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# Ion Exchange Distribution Coefficients for $^{137}Cs$ and $^{99}Tc$ removal from Hanford Tank Supernatants AW-101 (Envelope A) and AN-107 (Envelope C)

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# SUMMARY

The current BNFL Inc. flowsheet for the pretreatment of the Hanford High-Level tank wastes includes the use of Superlig® materials in a dual column system for the removal of $^{137}Cs$ and $^{99}Tc$ from the aqueous fraction of the waste. The Superlig® materials include the cesium selective Superlig®632 and Superlig®644 for removal of $^{137}Cs$ and Superlig®639 for the removal of $^{99}Tc$ present as $TcO_4^-$. These materials have been developed and supplied by IBC Technologies, Inc., American Fork, UT.

The work reported in this document includes an evaluation of the equilibrium behavior of the Superlig® materials for the removal of $^{137}Cs$ and $TcO_4^-$, information on the composition of process feeds, and information on selected physical properties for the Superlig® resins. The equilibrium behavior (reported as Kd's) was assessed with batch contacts between the Superlig® resins and subsamples of the waste from tanks AW-101 (Envelope A) and AN-107 (Envelope C). The AN-107 subsample was diluted with DI water to simulate the dilution due to the Sr/TRU precipitation process. Since these experiments were conducted, the Sr/TRU precipitation process has been changed from the addition of strontium and ferric nitrate to the addition of strontium nitrate and sodium permanganate. Some of the subsamples were spiked with $CsNO_3$ or $^{99}Tc$ (as pertechnetate) to provide equilibrium data that bounds the feed composition. The resin physical properties include the particle size distribution of the as-received resins, the dry density and the water content.

The $^{137}Cs$ and $TcO_4^-$ Kd values at the feed conditions are shown in Table S1. These values were estimated from plots showing the variation of the $^{137}Cs$ and $TcO_4^-$ Kd values as a function of $Na^+$:$Cs^+$ and $NO_3^-$:$TcO_4^-$ mole ratios respectively. Based on earlier studies, the SL-632 Kds are much lower than expected. An investigation by IBC Technologies revealed that manufacturing difficulties resulted in a batch of resin that accounted for the relatively poor performance. Subsequent experimental results not reported in this document, indicate Kd's on the order of 400-500 mL/g.

Table S1. $^{137}Cs$ and $TcO_4^-$ Kd Values at Feed Conditions

| Waste tank | Feed conditions | $^{137}Cs$ Kd's SL-632 (mL/g) | $^{137}Cs$ Kd's SL-644 (mL/g) | $TcO_4^-$ Kd's SL-639 (mL/g) |
|---|---|---|---|---|
| AW-101 | $Na^+$=6.59 M, $Na^+/Cs^+$ = 79,400<br>$K^+/Cs^+$ = 7,400<br>$NO_3^-$:$TcO_4^-$ = 37,800<br>$NO_3^-$:$^{99}Tc$ = 36,600 | 130 (1) | 450 | 450-500 |
| AN-107 | Na+=5.61 M, Na+/Cs+ = 85,300<br>$K^+/Cs^+$ = 350<br>$NO_3^-$:$TcO_4^-$ = 265,000<br>$NO_3^-$:$^{99}Tc$ = 61,500 | 100 (1) | 570 | ≈ 125(2) |

(1) The SL-632 resin was determined by IBC Technologies to be improperly manufactured resulting in lower than expected Kds

(2) value not obtained at feed conditions; $NO_3^-$:$TcO_4^-$ = 577,000

The $TcO_4^-$ Kds are estimated on the basis of analyses of the total $^{99}Tc$ concentration and the fraction of $^{99}Tc$ present as nonpertechnetate (assumed to be inextractable by SL-639). Short duration contacts with a large excess of SL-639 removed 22-25% of the $^{99}Tc$ from the AN-107 sample indicating that 75-78% of the $^{99}Tc$ is likely present as a nonpertechnetate species. Recent small column runs with the AW-101 sample indicate that 2.9% of the $^{99}Tc$ was not extracted, presumably because it is present as a nonpertechnetate species. A series of batch contacts with SL-639 and AW-101 simulant ($Na^+$ = 5 M) spiked with pertechnetate indicated a maximum Kd of 685 mL/g. The $TcO_4^-$ Kd determinations as a function of time also indicated that equilibrium may not have been attained in the batch contact experiments for $^{99}Tc$ removal. If equilibrium was not obtained, the Kd values would be underestimated.

# TERMS AND ABBREVIATIONS

| | |
|---|---|
| AEA | alpha energy analysis |
| ALARA | as low as reasonably achievable |
| BNFL | BNFL, Inc; subsidiary of British Nuclear Fuels, Ltd. |
| EQL | estimated quantitation level |
| GEA | gamma energy analysis |
| HLRF | High Level Radiation Facility |
| IC | ion chromatography |
| ICP | inductively coupled plasma/atomic emission spectrometry |
| ICP/MS | inductively coupled plasma/mass spectrometry |
| MDL | method detection limit |
| MRQ | minimum reportable quantity |
| RPL | Radiochemical Processing Laboratory |
| SAL | Shielded Analytical Laboratory |
| $TcO_4^-$ | pertechnetate |
| TC | total carbon |
| TRU | transuranic |

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## FIGURES



## TABLES

# 1.0 INTRODUCTION

The current BNFL Inc. flow sheet for the pretreatment of the Hanford High-Level tank wastes includes the use of Superlig® materials in a dual column system for the removal of $^{137}Cs$ and $^{99}Tc$ from the aqueous fraction of the waste. The Superlig® materials include the cesium selective Superlig®632 and Superlig®644 for removal of $^{137}Cs$ and Superlig®639 for the removal of $^{99}Tc$ present as $TcO_4^-$. These materials have been developed and supplied by IBC Technologies, Inc., American Fork, UT.

The objectives of this work were to:

- Evaluate the equilibrium behavior of the Superlig materials for the removal of $^{137}Cs$ and $^{99}Tc$ (as pertechnetate) from AW-101 (Envelope A) and AN-107 (Envelope C) clarified supernatants.

- Obtain information of the composition of ion exchange feed streams and the pertechnetate/nonpertechnetate fraction in the samples.

- Determine some of the Superlig material physical properties including particle size distribution, dry density and water content.

To evaluate the equilibrium behavior, batch contacts at a phase ratio of 100 (5 mL of waste solution:0.05 g of exchanger) were conducted with each of the Superlig materials and each of the waste envelope samples. In order to obtain equilibrium data that bounds the expected feed compositions, some of the envelope subsamples were spiked with either $CsNO_3$ or $^{99}Tc$ as pertechnetate. The fraction of nonpertechnetate in the AN-107 sample was estimated by contacting some of the AN-107 sample with a large excess of Superlig®639 (phase ratio of about 1).

# 2.0 EXPERIMENTAL

## 2.1 Ion Exchange Materials

The ion exchange materials evaluated are listed in Table 2.1 along with the identification used in this report, the target component and the batch number. The SL-632 and SL-644 materials are cation exchangers that are selective for $Cs^+$ while the SL-639 material is selective for $^{99}Tc$ that is present as pertechnetate ($TcO_4^-$). Although the SL-639 material is commonly referred to as an ion exchange material, it actually extracts a neutral salt which is primarily $NaTcO_4$. These materials were supplied by IBC Technologies Inc. (American Fork UT).

The SL-632 and SL-644 resins were received in the $H^+$ form from IBC and were used without resin conditioning. Normally, these materials are used in the sodium form but this is not necessary for batch contacts due to the small amount of $H^+$ relative to the ionic content of the waste solution. The SL-639 material was conditioned by adding 5 g of resin to: (a) 10 mL of 1.0 M NaOH solution; (b) stirring for 1-hour; (c) filtering the resin, (d) washing the filtered resin with deionized water; and (e) drying with a low airflow for approximately 16-hours at room temperature. It should be noted that IBC recommends various resin bed conditioning steps prior to initiating column operations for each of these materials. For these batch contacts a large excess of waste solution acted as the conditioning solution.

**Table 2.1.** Ion Exchange Materials

| Exchanger | ID | Target component | Batch Number |
|---|---|---|---|
| Superlig®632 | SL-632 | $^{137}Cs$ | 981015SCM-II-80 |
| Superlig®644 | SL-644 | $^{137}Cs$ | 644BZ |
| Superlig®639 | SL-639 | $^{99}Tc$ | 980624001DC |

## 2.2 Resin Physical Properties

Several of the physical properties of the Superlig materials were measured including the dry density, F-factor, and the particle size distribution. The density was determined by weighing approximately 10 ml of exchanger in a 50 mL graduated cylinder. The cylinder was tapped repeatedly to settle the bed until a constant bed volume was obtained. The graduated cylinder had a diameter of approximately 1 inch and was of sufficient diameter to minimize wall effects. The amount of water in the exchangers was determined by heating approximately 0.5 g resin samples in an oven until the mass of successive weighings was reasonably constant. Drying was conducted at temperatures of 85 °C and 105 °C. This allowed a determination of the F factor which is the ratio of the mass of the dried exchanger to the initial mass of the exchanger. The particle size distribution of the dry as-received resin was determined by sieve analysis. All sieves had a diameter of 3-inches with U.S. Standard Sieve Numbers; 40 (425 μm), 70 (212 μm), 100 (150 μm) and 200 (74 μm).

## 2.3 Feed Preparation

Samples of the waste from tanks AW-101 (Envelope A) and AN-107 (Envelope C) were received in the High Level Radiation Facility (HLRF) in the Radiochemical Processing Laboratory (RPL) during the 4th quarter of 1998. The homogenization, dilution, caustic adjustment and subsampling of these samples is described in (Urie, 1999). Subsamples of the diluted waste samples were obtained in the HLRF and transferred to the Shielded Analytical Facility (SAL). Approximately, 141 mL of diluted AW-101 sample, with a sodium concentration of ≈ 6.6 M, and 109 mL of diluted AN-107 sample with a sodium concentration of about 7.7 M was provided for the batch contacts. The AN-107 subsample was diluted from ≈ 7.7 M Na to ≈ 5.6 M sodium by the addition of DI water to simulate the dilution that would occur during the Sr/TRU removal process. At the time these experiments were conducted the Sr/TRU precipitation process involved the use of strontium and ferric nitrate. The process has been revised to use strontium nitrate and sodium permanganate which will slightly increase the sodium:cesium mole ratio. An additional process change is that the ion exchange feed solutions will be somewhat more dilute than the concentrations test in this study. The sodium concentration is currently being targeted at 5-5.5 M in order to prevent the SL-639 from floating.

Solids were separated from both liquid fractions prior to the batch contacts. The AW-101 subsample was easily filtered with a 0.45 μm nylon filter. A total of 181.9 g of liquid and 2.85 g of damp solids were separated. Most of the solids were removed from the diluted AN-107 subsample by centrifugation at 2500 rpm for 1 hr. Additional solids removal by filtration with a 0.45 μm nylon filter proved to be impractical due to a very slow filtration rate (5 mL in 30 minutes). The AN-107 subsample was centrifuged at 2500 rpm for an additional hour and the supernatant decanted from the solids prior to contact with the ion exchange materials. A total of 182.6 g of liquid and 4.8 g of damp centrifuged solids were separated. Due to the inability to filter the AN-107 sample some of the very fine particulates were not removed. The solids from both subsamples were archived for washing and caustic leaching studies. The supernatants were used for contacts with the materials designated SL-632, SL-644 and SL-639.

