-ionized water (DI). Technetium was eluted from the Reillex™-HPQ beds with a solution of 1.0 M NaOH, 1.0 M ethylene diamine, and 0.005 M SnCl<sub>2</sub>. The system was run at 30 to 50 psi throughout the tests. The process steps and the specific conditions used during each stage of the flow testing are summarized in Table 2.5.

Table 2.5. Test Steps and Conditions

Material	Process Step	Feed	Flow Rate
ABEC 5000	Exchanger Conditioning	Deionized Water DSSF Simulant	20.0 BV (9.0 BV/hr) 6.0 BV (9.0 BV/hr)
	Loading	AW-101 Feed	(9.0 BV/hr)
	Caustic Wash	2.0 M NaOH	(9.0 BV/hr)
	Elution	Deionized Water	(4.5 BV/hr)
Reillex™-HPQ	Exchanger Conditioning	Deionized Water DSSF Simulant	10.0 BV (9.0 BV/hr) 6.0 BV (9.0 BV/hr)
	Loading	AW-101 Feed	(10.0 BV/hr)
	Caustic Wash	1.0 M NaOH	(12.0 BV/hr)
	Elution	1.0 M NaOH, 1.0 M ethylene diamine, and 0.005 M SnCl <sub>2</sub>	(4.5 BV/hr)

## 2.6 Analytical

### General

Cation concentrations were determined by inductively coupled plasma / atomic emission spectroscopy (ICP/AES). Anion concentrations were determined by ion chromatography (IC). Tc-99 concentrations were determined by inductively coupled plasma / mass spectrometry (ICP/MS). For this analysis, all  $m/z = 99$  signal was attributed to Tc-99. The only other likely mass 99 isotope is Ru-99. The Ru isotope distribution in all samples appeared to be non-natural. This is consistent with fission production of Ru, rather than addition of natural Ru during fuel processing. Ru-99 is not a significant fission product, so the assumption should be valid that Tc is the only mass 99 isotope in the samples.

As a check on the ICP-MS, about half the samples were analyzed for Tc-99 concentration using a radiochemical procedure. The samples are vigorously oxidized, then pertechnetate is chemically separated from each sample. The activity of the separated pertechnetate is determined by either proportional beta counting or liquid scintillation counting. The vigorous oxidation is necessary to completely convert non-pertechnetate species found in the actual waste to pertechnetate, as described and demonstrated previously (Blanchard *et al*, 1996). Although more expensive and time consuming than ICP-MS, this method distinguishes between Tc-99 and other mass 99 isotopes, providing an excellent check on the ICP-MS results.

### Gamma Energy Analysis (GEA)

Tc-99m  $C/C_0$  values were determined through the use of a portable gamma spectroscopy system. This consists of a lap top computer, an electronics unit, and a high-purity germanium (HPGe) detector. The HPGe is a 20% relative-efficiency semiconductor detector, which (along with a preamplifier) converts incident gamma into small voltage pulses. These pulses are amplified, shaped, and converted to digital pulses in the electronics unit. The resulting histogram of digital pulses is plotted versus energy, and may be appropriately analyzed with the computer system.

To determine Tc-99m  $C/C_0$  values, the gamma spectra of the samples were collected using identical conditions (sample size, position, count time, etc.) The maximum count in the Tc-99m 142.7 eV gamma emission peak was then normalized to the maximum count in the same peak for the feed sample. The values were decay corrected using the time recorded with the spectra. Glass 20 mL scintillation vials were used for the samples. They were placed approximately 3" from the end of the detector, and spectra were collected for 120 s (active counting) for each sample. Saturation of the detector was not observed. The samples were shielded during counting to reduce background.

## 3.0 Results

As discussed in Section 2.4, preparation of the feed received from the Cs decontamination demonstration was limited to mixing the bottles of feed and adding a Tc-99m tracer to follow breakthrough progress. The activity of the last 1.5 L of feed was reduced by contacting with CST material to remove Cs-137 before mixing with the rest of the feed. Analysis of the concentration of Tc-99 in the feed for the ABEC 5000 run by ICP-MS indicated 4.40 ug/mL. ICP-MS analysis of the feed for the Reillex™-HPQ run indicated 4.28 ug/mL.

### 3.1 Tc Loading

The ABEC 5000 columns were loaded downflow with the AW-101 feed at a rate of 9 BV/hr. The effluent from the first column was sampled during loading and the Tc-99m  $C/C_0$  values were immediately determined as described in Sec. 2.6. The resulting Tc-99m breakthrough curve is shown in Figure 3.1. A log-probability plot is used, which largely converts the sigmoidal loading curve to a straight line. The data shows just over 1% breakthrough of the Tc-99m pertechnetate at 1 BV, for a DF of 80. The breakthrough began to increase more quickly after the 10th BV, and 50% breakthrough occurred at approximately 60 BV.

Subsequent determination of the Tc-99 concentration in the samples by ICP-MS gave significantly different results (also shown in Figure 3.1). Both Tc-99m and Tc-99 breakthrough curves are plotted on a linear-log scale to allow comparison. The initial ABEC 5000 samples show immediate Tc-99 breakthrough of 20%, for a DF of 4. Fifty percent (50%) breakthrough occurred much sooner for the Tc-99 than for the Tc-99m, at approximately 38 BV.

A small peak in  $C/C_0$  appears between 1 and 10 BV. Because it is present in both the Tc-99m and Tc-99 breakthrough curves, it appears real, and is probably caused by changes in the bed packing and flow rate. (The volume of feed processed in this region was estimated from the expected flow rate.) This peak does not significantly affect the breakthrough curve.

Analysis of a sample of the load effluent composite gives a Tc-99 concentration of 1120 ug/mL, or  $C/C_0$  of 0.25. This effluent passed through both columns; the second column is expected to pick up much of the pertechnetate Tc that passed through the first column. A Tc-99  $C/C_0$  in this effluent that is the same as the Tc-99  $C/C_0$  seen for the immediate breakthrough on the first column suggests that the Tc-99 that immediately broke through the first column also passed straight through the second column.

