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Technetium Partitioning for the Hanford Tank Waste Remediation System: Anion Exchange Studies for Partitioning Technetium from Synthetic DSSF and DSS Simulants and Actual Hanford Wastes (101-SY and 103-SY) Using Reillex™-HPQ Resin

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List of Acronyms

ALARA	As low as reasonably achievable
BV	Bed volume
BT	Breakthrough
CST	Chemical Science and Technology Division
CST-11	CST Division's Nuclear and Radiochemistry Group
DOE	Department of Energy
DSS	Double-shell slurry
DSSF-5	Double-shell slurry feed @ 5.00 M NaOH
DSSF-7	Double-shell slurry feed @ 7.00 M NaOH
DST	Double-shell tank
EDTA	ethylenediaminetetraacetic acid
en	ethylenediamine
EPA	Environmental Protection Agency
ETSU	East Texas State Unuversity
HLW	High-level waste
HPQ	Highly porous quaternary
IPM	Initial pretreatment module
LANL	Los Alamos National Laboratory
LLW	Low-level waste
LSC	Liquid scintillation counting
MP	Macroporous resin
NMR	Nuclear magnetic resonance
NTA	nitilotriacetic acid
SF	Separation factor
SST	Single-shell tank
TPA	Tri-Party Agreement
TWRS	Tank Waste Remediation System

Technetium Partitioning for the Hanford Tank Waste Remediation System: Anion Exchange Studies for Partitioning Technetium from Synthetic DSSF and DSS Simulants and Actual Hanford Waste (101-SY and 103-SY) Using Reillex™-HPQ Resin

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Abstract

This combined annual report fulfills the FY95 milestones for the TWRS technetium partitioning programs (1) "Column Ion Exchange Test for Technetium Removal from Synthetic DSSF Waste" and (2) "Column Ion Exchange Test for Technetium Removal from Actual DSSF Waste." This report describes batch and column experiments on the sorption of technetium from DSSF-7, DSSF-5, DSS, 101-SY and 103-SY simulants by Reillex™-HPQ anion exchange resin and other resins. It provides the first experimental data of the performance of Reillex™-HPQ anion exchange resin with a Hanford waste. As a courtesy to our funding agent, we have attached a copy of the paper entitled "Sorption Behavior of Perrhenate Ion on Reillex™-HPQ Anion Exchange Resin from Nitric Acid and Sodium Nitrate/Hydroxide Solutions." which we have submitted to the journal of "Solvent Extraction and Ion Exchange." The article fulfills part of a milestone for the DSSF Simulant work.

Reillex™-HPQ anion exchange resin continues to show good performance as a technology for partitioning technetium from Hanford waste streams. It efficiently sorbs technetium from DSSF-5, 101-SY and 103-SY simulants; distribution coefficients are >200 from these matrixes. Reillex™-HPQ sorbs technetium faster from DSSF-5 simulant than AG™MP-1 resin.

The fundamental behavior of pertechnetate with Reillex™-HPQ resin is understood in caustic nitrate solutions. This behavior is described by the relationship $K_d = K_2 \bullet R_t / \{K_4 \bullet [OH^-] + [NO_3^-]\}$ where K_2 and K_4 are the equilibrium constants, respectively, for the exchange of TcO_4^- and OH^- with the nitrate form of Reillex™-HPQ, and R_t is the total concentration of resin sites in either the nitrate or hydroxide form. This information can be used at Hanford to estimate the sorption of pertechnetate onto Reillex™-HPQ resin from tank supernates, and sludge washing and leaching solutions.

A 2.54 x 50 cm Reillex™-HPQ resin column can be used repetitively over a 100 day service period. Recovery of technetium over this period service is nearly quantitative. Flow rate studies with 2.54 x 50 cm Reillex™-HPQ resin columns shows that the 1% breakthrough point varies inversely and linearly with the flow rate. Full breakthrough experiments shows that Reillex™-HPQ columns are more efficient than AG™MP-1 columns.

Technetium K_d values, radiochemical analyses and ^{99}Tc NMR data show that ≈ 70% of the technetium in the 101-SY and 103-SY waste samples is not pertechnetate. Oxidation of these non-pertechnetate forms is not readily achieved. This problem is significant because it may effect the feasibility of separating technetium from tank waste.

INTRODUCTION

Background: The Department of Energy (DOE) is preparing to stabilize the waste generated from the production of plutonium at the Hanford facility. Over the last 50 years, acidic processing waste has been neutralized (actually made caustic, pH > 12) and placed in either single-shell tanks (149 SST) or, in more recent time, double-shell tanks (28 DST).[1] Many of the SST are approaching their engineered design life-time. As a result approximately half of the SST are leaking. Compounding the waste burden are safety problems associated with incompatible chemical mixtures that are being digested by radiolytic heating. In addition, chemical transformations, initiated by radiolytic processes, produce reactive radical species and generate explosive gases (i.e. H_2).[2-6] Thus, it is imperative that this waste be stabilized before a major environmental catastrophe occurs.

The plan to remediate the Hanford tank waste is to separate it into low-level waste (LLW) and high-level waste (HLW) fractions; "pretreatment" is the term given to this general partitioning plan.[7] The LLW will be converted to glass and stored on the Hanford reservation while the HLW will be vitrified into glass logs and placed in a geologic repository. Constraints on the number of glass logs that can be accommodated by the repository and the activity level in the LLW glass will require that chemical separation of many radioactive components be made from the bulk waste to get them into their proper waste stream. The "Current Hanford Pretreatment Flow Diagram" (Figure 1), addresses these separation issues.[8] In this process, actinides, cesium, strontium and technetium are separated from the bulk waste and then vitrified with the HLW. The rationale for placing technetium in the HLW component is due to its long half-life (213,000 years) and ability to migrate in the environment.[9] If left in the LLW, these factors cause technetium to be a major contributor to the long-term hazard associated with the LLW form.[10]

It should be noted that the current baseline remediation strategy of the new Hanford Tri-Party Agreement (TPA) between DOE, the Environmental Protection Agency (EPA), and the State of Washington does not formally incorporate technetium partitioning.[11] However, because of the uncertain behavior of technetium in the LLW form, the agreement still recommends further research