Portions of the supernatants were spiked with $^{133}Cs$ or $^{99}Tc$ stock solutions to obtain additional concentrations of the cesium and technetium species. The cesium spike solutions were either 0.1 or 0.5 M $CsNO_3$. The $^{99}Tc$ spike solution was 45 mg/mL (0.455 M) ammonium pertechnetate in 1 M ammonium hydroxide. The initial cesium and technetium concentrations in the AW-101 and AN-107 supernatant solutions are given in Tables 2.2 and 2.3 along with the target values. $^{99}Tc$ spikes were not added to the AN-107 solution due to the uncertainty introduced by the expected high fraction of nonpertechnetate species which are not extracted by the SL-639. The actual cesium and technetium concentrations are based on analytical results obtained with ICP-MS. The purpose of these spikes was to ensure that the equilibrium composition of the solutions bracketed the feed concentrations of the components of interest.

**Table 2.2.** Initial Cs Concentrations in the Solutions Used for the Batch $K_d$ Determination Tests

| *Waste* | *Solution* | *Initial Cs Conc. [M]* | | *Initial Na/Cs (a)* | | *Initial K/Cs (a)* |
|---|---|---|---|---|---|---|
| | | target | Actual | target | Actual | Actual |
| AW-101 | Un-spiked | NA | 8.29E-5 | NA | 79,400 | 7400 |
| (6.59 M $Na^+$) | Cs Spike 1 | 6.59E-04 | 5.88E-4 | 10,000 | 11,200 | 1040 |
| (0.61 M $K^+$) | Cs Spike 2 | 6.59E-03 | 5.09E-3 | 1,000 | 1,300 | 120 |
| AN-107 | Un-spiked | NA | 6.57E-5 | NA | 85,300 | 350 |
| (5.61 M $Na^+$) | Cs Spike 1 | 5.61E-04 | 5.32E-4 | 10,000 | 10,500 | 43 |
| (0.023 M $K^+$) | Cs Spike 2 | 5.61E-03 | 4.98E-3 | 1,000 | 1,100 | 5 |

(a) Na+ and K+ are the primary cations that compete with Cs+ for ion exchange with SL-632 and SL-644.

**Table 2.3.** Initial $^{99}Tc$ Concentrations in the Solutions Used for the Batch $K_d$ Determination Tests

| *Waste* | *Solution* | *Initial $^{99}Tc$ Conc. [M]* | | *Initial $NO_3^-/^{99}Tc$ (a)* | |
|---|---|---|---|---|---|
| | | target | Actual | target | actual |
| AW-101 | Un-spiked | NA | 5.43E-5 | NA | 36,100 |
| (1.99 M $NO_3^-$) | Tc Spike 1 | 4.98E-4 | 4.18E-4 | 4,000 | 4,760 |
| | Tc Spike 2 | 1.99E-3 | 1.58E-3 | 1,000 | 1,260 |
| AN-107 | Un-spiked | NA | 3.35E-5 | NA | 61,400 |
| (2.06 M $NO_3^-$) | | | | | |

(a) Nitrate, perrhenate and permanganate are known to compete with pertechnetate for adsorption by SL-639. Nitrate is the only anion present in significant quantities.

## 2.4 Batch Contacts

Sample flow diagrams for the supernatant spiking with cesium and $^{99}Tc$ and the batch contacts are shown in Figures 2.1 and 2.2. The batch Kd tests were performed at a phase ratio of approximately 100 (liquid volume to exchanger mass). Typically, 0.05 g of exchanger was contacted with 5 mL of solution. The exchanger mass was determined to an accuracy of 0.0001 g. The waste volume was transferred by pipette and the actual volume was determined by mass difference with an accuracy of 0.0001 g and the solution density. Agitation was provided by an orbital shaker set at 200 rpm for approximately 72 hours. The temperature was not controlled but was generally constant at 21 °C over the course of the 3 days of contact.

All $K_d$ measurements were made in duplicate and blank samples (i.e., without the ion exchange resin) were used to determine the initial concentration of the species of interest. All initial and final solutions were analyzed by GEA to determine the $^{134}Cs$ and $^{137}Cs$ concentrations. Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) was used to determine the $^{133}Cs$ and $^{99}Tc$, concentrations in the SL-639 batch contact and initial Cs and $TcO_4^-$ spiked solutions. The initial sodium and potassium concentrations were determined with Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).

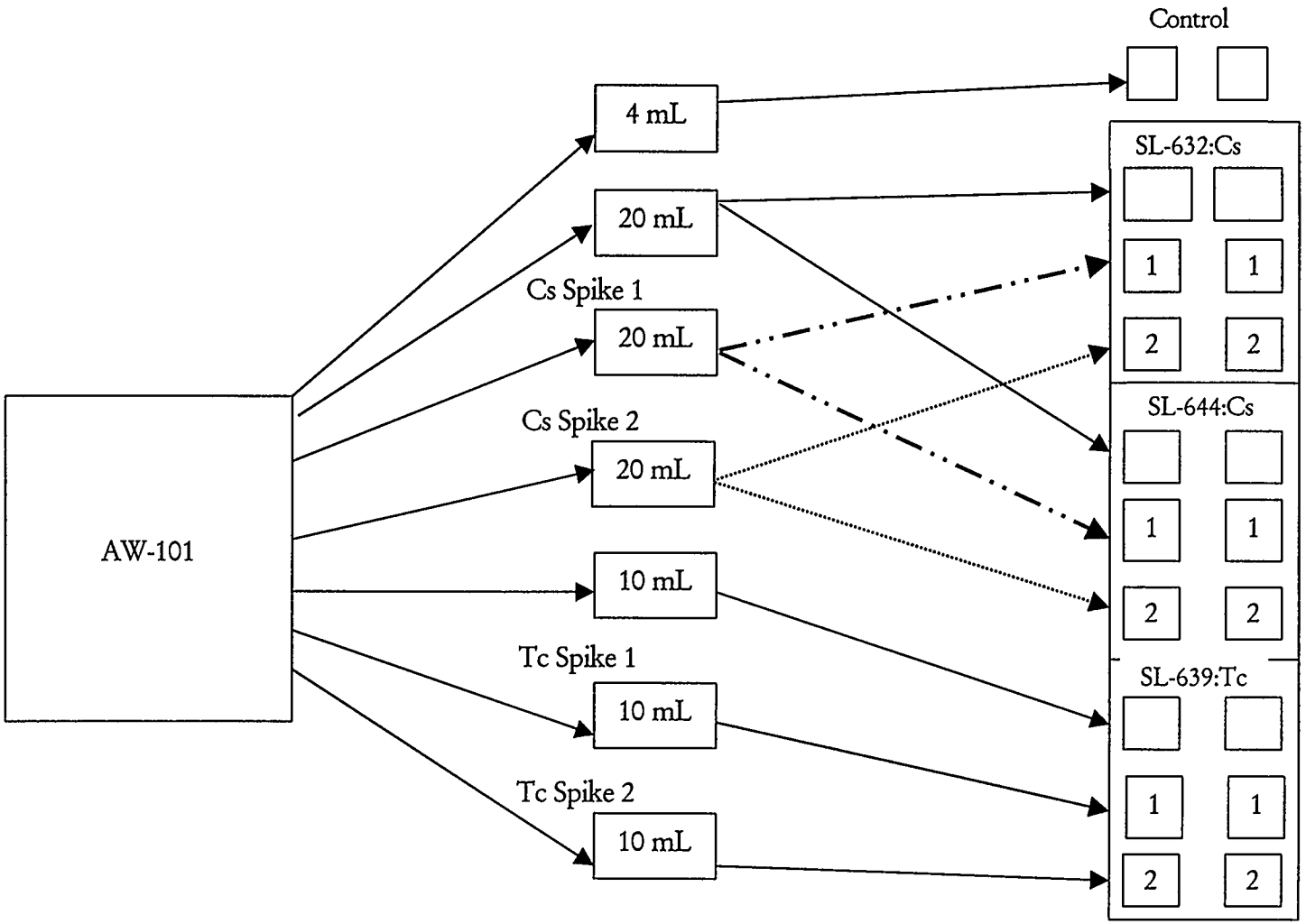


**Figure 2.1** Preparation of AW-101 Cesium and Technetium Spike Solutions and Batch Contacts

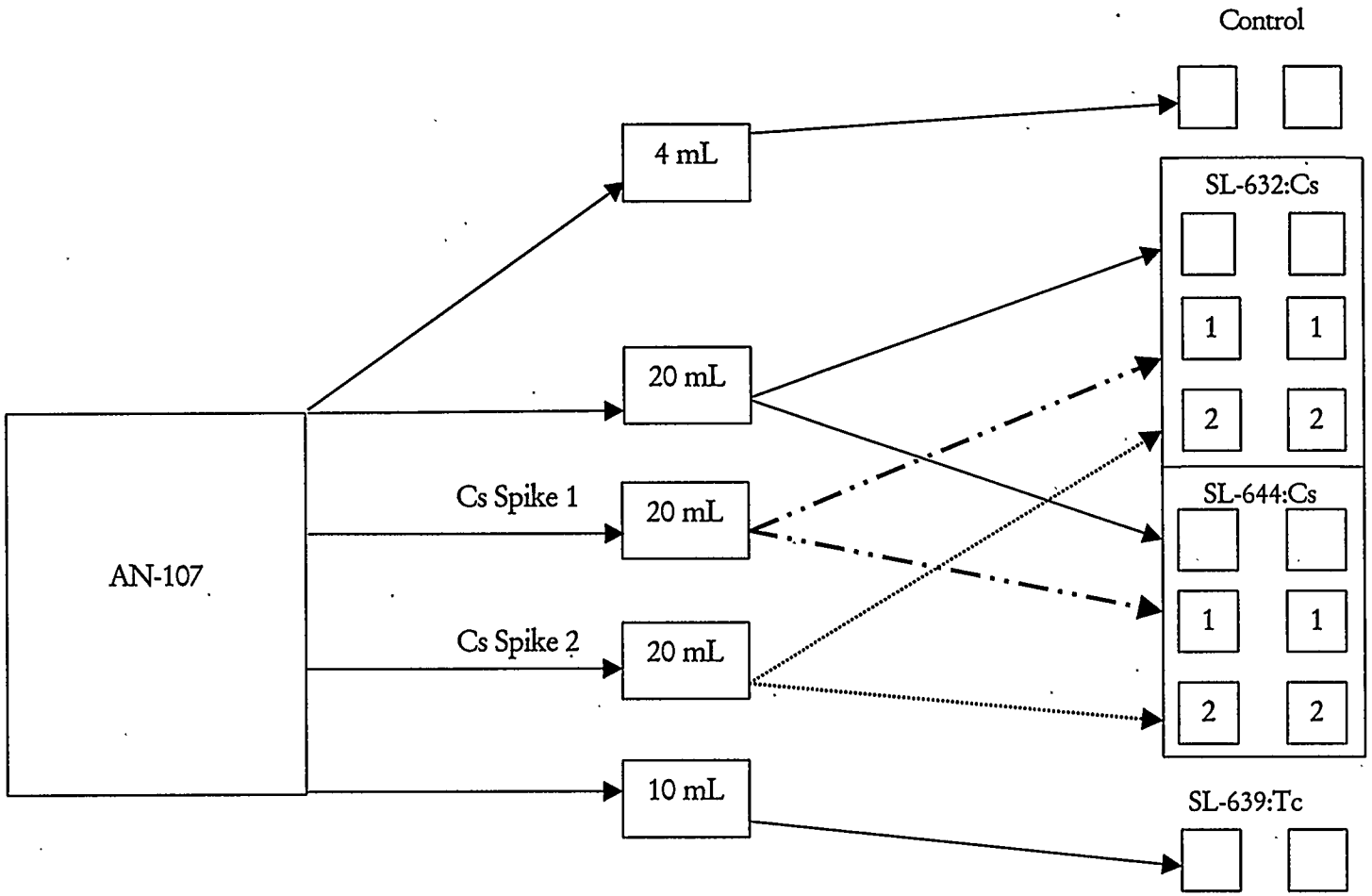


**Figure 2.2** Preparation of AN-107 Cesium and Technetium Spike Solutions and Batch Contacts

The batch distribution coefficient, $K_d$ (with units of mL/g), was determined using the following relationship;

$$K_d = \frac{(C_0 - C_1)}{C_1} * \frac{V}{M * F} \quad (1)$$

Where: $C_0$ and $C_1$ are the initial and final concentrations, respectively, of the species of interest (i.e., $^{137}Cs$ or $^{99}Tc$), V is the volume of the liquid sample (mL), M is the mass of the ion exchanger (g), and F is the mass of the dried resin divided by the mass of the as received or conditioned resin.