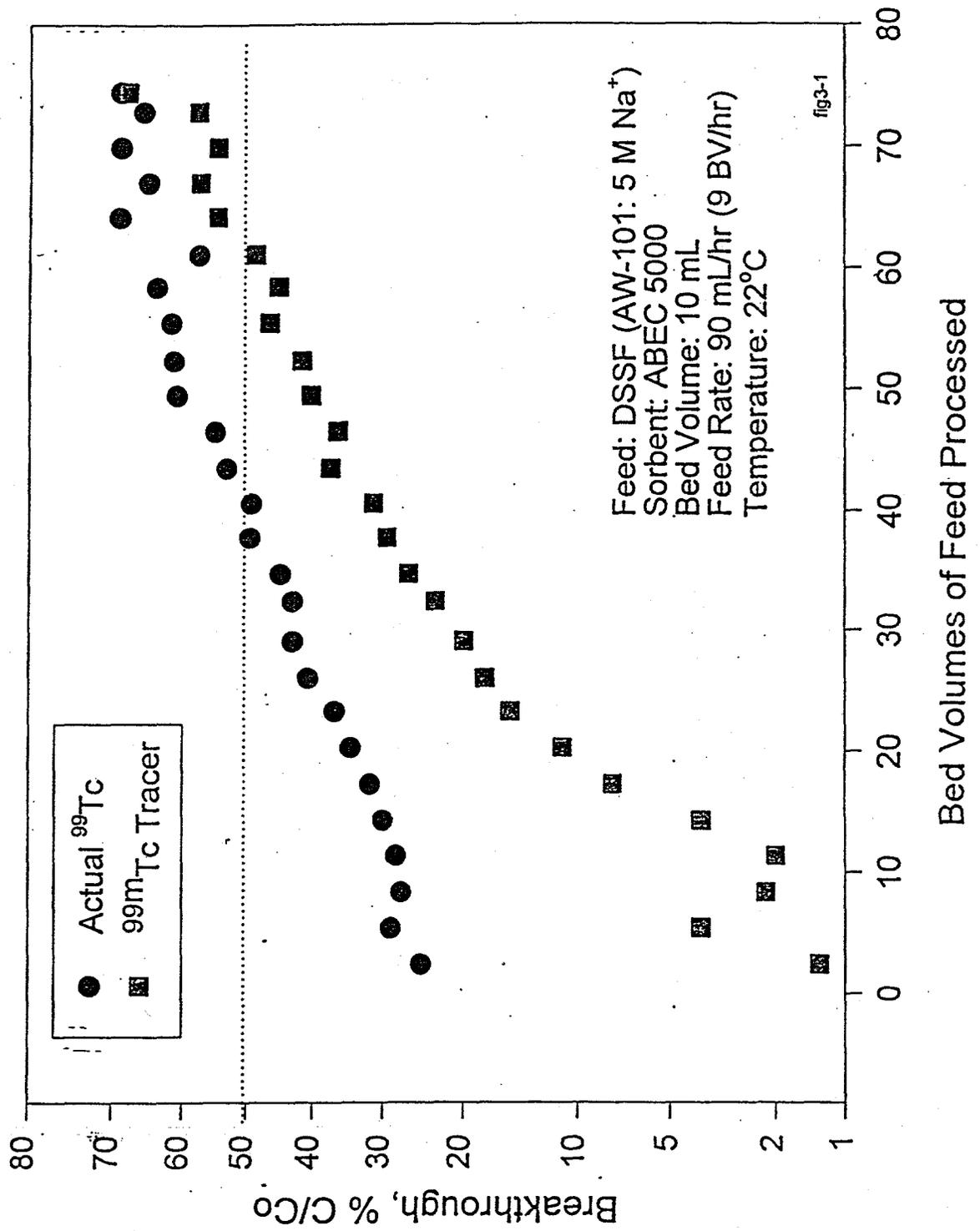
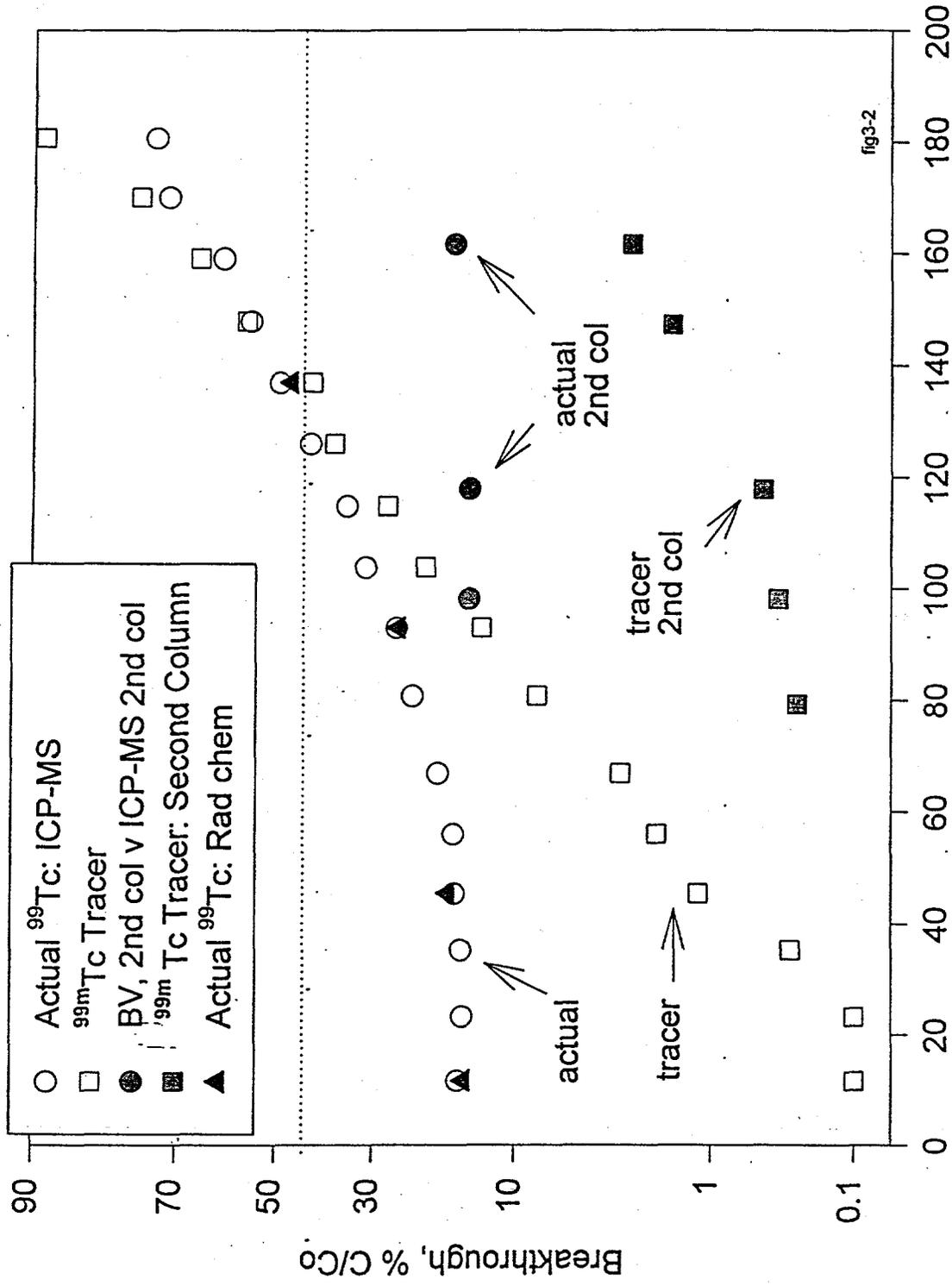