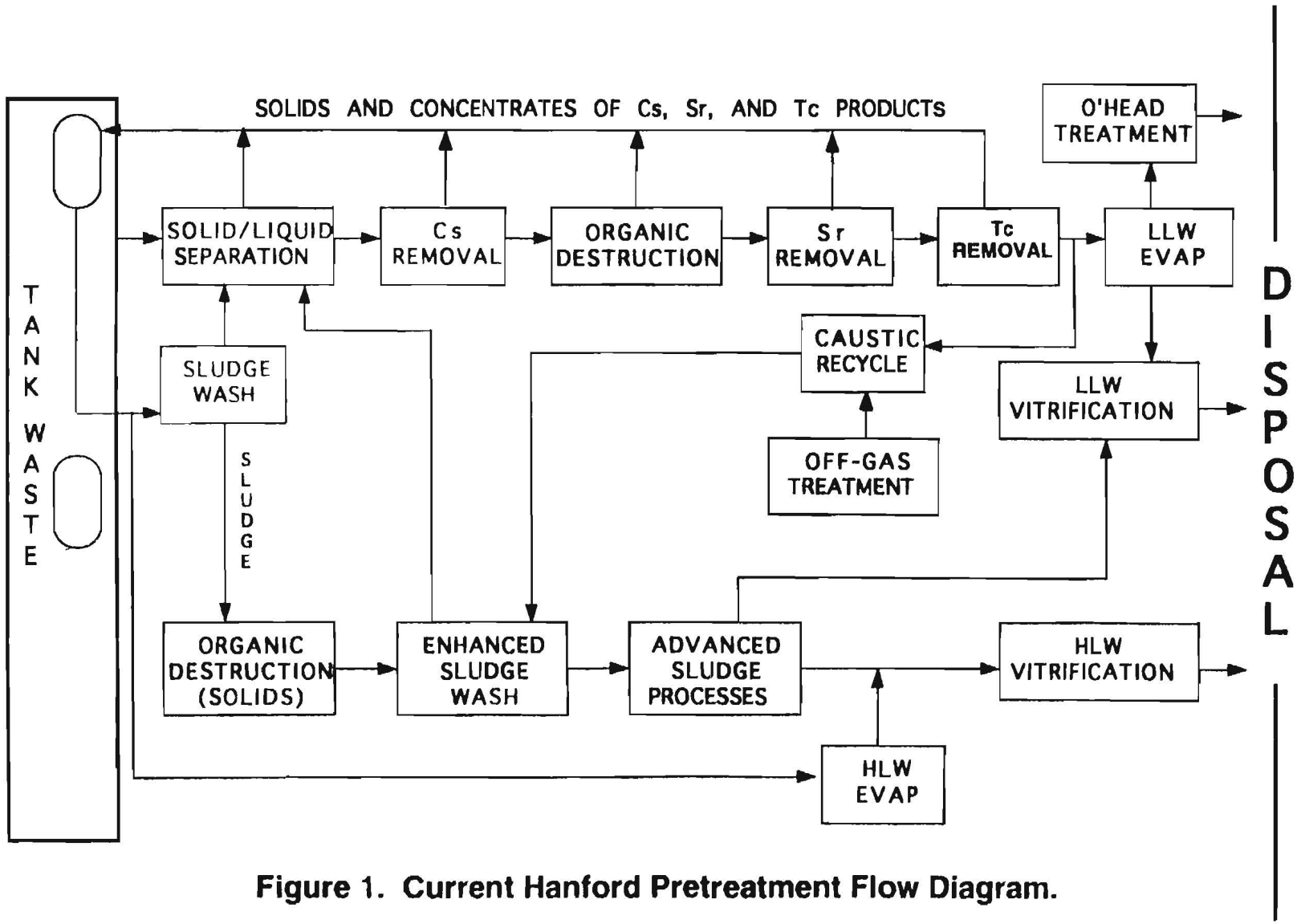


Figure 1. Current Hanford Pretreatment Flow Diagram.

on technetium partitioning from Hanford waste streams. Application of a technetium partitioning technology would help Hanford and other potential DOE sites meet the performance assessment criteria for their LLW forms.

The scope of the technetium problem is estimated by its inventory in the waste, ~ 2000 Kg.[12] Technetium is generally highly oxidized and stable in aqueous solution as the pertechnetate anion, TcO_4^-. However, the combination of radiolytic effects, heating, organic solvents and complexants (EDTA, NTA, oxalate, citrate, etc.) and time may have reduced and complexed a significant fraction of the technetium in the tank waste. These species may be in a form that is not readily amenable to separation techniques based on removing pertechnetate. This problem was anticipated by this project at its inception and is addressed in this report.[13]

Technetium Partitioning Technology Development: An early attempt to separate technetium from neutralized Hanford waste was performed by Wheelwright's group during the early 1960's.[14] They used Dowex-1 anion exchange resin to recover technetium from freshly generated waste. This work clearly demonstrated anion exchange as a baseline technology for this separation. Thirty years of anion exchange resin development has produced resins that have improved performance compared to Dowex-1. Their application may exceed the decontamination factor of five obtained by Wheelwright's group. For instance, F. Marsh at LANL, in collaboration with Reilly Industries, has developed a new resin, Reillex™-HPQ, to separate plutonium nitrate complexes from concentrated nitric acid solutions (~8 M).[15] This resin is a co-polymer of divinylbenzene and 4-vinylpyridine that has been subsequently methylated at the pyridine nitrogen to give pyridinium [-$C_5H_4N(CH_3)^+$] strong base anionic sites (Figure 2). The pyridinium functionality of Reillex™-HPQ resin is unique; most other strong base anion resins like Dowex-1 (Figure 3) are alkyl quaternary amine resins. Reillex™-HPQ, compared to other resins, has superior stability to radiolysis and nitric acid.[16,17] At LANL's plutonium facility the resin's life time is at least four times that of conventional resins under normal processing conditions. More specifically for technetium, we have found that this resin was included in a thesis project that evaluated 22 anion exchange resins for their ability to separate technetium from acidic, neutral, and highly salted solutions.[18] Reillex™-HPQ was the highest

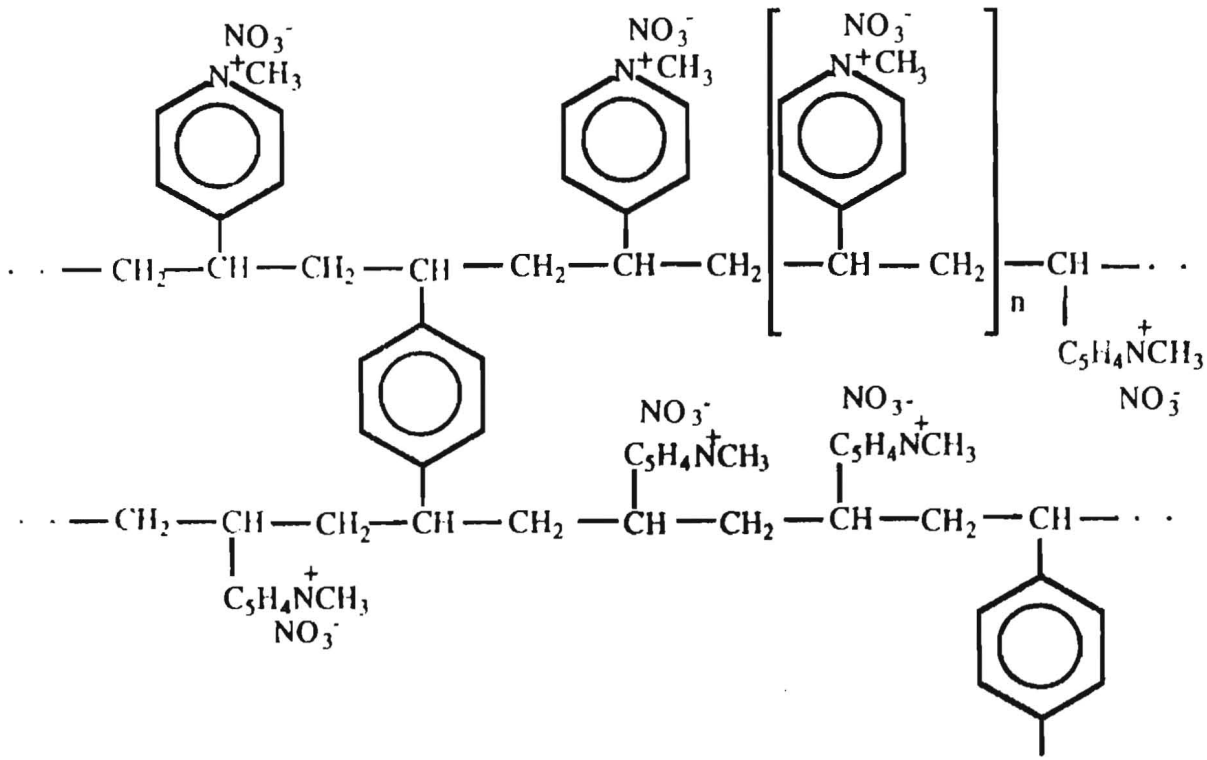


Figure 2. Structure of Reillex™—HPQ Anion Exchange Resin.