## 2.5 $TcO_4^-$ Kd Versus Time Contacts

In an effort to determine the length of time required for batch contacts to reach equilibrium for SL-639 and pertechnetate, a series of batch contacts were conducted with contact times of 4 hr, 8 hr, 16 hr, 24, 48 and 72 hrs. A simulant representing AW-101 with a sodium concentration of 5 M (Table 2.4) was spiked with a $TcO_4^-$ stock solution to provide a simulant with a target $TcO_4^-$ concentration of 5.07E-5M (5028 ng/mL). The target $NO_3^-$:$TcO_4^-$ mole ratio was 3E+04. The batch contacts were conducted in the same manner as the contacts with actual waste except that the contact times were varied. The phase ratio was 100 (5 mL of solution:0.05 g of exchanger). Previous testing (Brown et.al., 1996) demonstrated that cesium uptake by SL-644 reached steady state in 20 hours. Therefore additional batch contacts as a function of time were not conducted for the cesium ion exchange materials.

**Table 2.4.** Simulant Composition (Envelope A, AW-101) for $TcO_4^-$ kd versus Time Experiment

| Cations, M | |
|---|---|
| $Na^+$ | 5.0 |
| $K^+$ | 0.43 |
| $Cs^+$ | 6.4E-5 |
| Na/Cs mole ratio | 78,100 |
| K/Cs mole ratio | 6,700 |
| Anions, M | |
| $AlO_2^-$ | 0.51 |
| $Cl^-$ | 0.07 |
| $CO3^-_2$ | 0.10 |
| $NO_2^-$ | 0.79 |
| $NO_3^-$ | 1.52 |
| $OH^-$ | 2.27 |
| $PO_4^{-3}$ | 1.73E-03 |
| $SO_4^{-2}$ | 2.36E-03 |
| Radionuclides | |
| $^{99}Tc$ (μCi/mL) | 8.55E-2 |
| $^{99}Tc$ (ng/mL) | 5028 |
| $^{99}Tc$ (M) | 5.07E-5 |
| $NO_3^-$:$TcO_4^-$ mole ratio | 30,000 |

## 2.6 Nonpertechnetate fraction in Envelope C (AN-107)

In an attempt to assess the fraction of nonpertechnetate in the AN-107 sample, two quick contacts were conducted in which aliquots of the waste were contacted with a large excess of the SL-639. The large excess of resin is expected to remove essentially all of the pertechnetate. Two aliquots of approximately 1 mL each were contacted separately with 0.5 g quantities of the SL-639 resin. The samples were placed on the orbital shaker for 2 hours and 15 minutes at which point the mixture was separated with a syringe filter. The 2 hour contact time was chosen to more closely approximate the residence time of waste in the plant-scale columns. The plant design basis is to operate the Tc columns at 3-BV/hr, which equates to a contact time of 20 minutes in the lead column or 40 minutes total residence time in both columns.

# 3.0 RESULTS AND DISCUSSION

## 3.1 Resin Physical Properties

The bed densities and F factors for the Superlig® materials are shown in Table 3.1. The density for SL-632 and SL-644 is for the as-received material while the SL-639 was conditioned with 1 M NaOH and washed with DI water (Section 2.1). The F factor is the ratio of the dry mass of exchanger to the initial mass of the exchanger. The dry mass of the exchanger was obtained after 145 hours of drying although the majority of the water was lost in the initial 25 hours. The actual drying data as a function of time may be found in Appendix A. The SL-639 was dried for an additional 145 hours at 105 °C and the F factor was reduced from 0.98 to 0.93. The dry bed density is obtained by multiplying the bed density by the F factor (85 °C).

**Table 3.1** Bed Density and F Factors

| | Bed Density (g/mL) | F factor @ 85 °C | Dry bed density (g/mL) |
|---|---|---|---|
| SL-632 | 0.55 | 0.894 | 0.49 |
| SL-644 | 0.86 | 0.907 | 0.78 |
| SL-639 | 0.5 | 0.978 | 0.49 |

The particle size distribution of the as-received Superlig® materials is shown in Table 3.2. This distribution was determined with a sieve analysis utilizing about 5 g of exchanger.

**Table 3.2** Particle Size Distribution

| Sieve size | Size (μm) | SL-632 | SL-644 | SL-639 |
|---|---|---|---|---|
| 40 | >425 | 79.8 | 9.9 | 99.8 |
| 70 | 425-210 | 18.3 | 88 | 0.2 |
| 100 | 210-149 | 1.7 | 2.1 | 0 |
| 200 | 149-74 | 0.3 | 0 | 0 |
| | <74 | 0.04 | 0 | 0 |

## 3.2 Feed Composition

The initial composition of the feed subsamples is shown in Table 3.3. Most of the results are based on direct analyses of the subsamples. Some of the component concentrations are based on the characterization data reported in Urie, 1999. The total cesium concentration is estimated using the GEA results for $^{137}Cs$ and the isotopic ratios determined with thermal ionization mass spectroscopy. For the AW-101 sample the $^{137}Cs$:total cesium was 0.2465 and for the AN-107 sample the $^{137}Cs$:total cesium was 0.2455.

Table 3.3. Composition of Waste Subsamples

| | AW-101 (Envelope A) | AN-107 (Envelope C) |
|---|---|---|
| Cations, M | | |
| $Na^+$ | 6.59 | 5.61 |
| $K^+$ | 0.61 | 0.023 (1) |
| $Cs^+$ | 8.29E-5 | 6.57E-5 |
| Na/Cs mole ratio | 79,400 | 85,300 |
| K/Cs mole ratio | 7,400 | 350 |
| Anions, M | | |
| $AlO_2^-$ | 0.645 | 0.1 |
| $Cl^-$ | 0.099 | Not detected |
| $CO3^-_2$ | 0.18 (1) | 0.97 (1) |
| $CrO_4^{-2}$ | 1.07E-3 | 2.8E-3 |
| $NO_2^-$ | 1.28 | 0.717 |
| $NO_3^-$ | 1.99 | 2.06 |
| $OH^-$ | 3.1 (1) | 0.51 (1) |
| $PO_4^{-3}$ | 0.01 | 0.011 |
| $SO_4^{-2}$ | 0.019 (1) | 0.052 |
| oxalate | <8.6E-3 (1) | 1.07E-2 (1) |
| Radionuclides | | |
| $^{99}Tc$ (μCi/mL) | 9.13E-2 | 5.64E-2 |
| $^{99}Tc$ (ng/mL) | 5370 | 3320 |
| $^{99}Tc$ (M) | 5.43E-5 | 3.35E-5 |
| $^{134}Cs$ (μCi/mL) | 5.8E-2 | <1E-2 |
| $^{137}Cs$ (μCi/mL) | 243 | 192 |
| $NO_3^-$:$^{99}Tc$ mole ratio | 36,600 | 61,500 |
| Solution Density, g/mL | 1.318 | 1.235 |
| (1) These values have been estimated from the diluted feed characterization data reported in PNWD-2463, BNFL-RPT-003, rev 0. Unless otherwise noted the results are based on direct analysis of subsamples as prepared for the batch contacts. | | |

## 3.3 Cesium Kd's

The batch cesium $K_d$ results are shown in Figures 3.1 and 3.2 for the AW-101 and AN-107 supernatants respectively. The Kd values were calculated with Equation 1 and are based on the $^{137}Cs$ concentrations as measured by GEA. The Na/Cs ratio is calculated from the individual sodium and cesium concentrations. The sodium concentrations are based on an analysis of the initial subsamples as prepared for the batch contacts and is assumed to be constant for the batch contacts. Since the quantity of $H^+$ added with the resins is small relative to the moles of $Na^+$ and $OH^-$ (phase ratio of 100 mL of solution: gram of exchanger) this is a reasonable assumption. In these experiments the waste solutions are estimated to have 5-12.5 meq of $OH^-$ and 28-33 meq of $Na^+$, while the resin had 0.005 meq of $H^+$. The total cesium is based on the $^{137}Cs$ concentrations and the ratio of $^{137}Cs$:total cesium determined for the unspiked and spiked solutions.