Figure 3.1. Tc Removal from DSSF (AW-101) with ABEC 5000

The Tc-99m results for the Reillex™-HPQ test are shown in Figure 3.2. Only 0.1% breakthrough was observed after 1 BV, for a DF of 1000, with 50% breakthrough at approximately 140 BV. However, immediate Tc-99 breakthrough is also observed for the Reillex™-HPQ test. There is less immediate breakthrough (15%, for a DF of 6) for the Reillex™-HPQ than for the ABEC 5000. Fifty percent breakthrough of Tc-99 occurred at approximately 130 BV. Radiochemical data for Tc-99  $C/C_0$  are also shown in Figure 3.2, and are in excellent agreement with the ICP-MS values.

The  $C/C_0$  values for samples taken after the second column are also shown in Figure 3.2. The results parallel the 1st column data. The Tc-99m shows very little initial breakthrough, while the Tc-99 shows immediate breakthrough of 15%. The Tc-99m pertechnetate is effectively removed by both Reillex™-HPQ beds, but a significant fraction of the actual Tc-99 passed through both columns without removal.

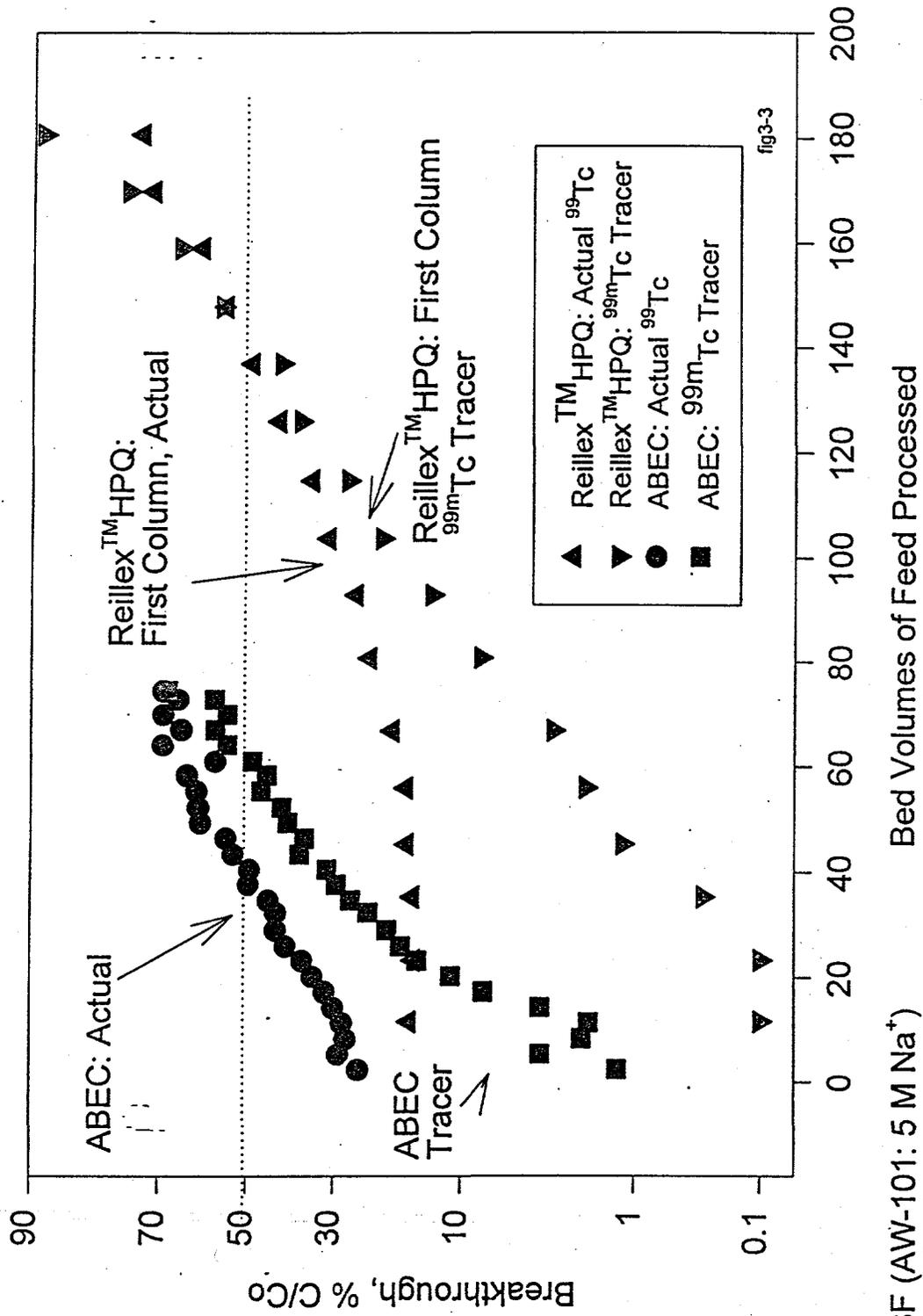
Technetium-99m and Tc-99 breakthrough curves for both the ABEC 5000 and Reillex™-HPQ tests are plotted together in Figure 3.3 for direct comparison. The Reillex™-HPQ is able to process a 2.2 X greater volume of feed than ABEC 5000 for the same bed volumes, to reach 50% breakthrough of Tc-99m. Reillex™-HPQ also shows better initial removal (0.1% initial Tc-99m breakthrough vs 1% for ABEC 5000). The difference between the  $\lambda_{50}$  values for the Tc-99m tracer data and the actual Tc-99 data is attributed to the non-pertechnetate fraction in the waste, as described below. It does not appear to be due to fouling of the materials by the waste, since this would affect both the Tc-99 and Tc-99m in the same way and to the same degree. No other interactions between the waste and the pertechnetate selective materials were observed.