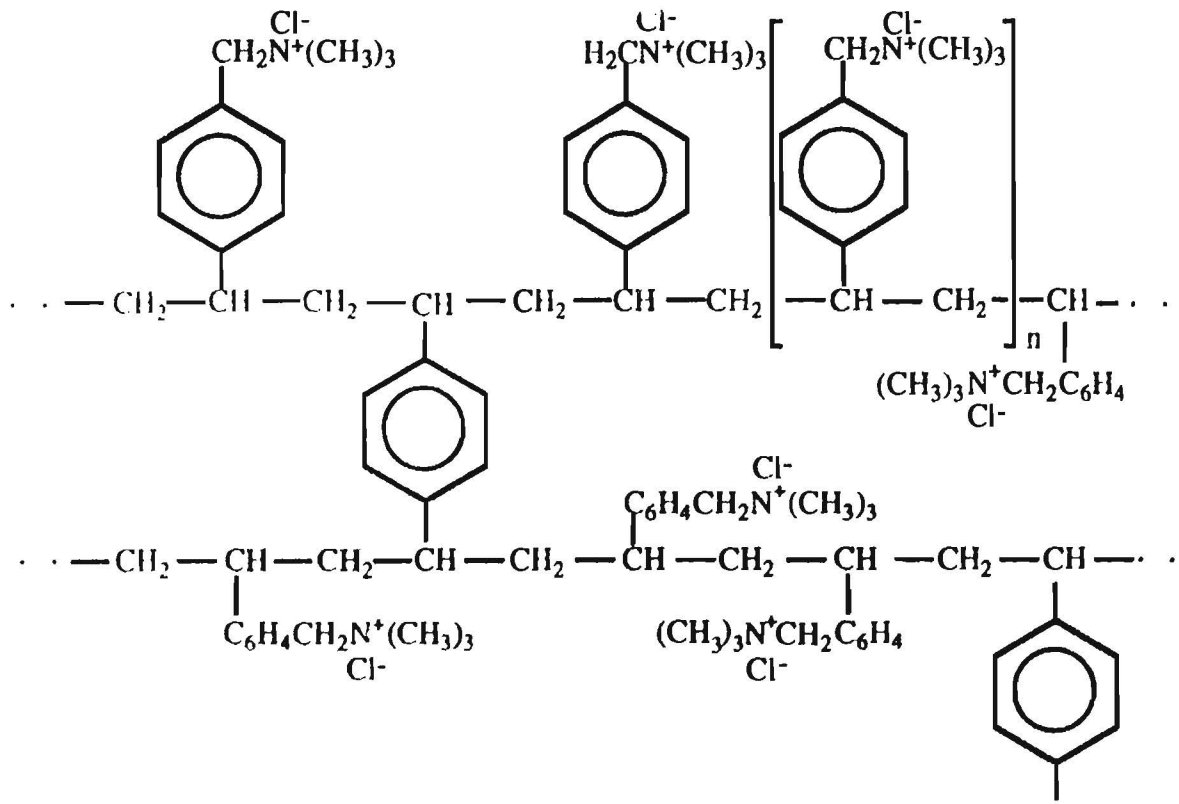


Figure 3. Structure of Dowex™—1 Anion Exchange Resin.

ranked resin in this study. On the basis of these data we chose to examine the qualities of Reillex™-HPQ to partition technetium from Hanford DSS and DSSF-7 waste simulant solutions.[19-21] Data from a recent scoping study of absorbers has reconfirmed the appropriateness of this decision.[22] Table 1 shows that Reillex™-HPQ was the best absorbers of the 63 tested for removing technetium from DSSF-7 simulant within 30 minutes. The time criterion is important because the anticipated residence time of feed in an anion exchange column may be 30 minutes or less.

Table 1. Distribution of Technetium by Absorbers from DSSF-7 Simulant.[a]

Absorber	30-min K_d [b]	2-hr K_d	6-hr K_d
Reillex™-HPQ	254	293	332
Purolite™ A-520-E	189	392	527
Aliquat™ 336	177	464	524
Cyanex™ 923	121	244	230
Ionac™ SR-6	45	105	188

[a] Data from Zita V. Svitra and S. Fredric Marsh, reference 22.

[b] Technetium distribution coefficients, K_d (mL/g), between resins and DSSF-7 simulant.

In a follow up study (Table 2), Reillex™-HPQ remained near the top of the list of efficient technetium sorbers.[23] It is important to note that of the seven sorbers in Table 2 only the Purolite™ A-520-E and Reillex™-HPQ resins are commercially available. In addition, the N-Butyl-HP, N-Hexyl-HP, and N-Octyl-HP resins are also pyridinium resins similar to Reillex™-HPQ.

Technetium Partitioning Objectives: This report describes research that is a continuation of two prior years of TWRS work.[19-21] It describes research that is developing a method to separate technetium, as pertechnetate, from Hanford waste streams by applying the baseline technology of anion exchange

Table 2. Distribution of Technetium by Absorbers from 101-SY Simulant.[a]

Absorber	30-min K_d [b]	2-hr K_d	6-hr K_d
N-Butyl-HP [c]	683	1208	1406
Aliquat™ 336	649	1262	1422
N-Hexyl-HP [c]	602	1165	1406
Purolite™ A-520-E	517	1007	1301
Reillex™-HPQ	465	648	669
Ionac™ SR-6	320	757	1171
N-Octyl-HP [c]	251	530	780

[a] Data from Zita V. Svitra and S. Fredric Marsh, reference 23.

[b] Technetium distribution coefficients, K_d (mL/g), between resins and 101-SY simulant.

[c] Experimental resins prepared by Reilly Industries, Indianapolis IN.

using Reillex™-HPQ resin. Thus, it assumes that an efficient organic destruction process will precede technetium partitioning as depicted in Figure 1.

The goals for FY95 were to develop a partitioning scheme for DSSF-7 simulant and apply it to a sample of actual Hanford DSSF waste supernate. In our development work we have striven to develop a process that is robust enough to handle a variety of waste streams including other supernates, dissolved salt cake, alkaline and acidic sludge washes and leaches, and if required it should be amenable for removing technetium from the vitrification plant's off-gas aqueous scrubbing stream. The robustness of our process is already being tested; instead of receiving DSSF waste we were shipped CS-100 treated 101-SY and 103-SY supernates.