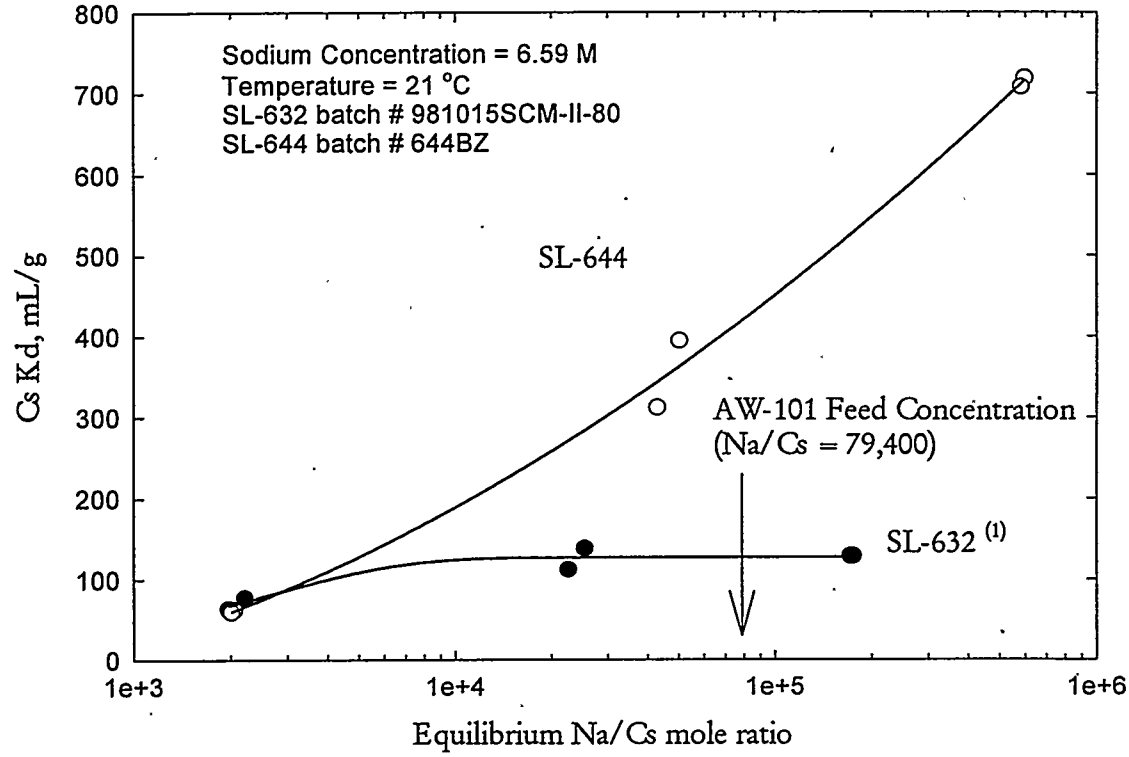


**Figure 3.1.** Cesium Kd's for SL-644 and SL-632 with AW-101 Supernatant.

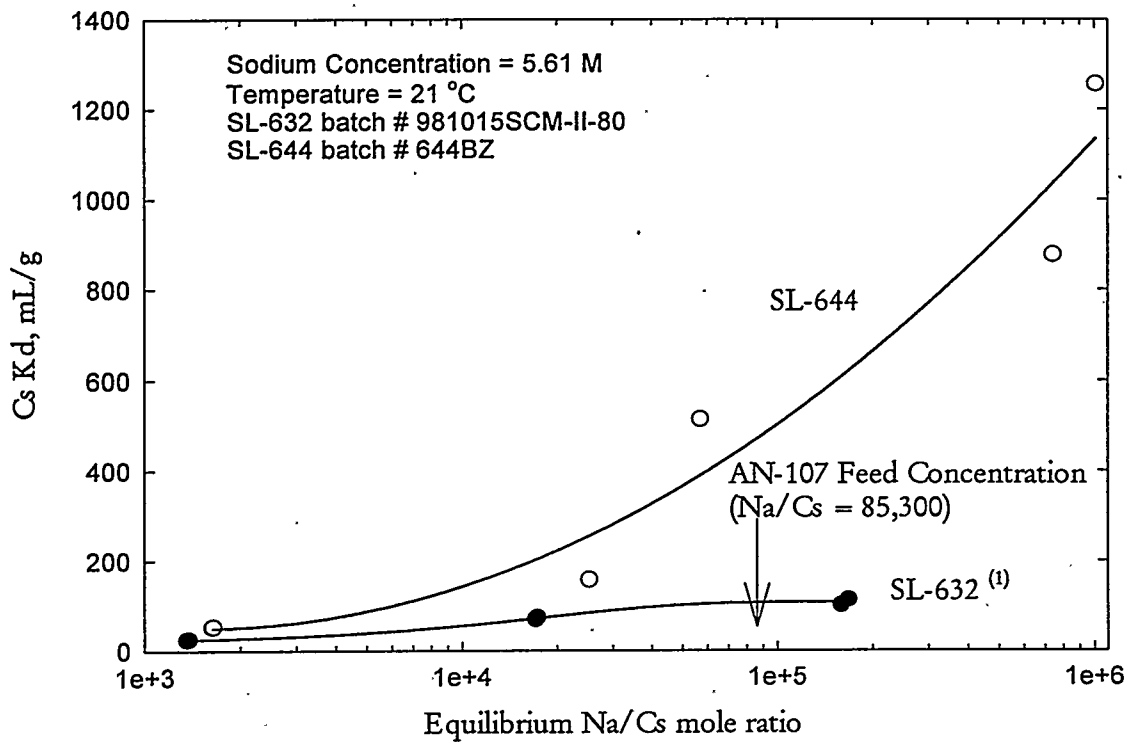


**Figure 3.2.** Cesium Kd's for SL-644 and SL-632 with AN-107 Supernatant.

(1) The SL-632 resin was determined by IBC Technologies to be improperly manufactured resulting in lower than expected Kds.

The Kd's for the SL-644 decrease significantly as the Na/Cs mole ratio decreases (e.g. cesium concentration increases) the Kds for the SL-632 decrease to a much smaller extent. The SL-632 Kds are much lower than expected. An investigation by IBC Technologies revealed that manufacturing difficulties resulted in a batch of resin that accounted for the relatively poor performance. Subsequent experimental results not reported in this document, indicate Kd's on the order of 400-500 mL/g. The result for SL-644 resin is typical of ion exchange materials that are becoming saturated because for a given mass of ion exchange resin, the total amounts of exchangeable sites are constant. Therefore as the initial cesium concentration increases, the amount of cesium removed from the solution begins to approach a constant value and the $K_d$ values decrease. The implication for waste processing is that as the Na/Cs mole ratio decreases, the volume of waste processed per column cycle will decrease.

The Kds at the waste feed conditions can be estimated from these plots as indicated in Table 3.4. These data could be used with the appropriate bed density to estimate the $\lambda$ value and estimate the bed size required to process a given amount of feed. This hasn't been done because the actual experimental feed conditions and expected plant processing conditions have changed since these experiments were conducted. The Sr/TRU precipitation process has been changed from the use of ferric nitrate to the use of sodium permanganate. This will have a small impact on the sodium:cesium mole ratio and may also impact the $^{99}Tc$ present as pertechnetate. It is also expected that the ion exchange feed solutions will be diluted to a sodium concentration that ranges from 5-5.5 M in order to prevent the SL-639 from floating.

**Table 3.4.** $^{137}Cs$ Kd Values at the Feed Conditions

| Waste tank | Feed Conditions | SL-632 Kd's (mL/g) | SL-644 Kd's (mL/g) |
|---|---|---|---|
| AW-101 | Na=6.59 M, Na/Cs = 79 ,400<br>K/Cs = 7400 | 130 | 450 |
| AN-107 | Na=5.61 M, Na/Cs = 85,300<br>K/Cs = 350 | 100 | 570 |

## 3.4 $TcO_4^-$ Kd's as a Function of Contact Time

The $TcO_4^-$ Kd's are shown as a function of contact time in Figure 3.3 for a series of batch contacts involving SL-639 and an AW-101 simulant spiked with $TcO_4^-$. Since the Kd's do not reach a constant value, it appears that the 72 hour contact was not sufficiently long to allow equilibrium to be reached. This is somewhat surprising since the SL-639 is expected to have reasonably fast kinetics (actually reasonably fast diffusion rates) and equilibrium was expected to be obtained in less than 24 hours. One possible explanation is that the SL-639 tends to float in the batch contact solutions and this results in relatively poor contact between the solution and the exchanger. Another possible explanation is that analytical uncertainty could introduce enough error into the final data point so that it would appear that equilibrium was not obtained. The difference between the 48 hour and 72 hour $^{99}Tc$ concentrations was about 12% and analytical uncertainty is estimated at $\pm 10\%$.

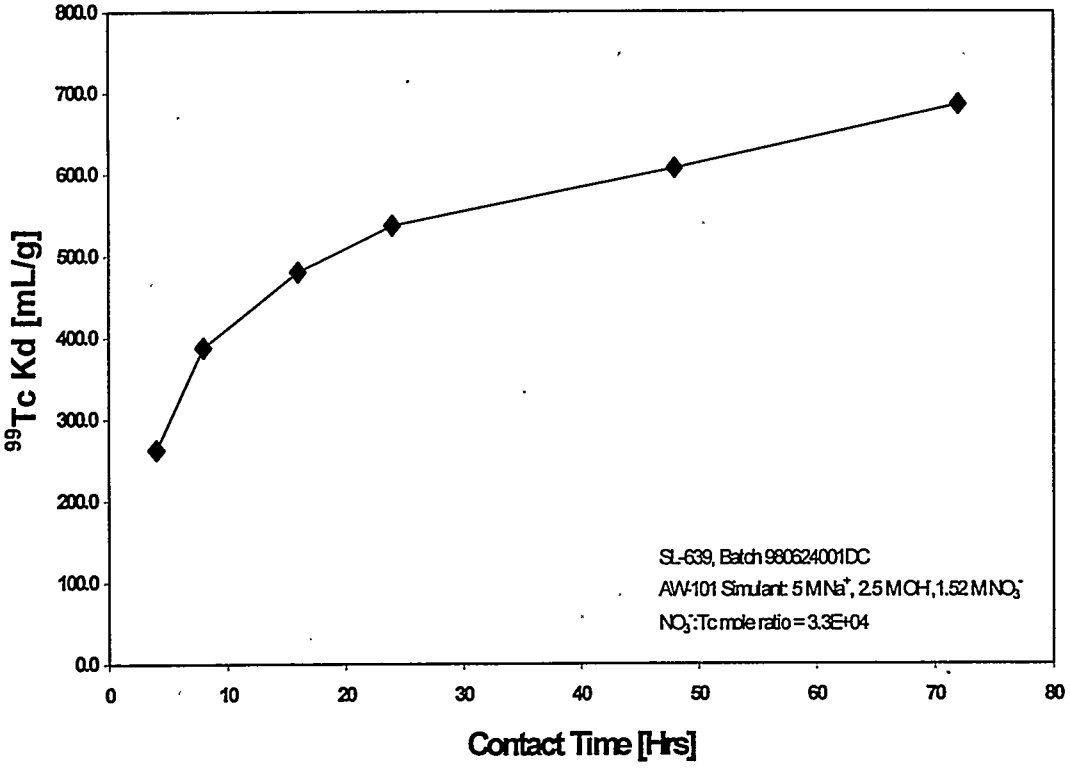


**Figure 3.3.** $TcO_4^-$ Kd's as a Function of Contact Time

## 3.5 $TcO_4^-$ and $^{99}Tc$ Kd's

The results of the batch technetium $K_d$ determinations based on estimates of the pertechnetate concentrations for the AW-101 and AN-107 supernatants contacted with the SL-639 ion exchange resin are shown in Figure 3.4. The Kds are plotted as a function of the $NO_3^-$:$TcO_4^-$ mole ratio since nitrate is the dominate competing anion. Since the nitrate concentration was constant for these experiments, a higher $NO_3^-$:$TcO_4^-$ indicates a decreasing pertechnetate concentration. The initial feed condition is also shown. The Kd values in Figure 3.4 for AW-101 appear to increase with the $NO_3^-$:$TcO_4^-$ mole ratio ($TcO_4^-$ concentration decreases) although the uncertainty in the data is to great to be conclusive.

Since only total $^{99}Tc$ concentrations were known, an estimate of the amount of $^{99}Tc$ present as nonpertechnetate was subtracted from the $^{99}Tc$ determinations. The amount of nonpertechnetate was estimated by determining the maximum amount of $^{99}Tc$ that could be removed by the SL-639 and assuming that the fraction not removed was some type of nonpertechnetate species. The amount of nonpertechnetate present in the AW-101 sample was estimated at 2.9% on the basis of the initial $^{99}Tc$ breakthrough from a small column run. The amount of nonpertechnetate present in the AN-107 sample was estimated at 75-78% on the basis of the short duration contacts with an excess quantity of SL-639 (see section 3.6).