Feed: DSSF (AW-101: 5 M Na<sup>+</sup>)  
 Exchanger: Reillex™HPQ  
 Bed Volume: 10 mL  
 Feed Rate: 100 mL/hr (10 BV/hr)  
 Temperature: 22°C

Bed Volumes of Feed Processed

Figure 3.2. Tc Removal from DSSF (AW-101) with Reillex™-HPQ



Feed: DSSF (AW-101: 5 M Na<sup>+</sup>)  
 Bed Volume: 10 mL  
 Feed Rate ABEC: 90 mL/hr (9 BV/hr)  
 Feed Rate Reillex: 100 mL/hr (10 BV/hr)

Figure 3.3. Comparison of ABEC 5000 and Reillex™-HPQ Tc Breakthrough Curves

The difference between the Tc-99 and the Tc-99m breakthrough curves is either real or an experimental artifact. The most probable artifact is the presence of a mass 99 isotope other than Tc in the feed. This would pass through the columns with little or no sorption by ABEC 5000 or Reillex™-HPQ because of their high selectivity for pertechnetate. This mass 99 isotope could then be reported as Tc-99 by the ICP-MS analysis. The most probable sources of mass 99 isotopes other than Tc are Ru-99 present in the tank waste or a mass 99 isotope inadvertently added with the Tc-99m tracer spike.

Ruthenium isotopic abundances characteristic of tank waste were observed in ICP-MS data for the samples. Ruthenium-99 is not a significant fission product, and has not interfered with ICP-MS analysis of Tc in CC and DSSF tank waste, as shown by a comparison of ICP-MS and radiochemical data (Blanchard *et al*, 1996). The ICP-MS data are in excellent agreement with the radiochemical data in this study as well. Analysis of the decayed tracer solution and the unspiked feed indicates no contamination of the feed by the tracer spike, as expected from process knowledge of the tracer spike composition. Therefore it is unlikely that the difference in the curves is an experimental artifact.

Since the Tc-99m was added to the feed as pertechnetate, it is reasonable to assume that the Tc-99m breakthrough curve represents that of pertechnetate in the feed. So it is likely that the immediate breakthrough of Tc-99 is due to the presence of a non-pertechnetate species that is not sorbed by ABEC 5000 or Reillex™-HPQ.

Removal of this baseline breakthrough (by subtraction from  $C_0$  and from all C values) results in Tc-99 curves that look almost identical to the Tc-99m tracer breakthrough. This suggests that the Tc-99 pertechnetate in AW-101 is effectively removed by ABEC 5000 and Reillex™-HPQ, and that it is well modeled by the Tc-99m tracer. This "normalization" is shown in Figure 3.4. Both the Tc-99m and the "normalized" Tc-99 breakthrough curves for the ABEC 5000 and Reillex™-HPQ tests are plotted on a linear-probability scale to allow comparison.

Previous batch contacts performed at PNNL with a DSSF composite supernate suggested that there may be a small amount (less than 5%) of non-pertechnetate Tc present. The column test results indicate much more than this (22% or more) in the AW-101. The difference is probably due to the different feeds used in the two sets of tests. The DSSF composite tested in the initial batch contacts was being used for other tests as early as March, 1994 (Brown *et al*, 1996). Therefore the waste was taken from the tanks at least two years before the batch contacts performed in March 1996 to test Tc removal. As shown in Sec. 3.4, it appears likely that the non-pertechnetate species oxidizes to pertechnetate over time after removal from the tanks. So any non-pertechnetate Tc originally in this composite may well have oxidized to pertechnetate before the batch contacts were run. In contrast, the AW-101 sample used for the column tests reported here was taken from the tank in February, 1996. Evidently there was not time for much of the non-pertechnetate in the sample to oxidize to pertechnetate.

The 15-25% of the Tc-99 that was not extracted corresponds to a Tc-99 level in the effluent of  $1.65E-02 - 2.75E-02$  Ci/m<sup>3</sup>. This is 5.5-9.2% of the NRC Class A limit of 0.3 Ci/m<sup>3</sup>. The concentration in the final waste form would likely be higher.

The relatively high fraction of non-pertechnetate Tc-99 in the AW-101 waste suggests that this phenomena may be common in the tank wastes. It had been previously expected that significant fractions of non-pertechnetate Tc-99 would be restricted to tank wastes with a high organic content. The DSSF from AW-101 contains a relatively low amount of organic.