Our initial goals for the life cycle of the project were to design a technetium partitioning system using Reillex™-HPQ anion exchange resin that:

i) is selective for technetium,
ii) achieves the required separation factors (SF) under processing conditions,

iii) is sufficiently robust to caustic and acidic matrices under radiolytic conditions,
iv) interfaces with proposed IPM and pretreatment chemical separation flowsheets,
v) allows facile elution and recovery of technetium, and
vi) generates a minimum amount of secondary waste by recycling the resin and chemicals used in the separation.

In Figure 1, a technetium separation process is included as part of the LLW processing. During FY94 a new TPA was instituted that only requires a technetium separation factor (SF) of 10 for this operation to meet the performance assessment criteria of the LLW glass form.[11] Our work with Reillex™-HPQ anion resin at the bench scale has demonstrated that SF >100 are possible; thus we established a SF of 100 as our processing goal. Because of the ALARA philosophy and increasingly restrictive regulations, it is prudent to meet the technetium "Class A" (0.3 Ci/m^3, 18 g/m^3, 6000 ppb) level of compliance for waste disposal. This is an absolute level of compliance compared to the relative scale of a SF. Thus, we seek to leave < 50 ppb technetium in the LLW stream going to the melter. This absolute goal will produce a LLW glass containing 250 ppb or 0.5 g Tc/m^3. As we move our work toward a full scale process, this more rigorous level of compliance will help insure that the LLW glass meets it's performance criteria for on site storage.

FY95 Milestones: In FY95, our anion exchange work was administratively divided into two separate programs, one for simulant work and the second for actual waste experiments. The milestones for the program "Column Ion Exchange Tests for Technetium Removal from Synthetic DSSF Waste," are listed below.

1. Select column materials that are compatible with the DSSF-7 and DSS simulants.
2. Develop technetium elution, recycle, and recovery methods.
3. Determine technetium breakthrough and elution patterns at various flow rates for various Reillex™-HPQ anion exchange column sizes.
4. Determine the chemical stability of Reillex™-HPQ.

5. Further characterize the Reillex™-HPQ resin. This milestone is partially fulfilled by a journal article we submitted to "Solvent Extraction and Ion Exchange."[24] A draft copy of the paper is included in Appendix C.

The milestones for the program "Column Ion Exchange Test for Technetium Removal from Actual DSSF Waste," are listed below.

1. Measure batch K_d values for technetium between Reillex™-HPQ and actual waste.
2. Determine column sorption and elution behavior of technetium from actual waste.
3. Development feed adjustment chemistry to get technetium as pertechnetate in actual waste.
4. Determine the radiolytic stability of Reillex™-HPQ resin in the waste solution.
5. Optimize the technetium elution from Reillex™-HPQ resin after loading from the waste.

Finally, for both programs, we were to issue an annual report. This last milestone is this document.

EXPERIMENTAL

1. General

All water used in these experiments was 18-MΩ water (Millipore, Bedford, MA). Potassium perrhenate was acquired from Cleveland Refractory Metals (Solon, OH) and was used as received. Standard solutions of HNO_3 were prepared from concentrated HNO_3 (Baker) and standardized against primary standard sodium carbonate (Baker). Sodium hydroxide solutions were standardized against 0.16 or 8.00 N H_2SO_4 solutions (Hach Chemical, Ames, IA). All other reagents were analytical grade (except where noted) and obtained from either Aldrich Chemical Co., J. T. Baker, EM Science (Merck), or Mallinckrodt. Plots of data and nonlinear-least squares fits of data were done using the KaleidaGraph™ program for the Macintosh.®

2. Technetium Preparation and Assay Techniques

Lithium pertechnetate ($Li^{99}TcO_4$) was added to simulants to produce a macro technetium concentration of ≈ 5 x 10^{-5} M. The $Li^{99}TcO_4$ stock solution was metathesized from $NH_4{}^{99}TcO_4$ (Oak Ridge National Laboratory) by a procedure described previously.[20] The stock solution was 0.12 M $Li^{99}TcO_4$. A tracer technetium isotope, ^{95m}Tc ($t_{1/2}$ = 61 days), was also added to the simulant to give a concentration of < 10^{-9}M. This gamma emitting isotope was readily obtained from the Medical Radioisotopes Group in CST-11 at LANL. In order to insure that both macro and tracer technetium were in the same chemical form (i.e. TcO_4^-) before adding to the simulants, they were taken to incipient dryness separately, three times, in HNO_3, under mild heating conditions (< 200°C). Each technetium isotope was tested with a standard 60 minute batch contact experiment between either DSSF-7 or DSS simulant and Reillex™-HPQ resin; a batch K_d value 250 ± 25 mL/g with DSSF-7 simulant or 330 ± 30 mL/g with DSS simulant qualified the isotope.[20,21] The technetium isotopes were then added to the simulants and stirred for 24 hours before use.

Gamma counting of ^{95m}Tc was performed using a Packard Auto-Gamma® Model 5530 instrument (Packard Instrument Company, Downers Grove, IL). The detector is a three inch diameter thallium activated sodium iodide (NaI(Tl))

crystal that has a through-hole design. Technetium-95m decays by isomeric transition (4%), positron emission (0.4%) and electron capture with gamma emission (>95%). Seventy percent of all decay events produce a gamma photon of energy 204.2 keV.[25] These are the photons that are counted (the lower and upper limits of photon energies counted by the instrument were set as 165 and 245 keV, respectively). Counting efficiency for the 204.2 keV gamma peak of ^{95m}Tc is 45%. Samples were counted in 20 mL polyethylene scintillation vials. The number of counts-per-minute (cpm) for each sample and for several blanks (background, bkg) were recorded. Corrections for the decay of the ^{95m}Tc were automatically made by the instrument. The macro ^{99}Tc concentration does not interfere with the gamma counting of ^{95m}Tc since it decays 100% by β^- emission without producing any gamma photons. The instrument is equipped with a QA program to correct for background change and position of the calibration peak (^{137}Cs). An auto-calibration program adjusts the detector voltage to compensate for temperature and detector drift.