Due to the expected high concentration of $^{99}Tc$ present as nonpertechnetate, only one measurement (in duplicate) was made for the $TcO_4^-$ $K_d$ with the AN-107 supernatant. Two sets of results are available for the AW-101 supernatant because some of the samples were reanalyzed. Selected samples were reanalyzed because some of the initial $^{99}Tc$ and $^{133}Cs$ concentrations determined by

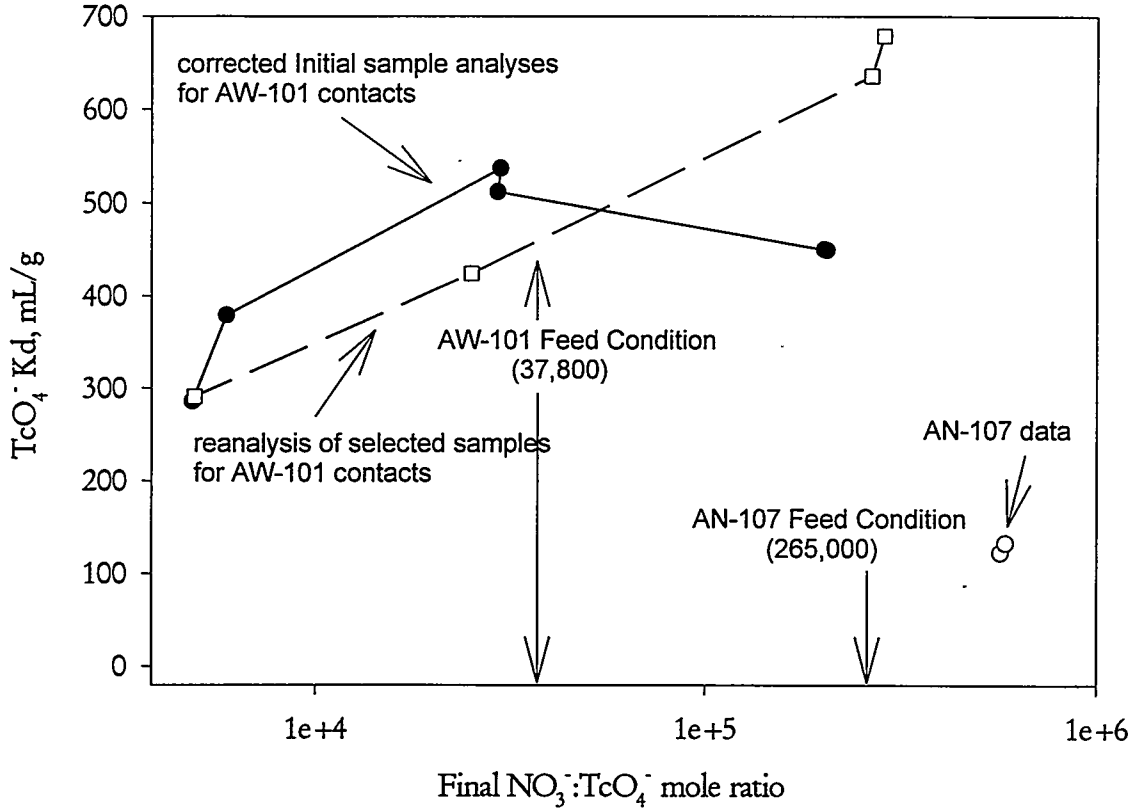


**Figure 3.4.** $TcO_4^-$ Kd's for SL-639 with AW-101 and AN-107 Supernatants

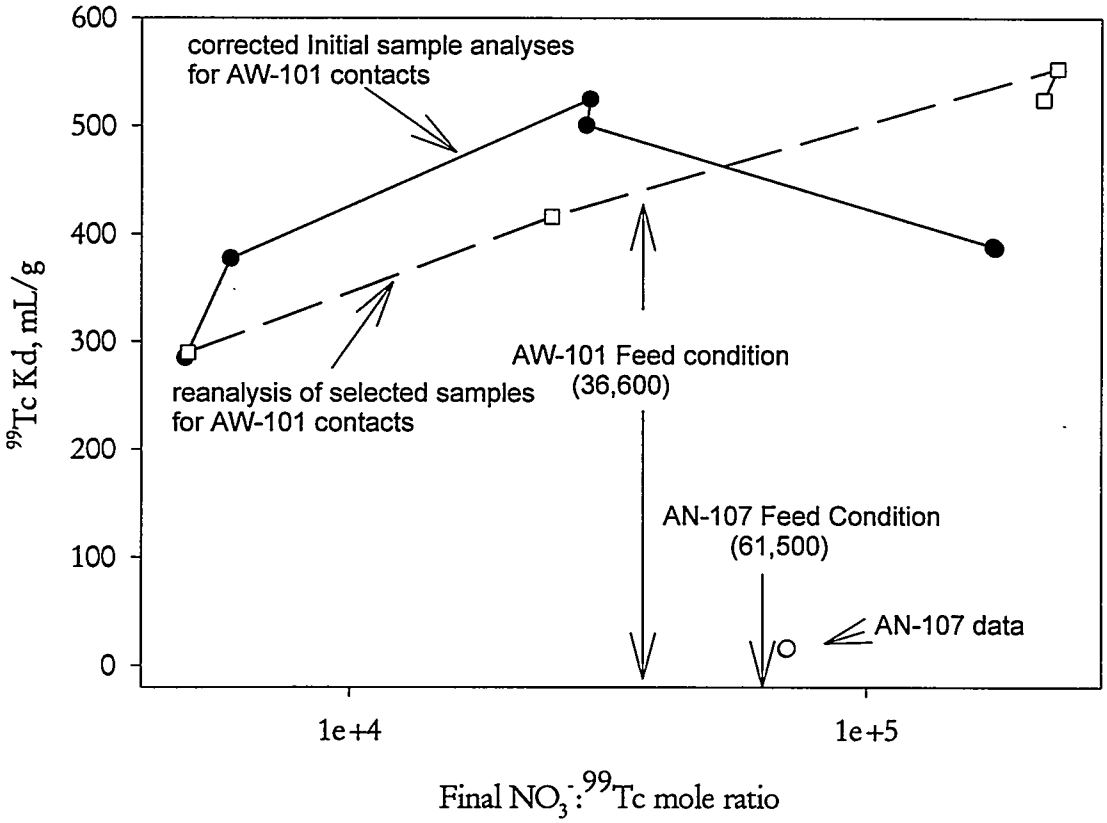


**Figure 3.5.** $^{99}$Tc Kd's for SL-639 with AW-101 and AN-107 Supernatants

ICP-MS were observed to be unusually low. The reanalyzed samples showed that the initial analytical results were indeed low and the cause was traced to dilution errors in the hot cell. The dilution errors were accounted for and the results based on the initial analyses are also shown. The reanalyzed samples probably reflect additional equilibration between the various species of $^{99}$Tc in solution and the $^{99}$Tc absorbed on the SL-639 since the SL-639 had not been separated from the waste samples. They were stored without agitation for approximately 3 months in sealed vials stored inside sealed plastic bags.

The apparent Kd values based on total $^{99}$Tc are shown in Figure 3.5 for comparison. The effect of the nonpertechnetate fraction is that it lowers the apparent Kd and is why the apparent Kd values for the AN-107 sample are so low relative to the Kds shown in Figure 3.4. The distinction between actual and apparent Kds should be noted. An actual Kd is a measure of equilibrium behavior of a component between the liquid and the solid phase. Since other species of $^{99}$Tc are present in the waste and are reflected in the total $^{99}$Tc analyses the apparent Kds do not represent the equilibrium behavior of a particular species of $^{99}$Tc.

## 3.6 Nonpertechnetate Fractions

In an effort to estimate the fraction of $^{99}$Tc present as nonpertechnetate some quick contacts (i.e. contacts at relatively short times) were performed with the AN-107 supernatant. Duplicate contacts resulted in the removal of only 22% and 25% of the $^{99}$Tc. While it is not certain that all of the pertechnetate was removed, the results are consistent with prior work with a different AN-107 sample that indicated a maximum of 26% of the $^{99}$Tc was removed (Blanchard, 1997). Similar batch contact work at the SRTC found that 27% of the $^{99}$Tc was removed (Hassan, 1997a). A small column test conducted at SRTC with SL-639 indicted that the initial removal of $^{99}$Tc was 42% indicating the fraction of $^{99}$Tc present in a nonpertechnetate form was 58% (Hassan, 1997b).

A recent small column run at PNNL with the AW-101 sample indicated that 2.9% of the $^{99}$Tc was present as a nonpertechnetate species. This is consistent with a prior small column test with AW-101 supernatant conducted at SRTC in phase 1A with SL-639 indicated that only 2% of $^{99}$Tc was nonpertechnetate (Hassan, 1997c). Prior small column tests at PNNL with a different sample of AW-101 supernatant indicate that the fraction of $^{99}$Tc present in a nonpertechnetate form is on the order of 15-25% (Blanchard 1997).

# 4.0 REFERENCES


Brown, G.N., L.A. Bray, C.D.Carlson, K.J. Carson, J.R. DesChane, R.J. Elovich, F.V. Hoopes, D.E. Kurath, L.E. Nenninger, P.K. Tanaka, 1996. *Comparison of Organic and Inorganic Ion Exchangers for Removal of Cesium and Strontium from Simulated and Actual Hanford 241-AW-101 DSSF Tank Waste,* PNL-10920, Pacific Northwest National Laboratory, Richland, WA.

Blanchard Jr., D.L., G.N. Brown, S.D. Conradson, S.K. Fadeff, G.R. Golcar, N.J. Hess, G.S. Klinger, and D.E. Kurath. 1997. *Technetium in Alkaline, High-Salt, Radioactive Tank Waste Supernate: Preliminary Characterization and Removal.* PNNL-11386, Pacific Northwest National Laboratory, Richland, WA.

Hassan, N.M., 1997a. *Hanford Tank AN-107 and AN-102 Samples Batch Ion Exchange Study.* SRTC-BNFL-03, Rev 1. Savannah River Technology Center, Westinghouse Savannah River Co. Aiken, SC, 29808.

Hassan, N.M., D.J. McCabe, 1997b. *Hanford Envelope C Tank Waste Ion Exchange Column Study.* SRTC-BNFL-018, Rev 0. Savannah River Technology Center, Westinghouse Savannah River Co. Aiken, SC, 29808.

Hassan, N.M.; D.J. McCabe, 1997c. *Hanford Envelope A Tank Waste Ion Exchange Column Study.* SRTC-BNFL-019, Rev 0. Savannah River Technology Center, Westinghouse Savannah River Co. Aiken, SC, 29808.

Urie, MW, JJ Wagner, LR Greenwood, OT Farmer, SK Fiskum, RT Ratner, CZ Soderquist, *Inorganic and Radiochemical Analysis of AW-101 and AN-107 "Diluted Feed" Materials,* May 1999, BNFL-RPT-003 Rev 0, PNWD-2463, Pacific Northwest National Laboratory, Richland, WA.

# APPENDIX A

Note: Raw data may be found in test instruction BNFL-TI-29953-034; BNFL Cs, Tc and $SO_4$ Batch Contact Test Instructions.

Figures A.1, A.2, and A.3 show the weight change as a function of the drying time for the SL-632, SL-644, and SL-639 ion exchange resins. Note that the exchanger mass becomes reasonably constant after 25 hours of drying.

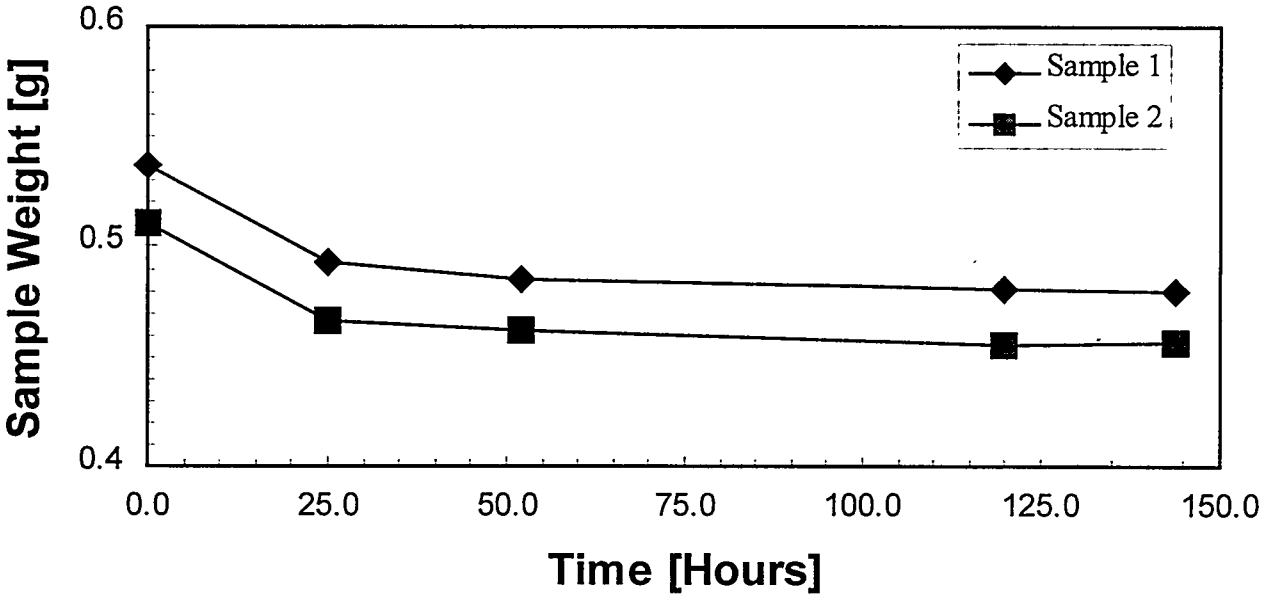


Figure A.1. Time Dependent Variation in the Weight of the SL-632 Ion Exchange Resin Samples at 85°C