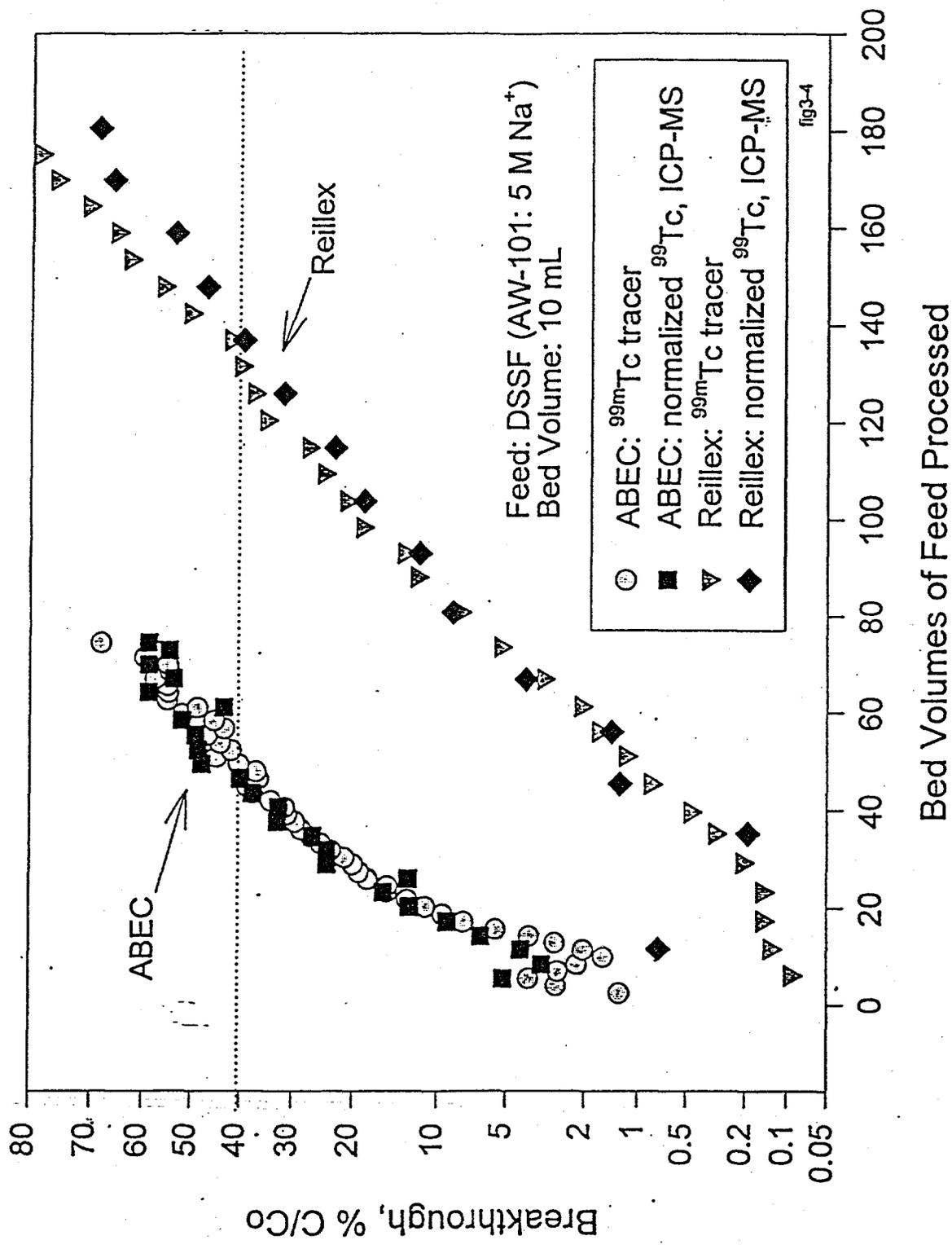


Figure 3.4. ABEC 5000 and Reillex™-HPQ Tc Breakthrough Curves: Normalized Data

### 3.2 Bed Washing

The ABEC 5000 bed was washed with 2 M NaOH at approximately 9 BV/hr before elution to prevent precipitation of aluminum oxides and hydroxides from the feed remaining in the column. A significant amount of Tc-99 was observed in the wash. Samples of the wash showed an increase in the concentration of Tc-99 from  $C/C_0 = 0.6$  to 1.1 during the wash cycle (2.5 BV).

Pertechnetate is sorbed to ABEC 5000 more completely the higher the ionic strength of the liquid phase (i.e., feed, wash, etc.). A higher hydroxide concentration in the wash probably would have resulted in less Tc being washed off during this step. This also shows that pertechnetate removal from tank waste supernates using ABEC 5000 would be best performed before dilution for other processing, such as Cs decontamination.

The Reillex™-HPQ bed was washed with 1 M NaOH at approximately 12 BV/hr before elution. The concentration of Tc-99 in the wash decreased from  $C/C_0 = 0.54$  to 0.022 during the wash cycle (5.25 BV), indicating little removal of pertechnetate from the resin.

### 3.3 Tc Elution

The ABEC 5000 was eluted with distilled de-ionized water at approximately 4.5 BV/hr. Greater than 99.8% of the Tc-99 loaded on the column was eluted within 5 BV (Figure 3.5). The bed expanded greatly, to a final volume of almost 20 mL. (For consistency, 1 BV is one bed volume in the feed, or 10 mL.) The elution curve was asymmetric, rising from  $C/C_0 = 1$  to 17.5 in 3.2 BV, and dropping 99.8% to  $C/C_0 = 0.035$  in just 0.4 BV. Elution curves for the Tc-99m tracer and the Tc-99 were very similar, although  $C/C_0$  for the tracer was consistently 60% higher.

The Reillex™-HPQ was eluted with an aqueous solution 1 M in NaOH, 1 M in ethylene diamine (en) and 0.005 M in  $\text{SnCl}_2$  at approximately 4.5 BV/hr. Greater than 99.9% of the Tc-99 loaded on the column was eluted within 6 BV (Figure 3.4). The bed contracted by approximately 1%. The elution curve is bell shaped, but broader than a Gaussian at the apex. Elution curves for the Tc-99m tracer and the Tc-99 were very similar, although  $C/C_0$  for the tracer was consistently 40% higher.

Both materials are efficiently eluted, but because ABEC 5000 is eluted with deionized water, very little is added to the final waste form other than Tc. Use of ABEC 5000 would require a column design that accommodated the large (2X) expansion that occurs upon elution.

No evidence of fouling or other interactions between the waste and the  $\text{TcO}_4^-$  selective materials was observed at any stage of the tests.