Liquid scintillation counting (LSC) of ^{99}Tc was performed using a Packard Model 2200 CA Tri-Carb® Liquid Scintillation Analyzer instrument, which has a counting efficiency of 98% for ^{99}Tc (β^- = 292 keV, branching ratio = 100%). The counting solution (cocktail) was prepared in 20 mL polyethylene scintillation vials by taking the desired volume (V) of the sample, (6.0 mL–V) of water, and 14.0 mL of Ultima Gold™ scintillation liquid (Packard). The cocktails were analyzed using an energy window of 0–200 keV, which encompasses >99.9% of the activity in the ^{99}Tc spectrum. The number of counts-per-minute (cpm) for each sample and for several blanks (bkg) were recorded. The net cpm of ^{99}Tc in the sample was converted to nanograms (ng) ^{99}Tc by equation (1):

$$\frac{\text{cpm } ^{99}Tc \quad + \quad 98}{37.2} = \text{ng } ^{99}Tc \qquad (1)$$

This equation was derived from a calibration curve established previously with an Amersham ^{99}Tc standard (Amersham Corporation, Arlington Heights, IL).[19] Less than 0.800 mmol of nitrate and 5 mmol of NaOH in the cocktail have no effect on the of the count rate of ^{99}Tc.[20]

3. Analytical Procedures for 101-SY and 103-SY Waste Samples

Two waste samples from tanks 101-SY and 103-SY were received at LANL this year. These samples were derived from the "101-SY Tank Comp 93D" sample and the "103-SY Whole-Tank Composite" sample, both of which had been diluted with 2 M NaOH to achieve a 5 M sodium concentration.[26] Thus, the original tank wastes were diluted by factors of 3.94 and 2.87 respectively. These dilutions formed slurries which were centrifuged to produce supernates. The supernates were passed through CS-100 columns to remove cesium. The samples sent to LANL were the first six column volume effluents from these experiments. The first column volume effluent, though, contained the void volume of 2 M NaOH from the column preparation. Thus, the supernates we received were diluted by additional 5% and have had some of the original constituents of waste removed by the CS-100 resin. Table 3 shows the activity levels of some of the constituents supplied to us by Westinghouse Hanford Company.[27]

Table 3. Activity Levels of Important Radionuclides in 101-SY and 103-SY Waste Samples.[a]

Nuclide	101-SY		103-SY	
	µCi/mL	M [b]	µCi/mL	M [b]
^{137}Cs	10	---	20	---
^{90}Sr	1.7	---	0.8	---
^{99}Tc	0.03	1.7×10^{-5}	0.06	3.5×10^{-5}
^{241}Am	0.0003	---	0.0006	---
$^{239/40}Pu$	0.00005	---	0.0001	---

[a] Data from reference 27.

[b] Calculated concentration based on the reported µCi/mL activity.

The 101-SY and 103-SY samples were analyzed by gamma counting with Ge(Li) or intrinsic Ge detectors. These counters are fully automated and the

data is processed by the *Gamanal* program. The accuracy of the counters is verified each day by calibrating the counting instrument for geometry and efficiency versus a NIST traceable standard.[28] The gamma spectra for the samples showed that ^{137}Cs was by far the dominant radionuclide in these samples.

Technetium was separated and analyzed by a method developed under the Efficient Separations and Processing Program.[29] Briefly, the method uses a ^{95m}Tc yield tracer and oxidizes the sample with Ce^{4+}/HNO_3. The sample (0.200 mL) and tracer are taken to incipient dryness at 200°C, four times, from concentrated nitric acid in the presence of ceric ion. The sample is passed through a 50W-X8 cation column and then sorbed onto Reillex™-HPQ resin. Extraneous species are removed from the resin by three 1M HNO_3 washes. Technetium is then eluted from the resin with 1 mL of 0.005 M Sn(II)/1 M NaOH/1 M en. Chemical yield is determined by gamma counting the ^{95m}Tc tracer in the sample relative to a ^{95m}Tc standard. Technetium-99 in the sample is determined by LSC. The ^{95m}Tc contribution to the sample's LSC spectrum is subtracted and the net ^{99}Tc count rate corrected for chemical yield. The ng of ^{99}Tc are obtained from equation (1).

4. ^{99}Tc NMR Spectroscopy of 101-SY and 103-SY Waste Samples

The pertechnetate concentrations in the 101-SY and 103-SY waste samples were measured using a ^{99}Tc nuclear magnetic resonance (NMR) technique developed under the Efficient Separations and Processing Program.[29] The method is currently selective for the $^{99}TcO_4^-$ anion and is able to detect it at concentrations > 8×10^{-6} M in Hanford waste matrices. The percentage of technetium that is present as pertechnetate in the waste samples was obtained by measuring the pertechnetate in 1.4 mL of the as received samples. A 0.6 mL aliquot of the as received sample was then put through the Ce^{4+}/HNO_3 oxidation and dry down steps discussed in section 3. After redissolving and determining the chemical yield, the pertechnetate NMR signal was measured.

5. Rhenium Preparation, Assay Techniques, and Batch Distribution Coefficient Measurements with Resin

Our collaborator at East Texas State University uses perrhenate (1.00-10.0 mM) as a surrogate for pertechnetate. The procedures used are described fully in the attached journal article (Appendix C) which has been accepted for publication in "Solvent Extraction and Ion Exchange."

6. Simulant Preparation and Characterization

DSSF-7 simulant (7.0 M Na^+) containing 5 x 10^{-5} M $Li^{99}TcO_4$ was prepared and its composition is shown in Table 4. This simulant mimics the waste in tank 101-AW or 105-AP.[30] The technetium concentration is slightly higher than the characterization data for tank 105-AP.[31] The appropriate weights of the reagents in the table were added to water in the sequence listed. Complete dissolution of each reagent was obtained prior to adding the next reagent. The simulant after preparation is a clear, slightly yellow solution, which yields a small amount of white precipitate upon cooling. Technetium-95m was added to give ~6000 cpm/4 mL. Reillex™-HPQ resin batch contact experiments were performed with the filtrate from the filtered DSSF-7 Simulant.

DSSF-5 simulant (5.0 M Na^+) was prepared from the filtered DSSF-7 simulant. A 1.00:1.40 dilution was performed by diluting 5.00 L of DSSF-7 simulant with 2.00 L of water. The proper amount of $Li^{99}TcO_4$ was added to give a macro concentration of 3.5 x 10^{-5} M. Technetium-95m was added to give ~6000 cpm/4 mL. Other dilutions of DSSF-7, 1:6 and 1:2, were made in a similar fashion; the $Li^{99}TcO_4$ concentration was adjusted accordingly.

Chromate free DSS simulants were prepared by the procedure described in LA-UR-93-4092.[19] This simulant mimics the waste in tank 241-AN-106.[32] The supernatant from centrifuging the DSS Simulant was used for batch contact and column experiments and contained 5 x 10^{-5} M $Li^{99}TcO_4$ and enough ^{95m}Tc activity to give ~6000 cpm/4 mL.

Table 4. Double-Shell Slurry Feed (DSSF-7) Simulant Formulation.

Material	Source	Grade	Molarity
$NaNO_3$	Baker	Reagent	1.162
KNO_3	Baker	Reagent	0.196
KOH	Baker	Reagent	0.749
$CsNO_3$	Baker	Reagent	7.0×10^{-5}
Na_2SO_4	Baker	Reagent	0.008
$Na_2HPO_4 \cdot 7H_2O$	Baker	Reagent	0.014
NaOH	Baker	Reagent	3.885
$Al(NO_3)_3 \cdot 9H_2O$	EM	Technical	0.721
Na_2CO_3	Baker	Reagent	0.147
NaCl	EM	Reagent	0.102
$NaNO_2$	Baker	Reagent	1.512
$Li^{99}TcO_4$	ORNL[a]	-------	5.0×10^{-5}
^{95m}Tc	LANL	-------	$<10^{-9}$

[a] $LiTcO_4$ derived from ORNL NH_4TcO_4; see ref. 20.