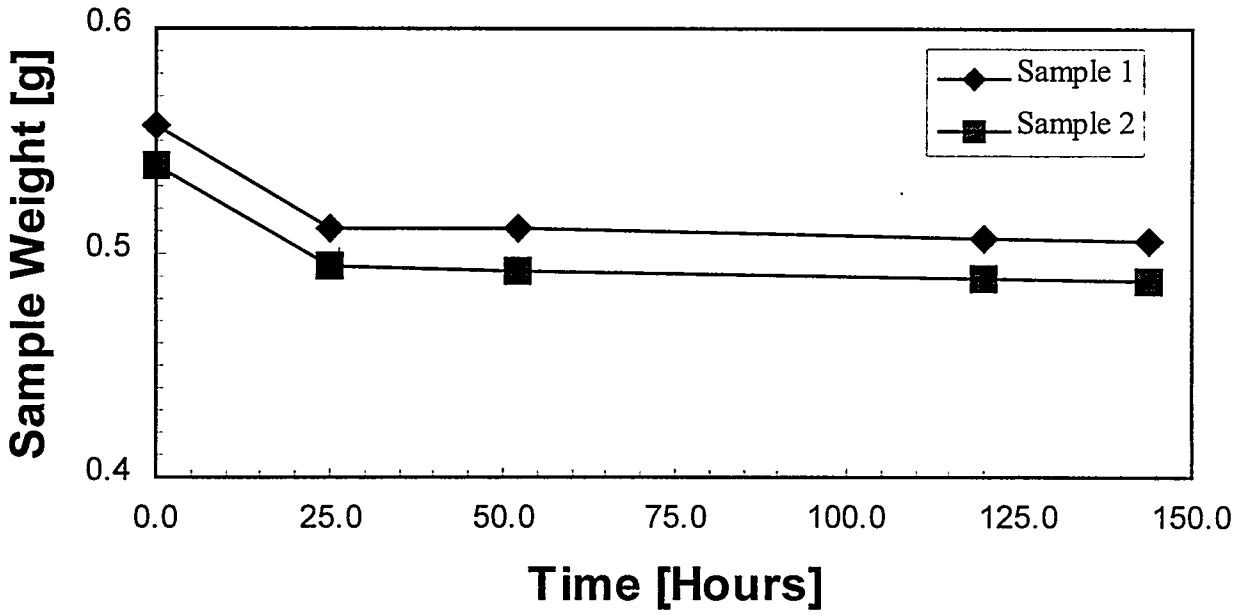


Figure A.2. Time Dependent Variation in the Weight of SL-644 Ion Exchange Resin Samples at 85°C

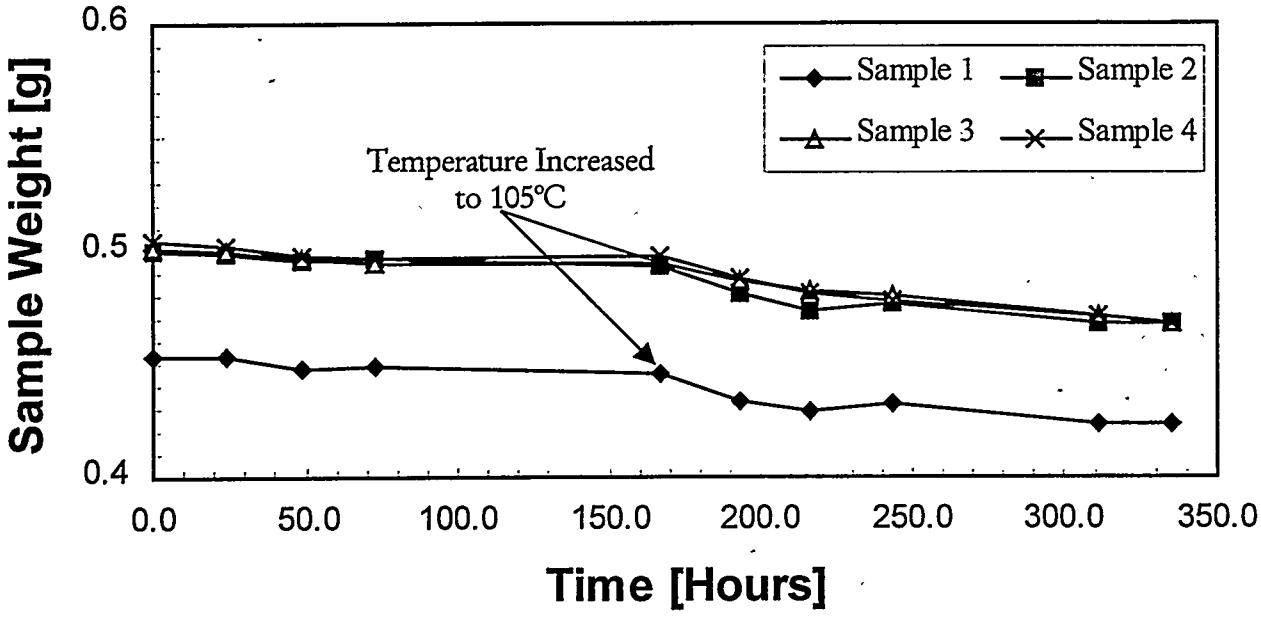


**Figure A.3.** Time Dependent Variation in the Weight of the SL-639 Ion Exchange Resin Samples at 85°C and 105°C

**Table A.1.** Sample Number Identification

| Sample ID | |
|---|---|
| W32, W32-D | SL-632 contact with AW-101 solution |
| W32-S1, W32-S1-D | SL-632 contact with Cs spike 1 AW-101 solution |
| W32-S2, W32-S2-D | SL-632 contact with Cs spike 2 AW-101 solution |
| W39, W39-D, W39-R, W39-D-R | SL-639 contact with AW-101 solution |
| W39-S1, W39-S1-D, W39-S1-R | SL-639 contact with Tc spike 1 AW-101 solution |
| W39-S2, W39-S2-D, W39-S2-R | SL-639 contact with Tc spike 2 AW-101 solution |
| W44, W44-D | SL-644 contact with AW-101 solution |
| W44-S1, W44-S1-D | SL-644 contact with Cs spike 1 AW-101 solution |
| W44-S2, W44-S2-D | SL-644 contact with Cs spike 2 AW-101 solution |
| N32, N32-D | SL-632 contact with AN-107 solution |
| N32-S1, N32-S1-D | SL-632 contact with Cs spike 1 AN-107 solution |
| N32-S2, N32-S2-D | SL-632 contact with Cs spike 2 AN-107 solution |
| N39, N39-D, N39-R, N39-D-R | SL-639 contact with AN-107 solution |
| N44, N44-D | SL-644 contact with AN-107 solution |
| N44-S1, N44-S1-D | SL-644 contact with Cs spike 1 AN-107 solution |
| N44-S2, N44-S2-D | SL-644 contact with Cs spike 2 AN-107 solution |
| | |
| W39-C | SL-632 contact with AW-101 simulant - control |
| W39-04, 08, 16, 24, 48, 72 | SL-632 contact with AW-101 simulant for 4, 8, 16, 24, 48 and 72 hours |
| | |
| | |
| | |

Key:

W = AW-101 solution
N = AN-107 solution
D = Duplicate
32= SL-632
39= SL-639
44= SL-644
S1= spike 1
S2= spike 2
C= control
R= reanalysis of contact solution

Table A.2. Cesium Kd Calculations for SL-632 and AW-101 Supernatant

| | Superlig SL-632 and AW-101 Supernatant | | | | | |
|---|---|---|---|---|---|---|
| Sample ID ------> | W32 | W32-D | W32-S1 | W32-S1D | W32-S2 | W32-S2D |
| Average Temperature [°C] | 21 | 21 | 21 | 21 | 21 | 21 |
| Mass of Exchanger [g] | 0.0527 | 0.0512 | 0.0505 | 0.0514 | 0.0509 | 0.0470 |
| Mass of AW-101 [g] | 6.6340 | 6.6544 | 6.4992 | 6.6673 | 6.5523 | 6.7030 |
| Avg. Density of AW-101 [g/mL] | 1.3176 | 1.3176 | 1.3176 | 1.3176 | 1.3176 | 1.3176 |
| Volume of AW-101 Taken [mL] | 5.0349 | 5.0504 | 4.9326 | 5.0602 | 4.9729 | 5.0873 |
| F-Factor | 0.8936 | 0.8936 | 0.8936 | 0.8936 | 0.8936 | 0.8936 |
| | | | | | | |
| Initial $^{133}$Cs Conc. [ng/mL] | 6.36E+03 | 6.36E+03 | 7.35E+04 | 7.35E+04 | 6.72E+05 | 6.72E+05 |
| Initial $^{137}$Cs Conc. [µCi/mL] | 2.43E+02 | 2.43E+02 | 2.43E+02 | 2.43E+02 | 2.43E+02 | 2.43E+02 |
| ratio of Cs-137:total Cs | 0.2465 | 0.2465 | | | | |
| Initial $^{133}$Cs Conc. [M] | 4.78E-05 | 4.78E-05 | 5.53E-04 | 5.53E-04 | 5.05E-03 | 5.05E-03 |
| Initial $^{137}$Cs Conc. [M] | 2.04E-05 | 2.04E-05 | 2.04E-05 | 2.04E-05 | 2.04E-05 | 2.04E-05 |
| Initial Cs Conc. [M] | 8.29E-05 | 8.29E-05 | 5.88E-04 | 5.88E-04 | 5.09E-03 | 5.09E-03 |
| Initial Na Conc. [M] | 6.59 | 6.59 | 6.59 | 6.59 | 6.59 | 6.59 |
| Initial Na/Cs | 79438 | 79438 | 11207 | 11207 | 1295 | 1295 |
| Initial [Cs]/[$^{137}$Cs] | 4.06 | 4.06 | 28.75 | 28.75 | 248.91 | 248.91 |
| | | | | | | |
| Final $^{134}$Cs Conc. [µCi/mL] | 2.80E-02 | 2.77E-02 | 2.30E-02 | 2.86E-02 | 3.54E-02 | 3.61E-02 |
| Final $^{137}$Cs Conc. [µCi/mL] | 1.10E+02 | 1.12E+02 | 1.07E+02 | 1.20E+02 | 1.42E+02 | 1.59E+02 |
| Final $^{137}$Cs Conc. [M] | 9.27E-06 | 9.44E-06 | 9.02E-06 | 1.01E-05 | 1.20E-05 | 1.34E-05 |
| Final Cs Conc [M] | 3.76E-05 | 3.83E-05 | 2.59E-04 | 2.91E-04 | 2.98E-03 | 3.34E-03 |
| Equilibrium [Na]/[Cs] | 1.75E+05 | 1.72E+05 | 2.54E+04 | 2.26E+04 | 2.21E+03 | 1.97E+03 |
| | | | | | | |
| Kd [mL/g] based on [$^{137}$Cs] | 128.74 | 128.72 | 138.42 | 112.40 | 77.40 | 63.60 |