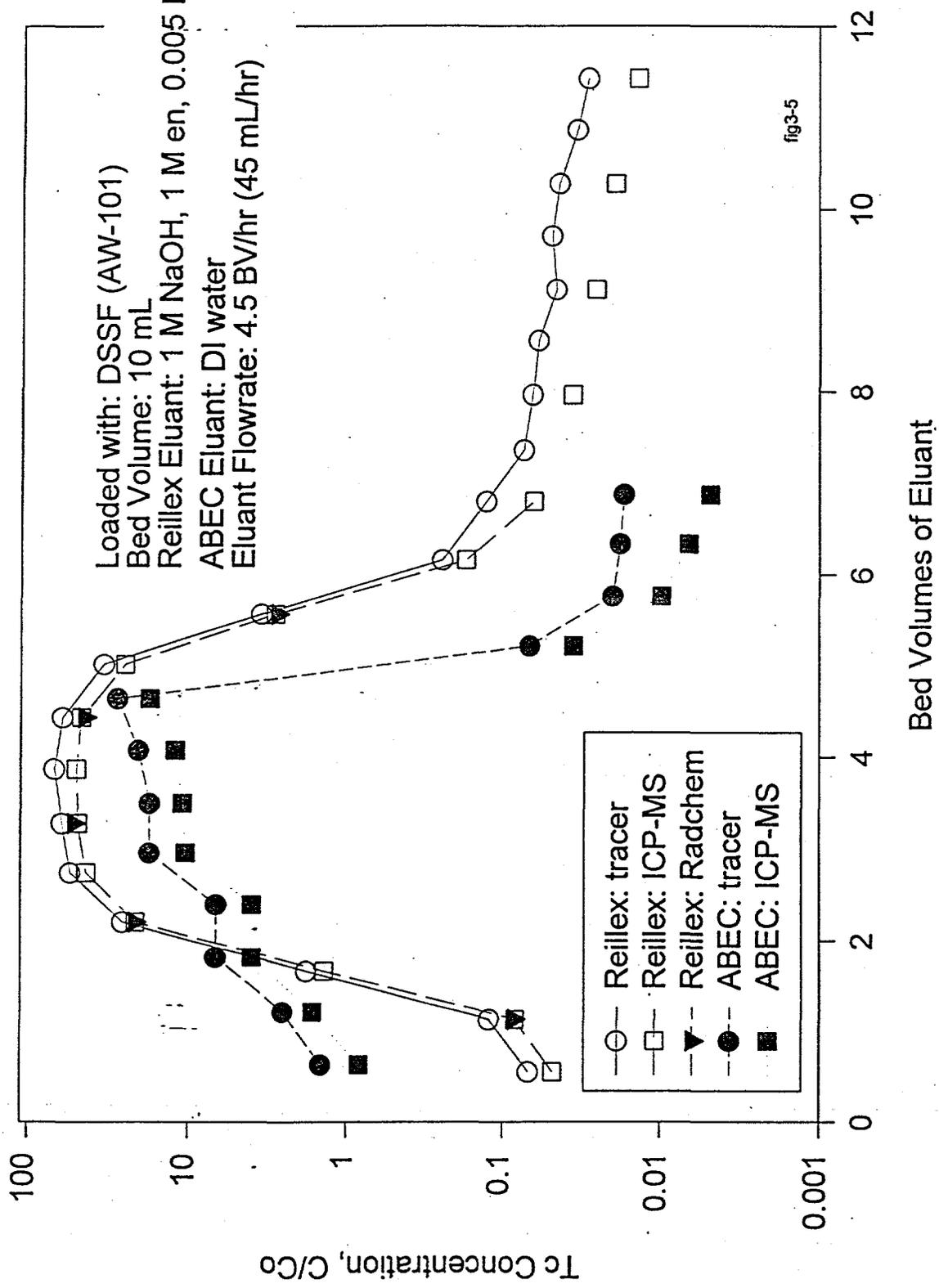


Figure 3.5. Elution of ABEC 5000 and Reillex™-HPQ

### 3.4 Tc Oxidation State and Species

The Tc oxidation state and chemical species in actual supernate samples of AW-101 and SY-103 were investigated by x-ray absorption spectroscopy (XAS). XAS spectra of the Tc K edge of the samples were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) in Stanford, California to determine 1) if the non-pertechnetate species previously observed (Blanchard *et al*, 1996) in SY-103 and other CC waste supernates is also present in a DSSF supernate, and 2) if the fraction of pertechnetate observed in CC waste changes with time outside tank conditions.

The principles of XAS were outlined previously (Blanchard *et al*, 1996), and are the subject of many books (Konigsberger and Prins, 1988; Stöhr, 1992; Teo, 1986; Teo and Joy, 1981). The x-ray absorption spectrum of an element near the absorption edge gives fingerprint type information that may be used to identify the oxidation states. A comparison of the edge position, and peaks that occur near or on it, can be made between a compound with a known oxidation state and an unknown to make this identification.

The absorption edge is that portion of the spectrum where the element begins to strongly absorb x-rays, so the absorption curve rises sharply. The edge position may be quantified by assigning it the value of the x-ray energy at the first inflection point (i.e., at the maximum in the 1st derivative) of this part of the curve. However, for the comparisons made in this report, visual inspection is sufficient. This portion of the XAS spectrum is called the x-ray absorption near edge structure (XANES). Data in a range from about 60 eV below the edge to 60 eV above the edge is used for XANES. The amount and reliability of information obtained by XANES analysis depends on the quality of the data (as measured by the signal-to-noise ratio, *s/n*). The data quality is largely determined by the concentration of the element in the sample. We have previously used the technique successfully for the investigation of the chemical states of Sr, U, Pu, Cr, and other elements in waste solids and solutions (Blanchard *et al*, 1994; Blanchard *et al*, 1995).

The XANES of six samples are presented here: "AW-101"; "AW-101, Contacted"; "SY-103, Apr, 1996"; "SY-103, Aug, 1996"; "SY-103, Contacted"; and "TcO<sub>4</sub><sup>-</sup>". "AW-101" is a sample of actual AW-101 supernate diluted and Cs decontaminated as described in Sec. 2.4. "AW-101, Contacted" is the same material contacted with Reillex<sup>TM</sup>-HPQ for several minutes. "SY-103, Apr, 1996" is a sample of actual SY-103 supernate, analyzed in April, 1996. It was prepared by dilution to 6.7 M Na followed by filtration, as described previously (Bredt and Tingey, 1996; Blanchard *et al*, 1996). "SY-103, Aug, 1996" was analyzed in August 1996, and is the same SY-103 sample after aging for approximately 5 months in an amber glass vial. "SY-103, Contacted" is the SY-103 August 1996 sample, contacted for several minutes with Reillex<sup>TM</sup>-HPQ. The "TcO<sub>4</sub><sup>-</sup>" sample is a reference solution with approximately 200 ppm ammonium pertechnetate (NH<sub>4</sub>TcO<sub>4</sub>). The concentrations of Tc in the AW-101 and the SY-103 samples were approximately 4.4 ppm (75 μCi/L) and 12 ppm (205 μCi/L), respectively. The concentration of Tc in the AW-101 contacted sample and SY-103 contacted sample was approximately 1 ppm (17 μCi/L) and 7 ppm (125 μCi/L), respectively. The tank samples were clear yellow, and the pertechnetate reference was clear and colorless.