One liter batches of 101-SY and 103-SY simulants were prepared to approximate the waste samples sent to Los Alamos. The formulations of the 101-SY and 103-SY simulants are based on the analyses made of the actual waste supernates (Tables 5 and 6) prior to passing them through the CS-100 columns.[26] They were prepared by adding the appropriate weights of the reagents in Tables 5 and 6 to 500 mL of water. The solutions were brought to 900 mL after all of the reagents were added and stirred for four hours while being heated on the hot plate at 60°C. The solutions were stirred overnight at room temperature and filtered to remove a small amount of insoluble crystalline material. The proper amounts of $Li^{99}TcO_4$ were added to give each simulant a macro concentration of 3.5×10^{-5} M. Technetium-95m was added to each to give ~6000 cpm/4 mL.

Table 5. 101-SY Simulant Formulation.

Element	g/L	Molarity[a]	Reagent	g
Na	119	5.26320	NaOH	141.65
Si	0.133	0.00468	SiO_2	0.2813
Al	15.4	0.54852	$NaAlO_2 \cdot 2H_2O$	64.709
Cu	0.0052	0.00007	$CuCl_2 \cdot 2H_2O$	0.0123
N	0.066	0.00109	$NiSO_4 \cdot 6H_2O$	0.2866
Ca	0.061	0.00142	$Ca(NO_3)_2 \cdot 4H_2O$	0.3359
Cr	0.05	0.00128	K_2CrO_4	0.2483
P	1.2	0.02250	---	---
S	0.738	0.02233	---	---
Mo	0.045	0.00045	Na_2MoO_4	0.0923
B	0.032	0.00282	$B(OH)_3$	0.1744
K	1.44	0.03555	KNO_3	3.3361
Cl^-	3.51	0.09886	NaCl	5.7691
NO_3^-	57.4	0.88541	$NaNO_3$	71.988
PO_4^{3-}	2.33	0.03017	$Na_2HPO_4 \cdot 7H_2O$	8.0869
SO_4^{2-}	1.76	0.01785	Na_2SO_4	2.3810
$C_2O_4^{2-}$	0.54	0.00668	$H_2C_2O_4 \cdot 2H_2O$	0.8422
TIC (CO_3^{2-})	2.69	0.04599	Na_2CO_3	4.8748

[a]Average molarity in the supernate derived from the "101-SY Tank Comp 93D" sample, reference 26.

One hundred milliliter portions of the 101-SY and 103-SY simulants were adjusted to have 4.27 g/L and 2.8 g/L total organic reagents to mimic the TOC content of the actual waste samples.[26] Since oxalate was already present in the simulants, we added equal weights (0.62 g/L and 0.30 g/L, respectively) of tetrasodium ethylenediaminetetraacetate (Na_4EDTA), sodium gluconate, sodium formate, trisodium nitrilotriacetate (Na_3NTA), sodium citrate, and trisodium (*N*-2-hydroxyethyl)ethylenediaminetriacetate ($Na_3HEEDTA$) to the 101-SY and 103-SY simulants.

Table 6. 103-SY Simulant Formulation.

Element	g/L	Molarity [a]	Reagent	g
Na	138.5	6.0244	NaOH	157.366
Si	0.0810	0.0029	SiO_2	0.17330
Al	16.8	0.6227	$NaAlO_2 \cdot 2H_2O$	73.4539
Cu	---	---	---	---
Ni	0.019	0.0003	$NiSO_4 \cdot 6H_2O$	0.08508
Ca	---	---	---	---
Cr	0.043	0.0008	K_2CrO_4	0.16060
P	1.525	0.0492	---	---
S	0.8285	0.0086	---	---
Mo	0.054	0.0034	Na_2MoO_4	0.7079
B	0.0395	0.0024	$B(OH)_3$	0.1463
K	1.605	0.0411	KNO_3	3.9834
Cl^-	4.13	0.1165	NaCl	6.8078
NO_3^-	70.05	1.1298	$NaNO_3$	92.5285
PO_4^{3-}	3.395	0.0358	$Na_2HPO_4 \cdot 7H_2O$	9.5829
SO_4^{2-}	2.175	0.0226	Na_2SO_4	3.1701
$C_2O_4^{2-}$	1.1	0.012	$H_2C_2O_4 \cdot 2H_2O$	1.5755
TIC (CO_3^{2-})	2.925	0.0487	Na_2CO_3	5.1662

[a] Average molarity in the supernate derived from the "103-SY Whole-Tank Composite" sample, reference 26.

The simulants were characterized by some of the qualification methods (density, percentage water, and [OH^-] titer) described previously.[21] Table 7 compares the composite characterization data for the DSSF tank AP-105 with the analytical data for the DSSF-7 simulant batches A through E. Table 8 compares the composite characterization data for tank 241-AN-106 with the analytical data for DSS simulant batches 11 through 16. Table 9 gives the characterization data for DSSF-5, 101-SY, and 103-SY simulants. The percentage of technetium retained by the solid phase was determined by gamma counting a known volume of simulant, centrifuging it, washing the solid phase three times with supernate from a technetium-free simulant, and counting

Table 7. Characterization Data for DSSF-7 Simulants.

	DSSF-7[a]	A	B	C	D	E
Density (23°C)	1.333	1.355[b]	1.346	1.342	1.353	1.359
Water (%)	60.3	57.4[b]	58.3	58.5	57.7	58.0
[OH^-] Titer	1.75[c]	1.167[b]	1.146	1.146	---	---
Tc Activity (Solid phase, %)	---	nd	nd	nd	---	---
% Solids (by volume)	<1	<1	<1	<1	<1	<1
% Solids (by weight)	<1	<1	<1	<1	<1	<1

[a] DSSF Tank AP-105 characterization data from reference 31.

[b] Density and % water measurements were made on uncentrifuged simulant solution; [OH^-] titer measurements were made on the centrifuged simulant supernate solution.

[c] Free OH^- titer for PNL prepared DSSF-7 simulant.

Table 8. Characterization Data for DSS Simulants 11 through 16.

	DSS[a]	11	12[b]	13[b]	14[b]	15[b]	16[b]
Density (23°C)	1.223	1.264	1.261	1.230	1.215	1.231	1.232
Water (%)	67	71	---	---	---	---	---
[OH^-] Titer	0.68	0.73	---	0.62	0.55	0.62	0.67
Technetium Activity (Solid phase, %)	---	0.24	---	---	----	---	---
Solids (by volume, %)	17	7.86	5.2	7.0	8.6	7.4	5.0
Solids (by weight, %)	---	6.45	---	---	---	6.5	---

[a] DSS composite values from reference 32.

[b] Density and [OH^-] titer measurements were made on the centrifuged simulant supernate solution.

Table 9. Characterization Data for the DSSF-5, 101-SY and 103-SY Simulants.

	DSSF-5	101-SY	103-SY
density, g/mL	1.266	1.234	1.257
free [OH^-], M	1.13	3.50	3.88

the solid phase; $[(cpm)_{solid} \times 100]/(cpm)_{simulant}$ = % Tc in the solid. The weight percent solids were determined from the corresponding weights of the uncentrifuged simulant and the solid phase; $[(g)_{solid} \times 100]/(g)_{simulant}$ = % solids by wt. In a similar manner, the volume percent solids were determined by comparing the height of the solid phase in the centrifuge tube after the simulant was centrifuged to the total height of the simulant in the tube.