**Table A.3.** Cesium Kd Calculations for SL-644 and AW-101 Supernatant

| | Superlig SL-644 and AW-101 Supernatant | | | | | |
|---|---|---|---|---|---|---|
| Sample ID ------> | W44 | W44-D | W44-S1 | W44-S1D | W44-S2 | W44-S2D |
| Average Temperature [°C] | 21 | 21 | 21 | 21 | 21 | 21 |
| Mass of Exchanger [g] | 0.0503 | 0.0503 | 0.0491 | 0.0504 | 0.0515 | 0.0518 |
| Mass of AW-101 [g] | 6.6098 | 6.6970 | 6.6273 | 6.6720 | 6.6194 | 6.7187 |
| Avg. Density of AW-101 [g/mL] | 1.3176 | 1.3176 | 1.3176 | 1.3176 | 1.3176 | 1.3176 |
| Volume of AW-101 Taken [mL] | 5.0165 | 5.0827 | 5.0298 | 5.0638 | 5.0238 | 5.0992 |
| F-Factor | 0.9069 | 0.9069 | 0.9069 | 0.9069 | 0.9069 | 0.9069 |
| | | | | | | |
| Initial $^{133}$Cs Conc. [ng/mL] | 6.36E+03 | 6.36E+03 | 7.35E+04 | 7.35E+04 | 6.72E+05 | 6.72E+05 |
| Initial $^{137}$Cs Conc. [µCi/mL] | 2.43E+02 | 2.43E+02 | 2.43E+02 | 2.43E+02 | 2.43E+02 | 2.43E+02 |
| ratio of Cs-137:total Cs | 0.2465 | 0.2465 | | | | |
| Initial $^{133}$Cs Conc. [M] | 4.78E-05 | 4.78E-05 | 5.53E-04 | 5.53E-04 | 5.05E-03 | 5.05E-03 |
| Initial $^{137}$Cs Conc. [M] | 2.04E-05 | 2.04E-05 | 2.04E-05 | 2.04E-05 | 2.04E-05 | 2.04E-05 |
| Initial Cs Conc. [M] | 8.29E-05 | 8.29E-05 | 5.88E-04 | 5.88E-04 | 5.09E-03 | 5.09E-03 |
| Initial Na Conc. [M] | 6.59 | 6.59 | 6.59 | 6.59 | 6.59 | 6.59 |
| Initial Na/Cs | 79438 | 79438 | 11207 | 11207 | 1295 | 1295 |
| Initial [Cs]/[$^{137}$Cs] | 4.06 | 4.06 | 28.75 | 28.75 | 248.91 | 248.91 |
| | | | | | | |
| Final $^{134}$Cs Conc. [µCi/mL] | 9.44E-03 | 8.35E-03 | 1.41E-02 | 1.26E-02 | 3.76E-02 | 3.77E-02 |
| Final $^{137}$Cs Conc. [µCi/mL] | 3.22E+01 | 3.30E+01 | 5.40E+01 | 6.35E+01 | 1.53E+02 | 1.56E+02 |
| Final $^{137}$Cs Conc. [M] | 2.71E-06 | 2.78E-06 | 4.55E-06 | 5.35E-06 | 1.29E-05 | 1.31E-05 |
| Final Cs Conc [M] | 1.10E-05 | 1.13E-05 | 1.31E-04 | 1.54E-04 | 3.21E-03 | 3.27E-03 |
| **Equilibrium [Na]/[Cs]** | **5.98E+05** | **5.84E+05** | **5.03E+04** | **4.28E+04** | **2.05E+03** | **2.01E+03** |
| | | | | | | |
| **Kd [mL/g] based on [$^{137}$Cs]** | **718.66** | **707.79** | **394.31** | **312.48** | **62.93** | **60.23** |

**Table A.4.** Cesium Kd Calculations for SL-632 and AN-107 Supernatant

| | Superlig SL-632 and AN-107 Supernatant | | | | | |
|---|---|---|---|---|---|---|
| Sample ID ------> | N32 | N32-D | N32-S1 | N32-S1D | N32-S2 | N32-S2D |
| Average Temperature [°C] | 21 | 21 | 21 | 21 | 21 | 21 |
| Mass of Exchanger [g] | 0.0492 | 0.0498 | 0.0516 | 0.0507 | 0.0499 | 0.0506 |
| Mass of AW-101 [g] | 6.4120 | 6.4512 | 6.4112 | 6.5096 | 6.4186 | 6.2175 |
| Avg. Density of AW-101 [g/mL] | 1.2353 | 1.2353 | 1.2353 | 1.2353 | 1.2353 | 1.2353 |
| Volume of AW-101 Taken [mL] | 5.1906 | 5.2224 | 5.1900 | 5.2697 | 5.1960 | 5.0332 |
| F-Factor | 0.8936 | 0.8936 | 0.8936 | 0.8936 | 0.8936 | 0.8936 |
| | | | | | | |
| Initial $^{133}$Cs Conc. [ng/mL] | 4.77E+03 | 4.77E+03 | 6.68E+04 | 6.68E+04 | 6.59E+05 | 6.59E+05 |
| Initial $^{137}$Cs Conc. [µCi/mL] | 1.92E+02 | 1.92E+02 | 1.92E+02 | 1.92E+02 | 1.92E+02 | 1.92E+02 |
| ratio of Cs-137:total Cs | 0.2455 | 0.2455 | | | | |
| Initial $^{133}$Cs Conc. [M] | 3.59E-05 | 3.59E-05 | 5.02E-04 | 5.02E-04 | 4.95E-03 | 4.95E-03 |
| Initial $^{137}$Cs Conc. [M] | 1.61E-05 | 1.61E-05 | 1.61E-05 | 1.61E-05 | 1.61E-05 | 1.61E-05 |
| Initial Cs Conc. [M] | 6.57E-05 | 6.57E-05 | 5.32E-04 | 5.32E-04 | 4.98E-03 | 4.98E-03 |
| Initial Na Conc. [M] | 5.61 | 5.61 | 5.61 | 5.61 | 5.61 | 5.61 |
| Initial Na/Cs | 85307 | 85307 | 10540 | 10540 | 1125 | 1125 |
| Initial [Cs]/[$^{137}$Cs] | 4.07 | 4.07 | 32.97 | 32.97 | 308.83 | 308.83 |
| | | | | | | |
| Final $^{134}$Cs Conc. [µCi/mL] | 1.00E-02 | 1.00E-02 | 1.00E-02 | 1.00E-02 | 1.00E-02 | 1.00E-02 |
| Final $^{137}$Cs Conc. [µCi/mL] | 1.03E+02 | 9.74E+01 | 1.18E+02 | 1.17E+02 | 1.58E+02 | 1.56E+02 |
| Final $^{137}$Cs Conc. [M] | 8.68E-06 | 8.21E-06 | 9.95E-06 | 9.86E-06 | 1.33E-05 | 1.31E-05 |
| Final Cs Conc [M] | 3.54E-05 | 3.34E-05 | 3.28E-04 | 3.25E-04 | 4.11E-03 | 4.06E-03 |
| **Equilibrium [Na]/[Cs]** | **1.59E+05** | **1.68E+05** | **1.71E+04** | **1.73E+04** | **1.36E+03** | **1.38E+03** |
| | | | | | | |
| **Kd [mL/g] based on [$^{137}$Cs]** | **101.40** | **113.34** | **70.07** | **74.05** | **24.72** | **25.34** |

**Table A.5.** Cesium Kd Calculations for SL-644 and AN-107 Supernatant.

| | Superlig SL-644 and AN-107 Supernatant | | | | | |
|---|---|---|---|---|---|---|
| Sample ID ------> | N44 | N44-D | N44-S1 | N44-S1D | N44-S2 | N44-S2D |
| Average Temperature [°C] | 21 | 21 | 21 | 21 | 21 | 21 |
| Mass of Exchanger [g] | 0.0496 | 0.0511 | 0.0517 | 0.0512 | 0.0499 | 0.0498 |
| Mass of AW-101 [g] | 6.4080 | 6.5488 | 6.5603 | 6.6945 | 6.5660 | 6.5640 |
| Avg. Density of AW-101 [g/mL] | 1.2353 | 1.2353 | 1.2353 | 1.2353 | 1.2353 | 1.2353 |
| Volume of AW-101 Taken [mL] | 5.1874 | 5.3014 | 5.3107 | 5.4193 | 5.3153 | 5.3137 |
| F-Factor | 0.9069 | 0.9069 | 0.9069 | 0.9069 | 0.9069 | 0.9069 |
| | | | | | | |
| Initial $^{133}$Cs Conc. [ng/mL] | 4.77E+03 | 4.77E+03 | 6.68E+04 | 6.68E+04 | 6.59E+05 | 6.59E+05 |
| Initial $^{137}$Cs Conc. [µCi/mL] | 1.92E+02 | 1.92E+02 | 1.92E+02 | 1.92E+02 | 1.92E+02 | 1.92E+02 |
| ratio of Cs-137:total Cs | 0.2455 | 0.2455 | | | | |
| Initial $^{133}$Cs Conc. [M] | 3.59E-05 | 3.59E-05 | 5.02E-04 | 5.02E-04 | 4.95E-03 | 4.95E-03 |
| Initial $^{137}$Cs Conc. [M] | 1.61E-05 | 1.61E-05 | 1.61E-05 | 1.61E-05 | 1.61E-05 | 1.61E-05 |
| Initial Cs Conc. [M] | 6.57E-05 | 6.57E-05 | 5.32E-04 | 5.32E-04 | 4.98E-03 | 4.98E-03 |
| Initial Na Conc. [M] | 5.61 | 5.61 | 5.61 | 5.61 | 5.61 | 5.61 |
| Initial Na/Cs | 85307 | 85307 | 10540 | 10540 | 1125 | 1125 |
| Initial [Cs]/[$^{137}$Cs] | 4.07 | 4.07 | 32.97 | 32.97 | 308.83 | 308.83 |
| | | | | | | |
| Final $^{134}$Cs Conc. [µCi/mL] | 9.00E-03 | 5.00E-03 | 6.00E-03 | 5.00E-03 | 8.00E-03 | 8.00E-03 |
| Final $^{137}$Cs Conc. [µCi/mL] | 1.61E+01 | 2.21E+01 | 7.99E+01 | 3.54E+01 | 1.32E+02 | 1.31E+02 |
| Final $^{137}$Cs Conc. [M] | 1.36E-06 | 1.86E-06 | 6.73E-06 | 2.98E-06 | 1.11E-05 | 1.10E-05 |
| Final Cs Conc [M] | 5.53E-06 | 7.59E-06 | 2.22E-04 | 9.84E-05 | 3.44E-03 | 3.41E-03 |
| **Equilibrium [Na]/[Cs]** | **1.01E+06** | **7.39E+05** | **2.53E+04** | **5.70E+04** | **1.63E+03** | **1.64E+03** |
| | | | | | | |
| **Kd [mL/g] based on [$^{137}$Cs]** | **1256.37** | **877.21** | **158.08** | **514.66** | **52.98** | **54.38** |