The samples were triply contained in a sample holder made of radiation- and chemical-resistant plastics, and stainless steel. The holder had 8 sample cells, each of which had a thin film plastic window that allowed visual inspection of the liquid sample, irradiation with the monochromatic synchrotron x-ray beam, and escape of the transmitted and fluorescent x-rays used for XAS analysis. A sample of powdered Tc metal was run with each spectrum as an energy reference.

Sample handling was minimized to maintain doses as low as reasonably achievable (ALARA). The contact dose rate was 120 mRem/hr beta, 17 mrem/hr gamma for the unshielded sample holder. All spectra were collected with the samples at ambient temperature. The holder was shielded with 1/2" lead. The shielding was segmented to allow analysis of each sample while all others were shielded. This reduced background in the detector caused by gamma radiation from Cs-137 and other isotopes in the samples. Data was collected on end station 4-2 at SSRL, under dedicated operating conditions (3.0 GeV, 40 to 90 mA current). Theta, the angle between the two crystals of the monochromator, was maintained at 0 (fully tuned) with harmonic rejection accomplished by critical angle reflection off a rhodium coated mirror. All measurements on the waste samples were performed in the fluorescence mode using a 13 element Ge detector. Intrinsic radiation emitted by the samples had only minimal effects on these data. The number of scans varied with the concentration, preferred data range, and beam quality.

The XANES data was analyzed using commercially available data analysis and plotting software packages on both Macintosh® and PC compatible computers. Each spectra was normalized to its edge step. This effectively converts the absorption scale to absorption per mole of Tc, including the edge step and all absorption features. The energy scale has been referenced to the first inflection point in the edge for Tc metal, which is denoted  $E_0$ . The prominent pre-edge peak observed in the  $\text{TcO}_4^-$  spectrum arises from transitions allowed because of the tetrahedral geometry of  $\text{TcO}_4^-$ . The  $\text{TcO}_4^-$  XANES is consistent with that previously published (Almahamid *et al*, 1995).

Evidence of non-pertechnetate Tc in the AW-101 sample is seen in Figure 3.6. The top plot shows the XANES of the contacted SY-103 sample, the (uncontacted) AW-101 sample, and the  $\text{TcO}_4^-$  reference. Although most of the Tc in the AW-101 sample is pertechnetate, as indicated by the similar intensity of the pre-edge peaks near -7 eV, there is a significant amount of non-pertechnetate. This is evident from the position of the AW-101 edge at approximately 5 eV, between the pertechnetate edge and the non-pertechnetate edge. (Contacting the SY-103 sample with Reillex™-HPQ removes most of the pertechnetate, leaving almost exclusively non-pertechnetate Tc, as seen by the distinct lack of a pre-edge peak and the position of the edge.)

The bottom plot of Figure 3.6 shows the XANES of the contacted SY-103 sample, the contacted AW-101 sample, and pertechnetate. The signal-to-noise of the contacted AW-101 is very poor because of the low concentration of the sample (1 ppm). It is clear from the coincidence of the edges of the two tank samples (from approximately 0 - 20 eV) that most of the Tc in the contacted AW-101 sample is non-pertechnetate. There is a small shoulder at the position of the pertechnetate pre-edge peak that indicates a small amount of residual pertechnetate in the contacted AW-101 sample.

Evidence that the non-pertechnetate Tc slowly oxidizes to pertechnetate when removed from tank conditions is shown in Figure 3.7. XANES collected in April, 1996 of an (uncontacted) SY-103 sample is compared to the XANES of the same sample taken 5 months later in August, 1996. The pertechnetate XANES is also shown for comparison. Changes in the pre-edge peak and the edge position make it clear that the fraction of pertechnetate in the sample is increasing. The sample was stored in an amber glass vial in a fume hood. The oxidation may be caused by a greater concentration of oxygen in the sample due to air exposure, or to lower concentrations of species that favor formation of the non-pertechnetate species. Species that favor non-pertechnetate formation may result from the high radiolysis in the tank, or from the solids present that are in intimate contact with the supernatant liquid.

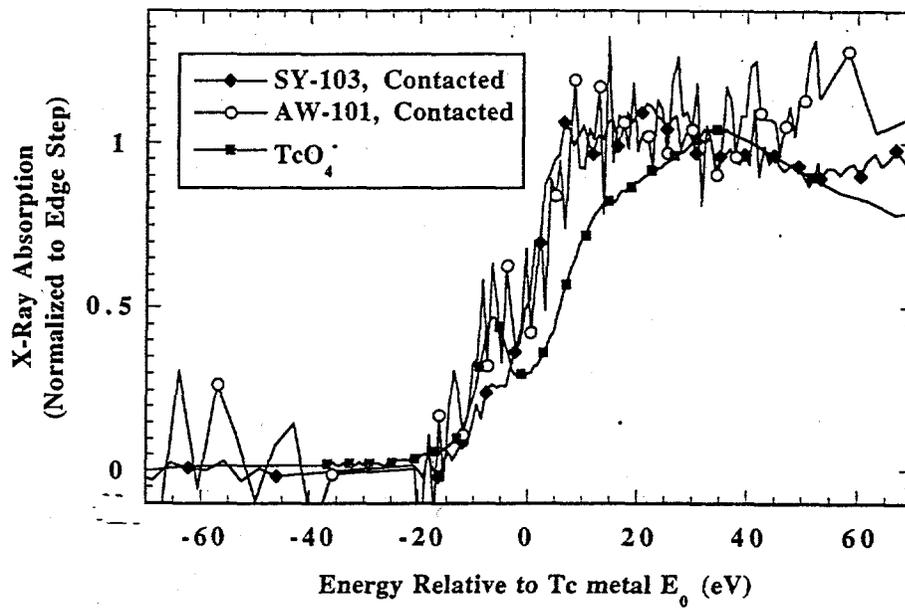
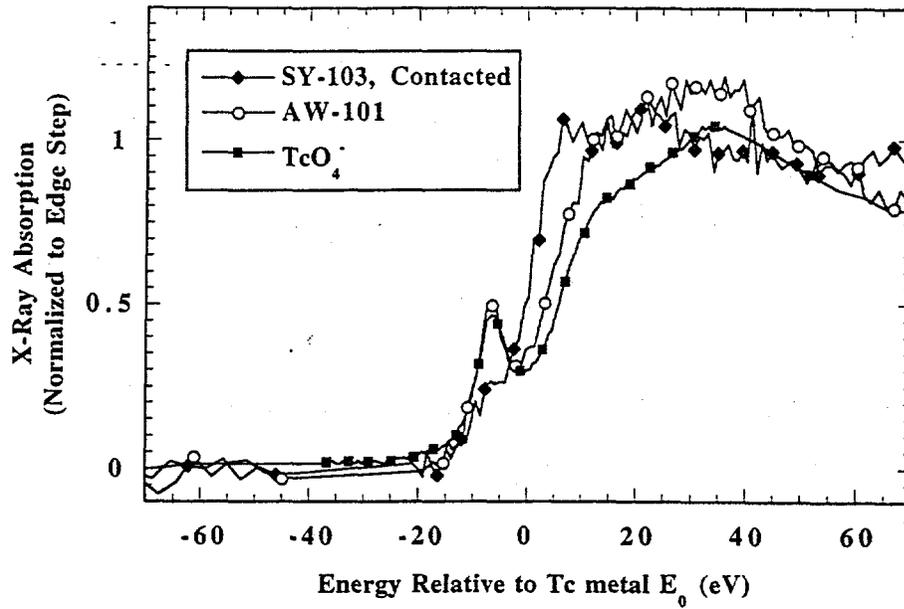