7. Preparation of Anion Exchange Resins

Table 10 summarizes the characteristics of the anion exchange resins evaluated. All Reillex™-HPQ and N-alkyl-HP type anion exchange resins were acquired from Reilly Industries (Indianapolis, IN) as 30–60 mesh resins in the chloride form. They are all co-polymers of divinylbenzene and 4-vinylpyridine and, except for Reillex™-HP, are macroporous strong base anion exchange resins. Reillex™-HPQ is ~25% cross-linked and 70% methylated at the pyridine nitrogen to give pyridinium anionic sites. The total exchange capacity provided by the manufacturer is 4.6 meq/g (dry) and 1.2 meq/mL (wet). Based on the % alkylation, the exchange capacity in basic solution would be 3.3 meq/g (dry) and 0.9 meq/mL (wet). Reillex™-HP is the unalkylated form of Reillex™-HPQ and is obtained in the chloride form. Its exchange capacity is 5.5 meq/g (dry) and 1.6 meq/mL (wet).

Reillex™-HPQ-4632-15 is 25% cross-linked and 85% methylated. The total exchange capacity is 4.2 meq Cl^-/g (dry); 1.2 meq Cl^-/mL (wet). Reillex™-HPQ-4632-17 is 18% cross-linked and 90% methylated. The total exchange capacity is 4.85 meq Cl^-/g (dry); 1.14 meq Cl^-/mL (wet).

Table 10. Anion Exchange Resins.

Resin	Exchange Capacity meq/g (dry)	Exchange Capacity meq/mL (wet)	Mesh Size	Cross Linking	Density g/mL	Quaternization
Reillex™-HPQ	4.6	1.2	30-60	25%	0.70	70%
Reillex™-HP	5.5	1.6	30-60	25%	0.70	-----
Reillex™-HPQ-4632-15	4.2	1.2	30-60	25%	0.70	85%
Reillex™-HPQ-4632-17	4.85	1.14	30-60	18%	0.70	90%
N-Butyl-HP (43)	2.22 [a]	-----	30-60	25%	0.70	43%
N-Butyl-HP (89)	3.75 [a]	-----	30-60	25%	0.70	89%
N-Hexyl-HP	2.15 [a]	-----	30-60	25%	0.70	45%
N-Octyl-HP	2.44 [a]	-----	30-60	25%	0.70	59%
Amberlite IRA-900	4.2	1.0	16-50	20-25% [b]	0.67	100%
Amberlite IRA-904	-----	0.7	20-50	20-25% [b]	0.67	100%
Amberlyst A-26	4.1-4.4	0.95-1.1	-----	20-25% [b]	-----	100%
Bio-Rad AG 1-X8 (Dowex type)	3.2	1.4	50-100	8%	0.7	100%
Bio-Rad AG®MP-1 (Dowex type)	4.2	1.2	50-100	20-25% [b]	0.7	100%
Ionac™SR-6	1.8	0.8	-----	20-25% [b]	0.64	100%
Purolite™A-520E	2.8	0.9	16-50	20-25% [b]	0.68	100%

[a] Strong base capacity

[b] No specific information available, but resin is described in literature as macroporous or macroreticular.

There are two different N-Butyl-HP Reillex™ resins. N-Butyl-HP (43) is 25% cross-linked and 43% quaternized with n-butyl groups. The exchange capacity is 2.22 meq/g (dry). N-Butyl-HP (89) is 25% cross-linked and 89% quaternized with n-butyl groups. The exchange capacity is 3.75 meq/g (dry). N-Hexyl-HP is 25% cross-linked and 45% quaternized with n-hexyl groups. The exchange capacity is 2.15 meq/g (dry). N-Octyl-HP is 25% cross-linked and 59% quaternized with n-octyl groups. The exchange capacity is 2.44 meq/g (dry).

The following strong base anion exchange resins are co-polymers of styrene and divinylbenzene containing quaternary amine (methyl groups except where noted) functional groups. They were obtained in the chloride form.

Amberlite IRA-900, Amberlite IRA-904, and Amberlyst A-26 were obtained from Rohm & Haas (Philadelphia, PA) and are macroreticular resins. Amberlite IRA-900, 16-50 mesh, has an exchange capacity of 4.2 meq/g (dry); 1 meq/mL (wet). Amberlite IRA-904, 20-50 mesh, has an exchange capacity of 0.7 meq/mL (wet). (Note: the 904 resin is being discontinued). Amberlyst A-26 has an exchange capacity of 4.1-4.4 meq/g (dry) and 0.95-1.1 meq/mL (wet).

Dowex-1 and AG MP-1 were obtained from Bio-Rad (Hercules, CA). Dowex-1 is a gel-type resin, mesh 50-100, with a total capacity of 3.2 meq/dry gram. AGMP-1 is a macroreticular resin, 50-100 mesh, with a total capacity of 4.2 meq/g (dry).

Ionac™ SR-6 was obtained from Sybron Chemicals, Inc. (Birmingham, NJ). It is a macroporous resin with tributylamine functional groups. The exchange capacity is 1.8 meq/g (dry) and 0.8 meq/mL (wet).

Purolite™ A-520E was obtained from the Purolite Company (Bala Cynwyd, PA). It is a macroporous resin, 16-50 mesh, with triethylamine functional groups. The total exchange capacity is 2.8 meq/g (dry) and 0.9 meq/mL (wet).

The resins were prepared in two different ways.[33] Resin prepared by the first method is called *acid washed resin.* Resin (~2 liters) was added to a 4-L beaker. One bed volume (BV) of 18 MΩ water was added and stirred with a stir rod (a magnetic stirrer will grind the resin) to completely suspend the resin.

After settling, the water and any floating resin beads were decanted. This washing procedure was repeated four times. The resins were transferred to a medium porosity sintered glass funnel/vacuum filter flask attached to a low vacuum source and then converted to various anionic forms.

Nitrate form: Resins were converted to the nitrate form by passing 20 bed volumes of 1.0 M HNO_3 through the resin; the effluent was monitored for the presence of Cl^- with a $AgNO_3$ solution. After conversion, the resin was washed with 20 bed volumes of water. Large quantities of resin were then stored in water. Smaller quantities of the resin were drained of free water while connected to the low vacuum source, then the damp resin was transferred to capped sample bottles. Resin used for experiments on a dry weight basis was dried at 60°C for 48 hours and kept in a desiccator over silica gel until ready for use. The dry Reillex™-HPQ nitrate form resin swells when placed in water. The conversion factor between grams of dry resin and bed volume (mL) of wet resin is 3.00 mL/g. Some studies used the undried resin but reported the results on a dry weight basis. For these types of experiments the moisture cor 'ent of the resin was determined from a separate sample of the resin by drying it at 60°C for 48 hours. While this sample was drying, resin samples for K_d measurements or stability studies were run.

Hydroxide form: The hydroxide form of the resin was obtained by making a column of the Reillex™-HPQ nitrate form and passing ten bed volumes of 1 M NaOH through the column, washing with > 10 column volumes of water until neutral and air drying the resin to constant weight. Note: drying the hydroxide form at 60°C may decompose the resin.