**Table A.6.** $^{99}$Tc Kd's as a Function of Time

| Kinetic Batch Distribution Coefficient Data for Tc-99 Using Superlig-639 Ion Exchange Material and AW-101 Simulant | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | | | | |
| Sample ID | W39-C | W39-04 | W39-08 | W39-16 | W39-24 | W39-48 | W39-72 |
| Contact Time (hrs) | 0 | 4 | 8 | 16 | 24 | 48 | 72 |
| Average Temperature (°C) | 23.2 | 22.5 | 22.5 | 22.5 | 22.5 | 22.5 | 22.5 |
| Mass of Exchanger (g) | 0.0000 | 0.0520 | 0.0519 | 0.0519 | 0.0500 | 0.0514 | 0.0519 |
| Mass of Simulant (g) | 6.3203 | 6.3557 | 6.3531 | 6.3404 | 6.3756 | 6.3394 | 6.2499 |
| Volume of Similant [mL] | 5 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 |
| Initial $^{99}$Tc Conc. [ng/mL] | 4580 | 4580 | 4580 | 4580 | 4580 | 4580 | 4580 |
| Initial $^{99}$Tc Conc. [moles/L] | 4.63E-05 | 4.63E-05 | 4.63E-05 | 4.63E-05 | 4.63E-05 | 4.63E-05 | 4.63E-05 |
| Final $^{99}$Tc Conc. [ng/mL] | 4580 | 1240 | 922 | 775 | 728 | 641 | 572 |
| Final $^{99}$Tc Conc. [moles/L] | 4.63E-05 | 1.25E-05 | 9.31E-06 | 7.83E-06 | 7.35E-06 | 6.47E-06 | 5.78E-06 |
| F-Factor | 0.9855 | 0.9855 | 0.9855 | 0.9855 | 0.9855 | 0.9855 | 0.9855 |
| $K_d$ [mL/g] | NA | **2.63E+02** | **3.88E+02** | **4.80E+02** | **5.37E+02** | **6.07E+02** | **6.85E+02** |
| | | | | | | | |
| note: The calculated (and target) $^{99}$Tc concentration is 5028 ng/mL | | | | | | | |

Table A.7. $^{99}$Tc Kd Calculations for SL-639 and AW-101 Supernatant

| | SL-639 & AW-101 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sample ID | W39 | W39-R | W39-D | W39-D-R | W39-S1 | W39-S1-R | W39-S1D | W39-S2 | W39-S2-R | W39-S2D |
| Average Temperature [°C] | 21 | 21 | 21 | 21 | 21 | 21 | 21 | 21 | 21 | 21 |
| Mass of Exchanger [g] | 0.0499 | 0.0499 | 0.0509 | 0.0509 | 0.0510 | 0.0510 | 0.0491 | 0.0502 | 0.0502 | 0.0504 |
| Mass of AW-101 [g] | 6.6903 | 6.6903 | 6.7034 | 6.7034 | 6.5986 | 6.5986 | 6.5231 | 6.5587 | 6.5587 | 6.6921 |
| Avg. Density of AW-101 [g/mL] | 1.3176 | 1.3176 | 1.3176 | 1.3176 | 1.3176 | 1.3176 | 1.3176 | 1.3176 | 1.3176 | 1.3176 |
| Volume of AW-101 Taken [mL] | 5.0776 | 5.0776 | 5.0876 | 5.0876 | 5.0080 | 5.0080 | 4.9507 | 4.9778 | 4.9778 | 5.0790 |
| F-Factor | 0.9855 | 0.9855 | 0.9855 | 0.9855 | 0.9855 | 0.9855 | 0.9855 | 0.9855 | 0.9855 | 0.9855 |
| | | | | | | | | | | |
| Init. ICP $^{99}$Tc Conc. [ng/mL] | 268.7 | 266.0 | 268.7 | 266.0 | 2070.0 | 2070.0 | 2070.0 | 7820.0 | 7820.0 | 7820.0 |
| Initial Dilution Factor | 20.0 | 20.5 | 20.0 | 20.5 | 20.0 | 20.0 | 20.0 | 20.0 | 20.0 | 20.0 |
| Initial $^{99}$Tc Conc. [ng/mL] | 5373.3 | 5460.2 | 5373.3 | 5460.2 | 41400.0 | 41400.0 | 41400.0 | 156400.0 | 156400.0 | 156400.0 |
| Initial $^{99}$Tc Conc. [M] | 5.43E-05 | 5.52E-05 | 5.43E-05 | 5.52E-05 | 4.18E-04 | 4.18E-04 | 4.18E-04 | 1.58E-03 | 1.58E-03 | 1.58E-03 |
| Initial $^{99}$Tc Conc. Ci/m$^3$ (uCi/mL) | 9.13E-02 | 9.28E-02 | 9.13E-02 | 9.28E-02 | 7.04E-01 | 7.04E-01 | 7.04E-01 | 2.66 | 2.66 | 2.66 |
| $NO_3^-$ concentration, M | 1.99 | 1.99 | 1.99 | 1.99 | 1.99 | 1.99 | 1.99 | 1.99 | 1.99 | 1.99 |
| Initial $NO_3^-$:$^{99}$Tc | 3.67E+04 | 3.61E+04 | 3.67E+04 | 3.61E+04 | 4.76E+03 | 4.76E+03 | 4.76E+03 | 1.26E+03 | 1.26E+03 | 1.26E+03 |
| **Initial $NO_3^-$:$TcO_4^-$** | **3.78E+04** | | | | | | | | | |
| Fin. ICP $^{99}$Tc Conc. [ng/mL] | 56.4 | 43.7 | 55.8 | 40.8 | 343.5 | 395.0 | 337.8 | 2039.5 | 1940.0 | 1669.0 |
| Final Dilution Factor | 20.0 | 20.6 | 20.0 | 20.7 | 20.0 | 20.3 | 20.0 | 20.0 | 20.8 | 20.0 |
| Final $^{99}$Tc Conc. [ng/mL] | 1128 | 898 | 1116 | 846 | 6870 | 7999 | 6756 | 40790 | 40283 | 33380 |
| Final $^{99}$Tc Conc [M] | 1.14E-05 | 9.07E-06 | 1.13E-05 | 8.55E-06 | 6.94E-05 | 8.08E-05 | 6.82E-05 | 4.12E-04 | 4.07E-04 | 3.37E-04 |
| **Final $NO_3^-$:$^{99}$Tc** | **1.75E+05** | **2.19E+05** | **1.77E+05** | **2.33E+05** | **2.87E+04** | **2.46E+04** | **2.92E+04** | **4.83E+03** | **4.89E+03** | **5.90E+03** |
| Final $^{99}$Tc Conc. Ci/m$^3$ (uCi/mL) | 1.92E-02 | 1.53E-02 | 1.90E-02 | 1.44E-02 | 1.17E-01 | 1.36E-01 | 1.15E-01 | 6.93E-01 | 6.85E-01 | 5.67E-01 |
| fraction Tc removed | 0.79 | 0.84 | 0.79 | 0.85 | 0.83 | 0.81 | 0.84 | 0.74 | 0.74 | 0.79 |
| | | | | | | | | | | |
| **$^{99}$Tc Kd [mL/g]** | **388.6** | **524.5** | **386.9** | **553.1** | **500.6** | **415.8** | **524.7** | **284.9** | **289.7** | **377.0** |
| assumed nonpertechnetate fraction | 0.029 | 0.029 | 0.029 | 0.029 | 3.74E-03 | 3.74E-03 | 3.74E-03 | 1.01E-03 | 1.01E-03 | 1.01E-03 |
| Final $TcO_4^-$ concentration, M | 9.83E-06 | 7.48E-06 | 9.71E-06 | 6.96E-06 | 6.78E-05 | 7.92E-05 | 6.67E-05 | 4.10E-04 | 4.05E-04 | 3.36E-04 |
| Final $NO_3^-$:$TcO_4^-$ | 2.02E+05 | 2.66E+05 | 2.05E+05 | 2.86E+05 | 2.93E+04 | 2.51E+04 | 2.98E+04 | 4.85E+03 | 4.91E+03 | 5.93E+03 |
| $TcO_4^-$ Kd [mL/g] | 450.4 | 635.8 | 449.2 | 679.3 | 512.1 | 424.0 | 537.0 | 286.0 | 290.9 | 378.8 |

**Table A.8.** $^{99}$Tc Kd Calculations for SL-639 and AN-107 Supernatant

| Ion Exchanger & Supernatant | SL-639 & AN-107 | | | | | SL-639 & AN-107: Quick Contacts | |
|---|---|---|---|---|---|---|---|
| Sample ID | N39 | N39-R | N39-D | N39-D-R | | N-QC | N-QC-D |
| Average Temperature [°C] | 21 | 21 | 21 | 21 | | 21 | 21 |
| Mass of Exchanger [g] | 0.0503 | 0.0503 | 0.0498 | 0.0498 | | | |
| Mass of AW-101 [g] | 6.5327 | 6.5327 | 6.6595 | 6.6595 | | | |
| Avg. Density of AW-101 [g/mL] | 1.2353 | 1.2353 | 1.2353 | 1.2353 | | | |
| Volume of AW-101 Taken [mL] | 5.2884 | 5.2884 | 5.3910 | 5.3910 | | | |
| F-Factor | 0.9855 | 0.9855 | 0.9855 | 0.9855 | | | |
| | | | | | | | |
| Init. ICP $^{99}$Tc Conc. [ng/mL] | 166.0 | 166.0 | 166.0 | 166.0 | | 166.0 | 166.0 |
| Initial Dilution Factor | 20.0 | 20.0 | 20.0 | 20.0 | | 20.0 | 20.0 |
| Initial $^{99}$Tc Conc. [ng/mL] | 3320.0 | 3320.0 | 3320.0 | 3320.0 | | 3320.0 | 3320.0 |
| Initial $^{99}$Tc Conc. [M] | 3.35E-05 | 3.35E-05 | 3.35E-05 | 3.35E-05 | | | |
| Initial $^{99}$Tc Conc. Ci/m$^3$ (uCi/mL) | 5.64E-02 | 5.64E-02 | 5.64E-02 | 5.64E-02 | | | |
| $NO_3^-$ concentration, M | 2.06 | 2.06 | 2.06 | 2.06 | | | |
| **Initial $NO_3^-$:$^{99}$Tc** | **6.14E+04** | **6.14E+04** | **6.14E+04** | **6.14E+04** | | | |
| | | | | | | | |
| Fin. ICP $^{99}$Tc Conc. [ng/mL] | 145.4 | 140.0 | 144.9 | 131.0 | | 130 | 125 |
| Final Dilution Factor | 20.0 | 21.2 | 20.0 | 21.3 | | 20.0 | 20.0 |
| Final $^{99}$Tc Conc. [ng/mL] | 2908.0 | 2961.2 | 2898.0 | 2784.8 | | 2600.0 | 2500.0 |
| Final $^{99}$Tc Conc [M] | 2.94E-05 | 2.99E-05 | 2.93E-05 | 2.81E-05 | | | |
| **Final $NO_3^-$:$^{99}$Tc** | **7.01E+04** | **6.89E+04** | **7.04E+04** | **7.32E+04** | | | |
| Final $^{99}$Tc Conc. Ci/m$^3$ (uCi/mL) | 4.94E-02 | 5.03E-02 | 4.93E-02 | 4.73E-02 | | | |
| fraction Tc removed | 0.12 | 0.11 | 0.13 | 0.16 | | 0.217 | 0.247 |
| | | | | | | | |
| **$^{99}$Tc Kd [mL/g]** | **15.12** | **12.93** | **15.99** | **21.10** | | | |
| assumed nonpertechnetate fraction | 0.768 | 0.768 | 0.768 | 0.768 | | | |
| Final $TcO_4^-$, concentration M | 3.62E-06 | 4.16E-06 | 3.52E-06 | 2.37E-06 | | | |
| **Final $NO_3^-$:$TcO_4^-$** | **5.69E+05** | **4.96E+05** | **5.86E+05** | **8.68E+05** | | | |
| **$TcO_4^-$ Kd [mL/g]** | **122.7** | **93.1** | **133.1** | **250.0** | | | |