Figure 3.6. Evidence of Non-Per technetate Tc in AW-101 Waste Feed.

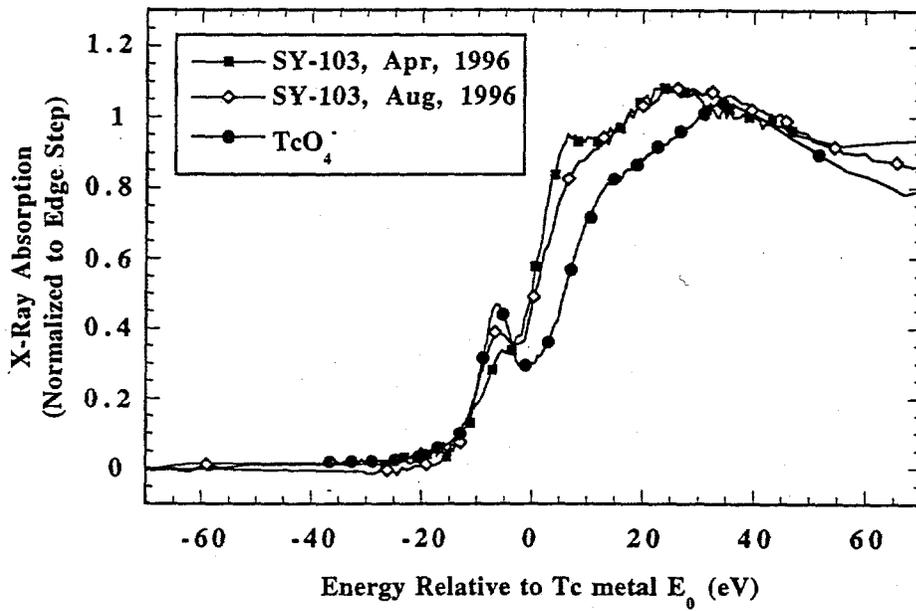


Figure 3.7. Evidence of Pertechnetate Increase in SY-103 Waste Feed.

## 4.0 Conclusions

- The low decontamination factors (4-6) for the actual Tc-99 indicate that 15-25% of the Tc-99 in the waste is in a non-pertechnetate chemical form. While the decontamination factors are not as great as expected, they are approximately equal to the estimated average required decontamination factor of 5.
- The significant decontamination factors for the Tc-99m tracer indicate that pertechnetate is effectively removed from the AW-101 feed. Based on the first sample from each run, the DF's are; ABEC 5000 (80), Reillex™-HPQ (1100). The larger DF for the Reillex™-HPQ is most likely a result of the greater effective capacity of the Reillex™-HPQ. The DF's achieved in a full-scale operation would be heavily dependent on the design and operation of the system implementing each material. The decontamination factors for the AW-101 waste will be controlled by the level of the non-pertechnetate Tc in the waste.
- The 15-25% of the Tc-99 that was not extracted corresponds to a Tc-99 level in the effluent of  $1.65 \times 10^{-02}$  Ci/m<sup>3</sup> to  $2.75 \times 10^{-02}$  Ci/m<sup>3</sup>. This is 5.5% to 9.2% of the NRC Class A limit of 0.3 Ci/m<sup>3</sup>. The concentration in the final waste form would likely be higher.
- The relatively high fraction of non-pertechnetate Tc-99 in the AW-101 waste suggests that this may be common in the tank wastes. Significant fractions of non-pertechnetate Tc-99 were expected to be restricted to tank wastes with a high organic content (10 - 40 g TOC/L). The DSSF from AW-101 contains a relatively low amount of organic ( about 2.5 g TOC/L in tank).
- As indicated by the  $\lambda_{50}$  values, the effective Tc-99 capacity of the Reillex™-HPQ is more than 2 times greater than that for the ABEC 5000 material for the same bed volume. The difference between the  $\lambda_{50}$  values for the Tc-99m tracer data and the actual Tc-99 data are attributed to the non-pertechnetate fraction in the waste.
- Both materials are efficiently eluted. Because ABEC 5000 is eluted with deionized water, very little would be added to the final Tc waste form other than Tc if ABEC 5000 is used.
- Few operational problems were experienced with either material, although a small portion of the Reillex™-HPQ bed on the second column was observed to float in solution and preparation of the ABEC 5000 column was tedious because of the difficulty in removing entrained air from the bed. Use of a larger particle size may alleviate this problem. Use of ABEC 5000 would require a column design that accommodated the large (2X) expansion that occurs upon elution.
- No evidence of fouling or other interactions between the waste and the pertechnetate selective materials was observed.
- XAS spectra confirm the presence of non-pertechnetate Tc in the AW-101 waste feed.
- XAS spectra taken in April 1996 and August 1996 of the same sample of SY-103 waste feed clearly show an increase in the fraction of pertechnetate in the sample. This suggests that the non-pertechnetate Tc in the sample is being oxidized to pertechnetate.

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