Chloride form: Even though Reillex™-HPQ is received in the chloride form, it was cleaned and "converted" to the chloride form by eluting with 10 bed volumes of 10.0 M HCl and then 20 bed volumes of water. This treatment also insured protonation of the un-methylated pyridine sites. The resins were dried in an oven at 60°C for 24 hours, cooled and stored in a desiccator. The chloride form of the resin was used to measure the total exchange capacity by a potentiometric titration with silver nitrate.[33] The capacity is 3.50 ± 0.14 meq/gram dry resin.

Resin prepared by the second method is called *cycled resins.* The procedure is the same through the vacuum filtration step. Then the following washing procedure was performed five times.

i. One BV of 2.0 M HNO_3 was added to the resin and stirred until the resin was completely suspended. Then the resin was vacuum filtered.

ii. One BV of water was added to the resin and stirred until the resin was completely suspended. Then the resin was vacuum filtered

iii. One BV of 2.0 M NaOH was added to the resin and stirred until the resin was completely suspended. Then the resin was vacuum filtered.

iv. One BV of water was added to the resin and stirred until the resin was completely suspended. Then the resin was vacuum filtered.

Following five cycles of these washings, steps I and ii were repeated. The resin was then transferred to a container and stored in 0.20 M HNO_3. Before use, the resin was washed with 5 BV of water and either used at this point, or else dried to constant mass at 60°C for 48 hours and stored over silica gel. The above procedure converts the resin to the nitrate form. Conversion to the chloride form is the same, but HCl is used instead of HNO_3.

8. Resin Stability Studies

Base Stability Determination: The experimental procedures for this study can be found in our collaborator's (Professor Kenneth Ashley) annual report.[33] The base stability of Reillex™-HPQ and Reillex™-HP were determined at 25 and 50°C. Briefly, the method involved placing weight amount of the nitrate form of the resins into 2 M NaOH at the desired temperature. Samples were removed at prescribed intervals and the chloride capacity determined. The capacity of this sample was compared to the well determined capacity of the resin without the NaOH treatment.

The total chloride capacity of the resin was determined by transferring the resin to a small chromatography column, rinsing with 10 mL of water, and converting to the chloride form by eluting with 150 mL of 2.0 M HCl. The resin was then washed with 5 mL of water then the chloride remaining on the resin was eluted with 50 mL of 1.0 M Na_2SO_4. The sulfate eluent was titrated for chloride

potentiometrically (Ag/AgCl versus saturated calomel electrode system) with a standard silver nitrate solution to an endpoint potential of 285 ± 10 mv.

The strong base capacity of the resin was determined by selectively converting the strong base sites to the chloride form by elution with two 10 mL portions of 0.1 M NH_4OH / 0.9 M NH_4Cl. At the end of the first elution, a few drops of the eluent were tested for the presence of sulfate ion with 0.1 M barium nitrate. No precipitate developed. The second elution was performed to ensure that no sulfate was present. The resin was then washed with two 10 mL portions of deionized water. After the first washing, the eluent was tested for presence of chloride with 0.1 M $AgNO_3$. No precipitate developed. The second elution was performed to ensure that no chloride was present. The chloride remaining on the strong base sites was eluted with 50 mL of 1.0 M Na_2SO_4. The sulfate elution was titrated as before. The difference in the total chloride capacity and the strong base capacity was defined as the weak base capacity.

Peroxide Evaluation Test: All the resin in Table 10, in their nitrate form, were tested by contacting a 0.5 g sample of dry resin with 100 mL of 5% H_2O_2 for 16 hours at 30°C. Technetium batch K_d measurements were made on each resin sample before and after the peroxide treatment.

9. Technetium Batch Distribution Coefficients with Reillex™-HPQ Resin

A weighed portion of resin was placed into a polyethylene vial (caps with polypropylene liners were used) with the desired amount of solution; the solution-to-resin ratio was usually 10:1 (5.00 mL : 0.5000 g). The sample was then contacted for the desired length of time using a Burrell Wrist-Action Shaker at ≈ 25°C or a Lab-Line Constant Temperature Shaker Bath at the desired temperature. At the end of the contact period, the resin/solution sample was poured into a Bio-Rad Econo-Column and the filtrate collected. Appropriate aliquots (4.00 mL) of the filtrate and the initial solution were analyzed by NaI or LS counting.

10. Technetium Stripping Reagent

The stripping eluent was a solution containing tin(II) chloride hemihydrate ($SnCl_2 \cdot 0.5H_2O$) or tin(II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$), ethylenediamine (en, $C_2H_8N_2$), and sodium hydroxide (NaOH). The en and NaOH were 1.0 M and the $SnCl_2$ was usually 0.005 M. The NaOH pellets, $SnCl_2$ crystals, and en liquid were added to 700 mL of N_2-purged water in a 1000 mL volumetric flask. Then the solution was diluted to the mark with N_2-purged water. A piece of mossy tin and a stirring bar were added and the solution stirred on a magnetic stirrer.

11. Resin Shrinking Experiments

Columns, 1 x 35 cm, were slurry packed with Reillex™-HPQ resin. The height of the resin bed was measured initially and then remeasured after the resin bed sat in various mixtures of NaOH and $NaNO_3$ and various dilutions of DSSF simulant. Each column was pretreated with 3 bed volumes of 1 M NaOH, which caused a shrinkage of 0.4 cm in every case. One column was allowed to sit in water to serve as a reference. No resin shrinking was observed with this column. Results of these experiments are summarized in Table 11. The mixtures of nitrate and hydroxide provided a reasonable trend. For this reason we decided to use a 6 M $NaNO_3$/2 M NaOH mixture as our shrinking solution; this solution is near the limit of solubility for this mixture.

12. Large Column (2.54 x 50 cm) Experiments

Chromaflex™ brand (Kontes, Vineland, NJ) chromatography columns and accessories were used for these experiments. The columns were 2.54 x 60 cm (1 x 24") size with a clear plastic safety/water jacket. The columns were connected to Masterflex (Cole-Parmer) peristaltic pumps. All tubing and fittings were PTFE. The two- and three-way valves were aluminum housing with PTFE plugs. The tubing arrangement was such that a solution could be pumped into the top (downflow) or the bottom (upflow) of the column. The column set-up is shown in Figure 4.

Table 11. Resin Shrinkage in Various Solutions.

Column	Solution	Decrease[a]
1	DSSF-7	-2.2 cm
2	DSSF-5	-1.4 cm
3	DSSF-3.5[b]	-1.5 cm
4	DSSF-2[c]	-1.4 cm
5	DSSF-1[d]	-1.2 cm
6	2 M $Al(NO_3)_3$	-0.4 cm
7	5 M $NaNO_3$	-0.4 cm
8	1 M $NaNO_3$ 1 M NaOH	-0.9 cm
9	2 M $NaNO_3$ 2 M NaOH	-1.2 cm
10	5 M $NaNO_3$ 2 M NaOH	-1.9 cm
11	5 M $NaNO_3$ 2 M NaOH	-1.5 cm

[a] Shrinkage relative to Reillex™-HPQ resin in water.
[b] 1->2 dilution of DSSF-7.
[c] 1->3 dilution of DSSF-7.
[d] 1->6 dilution of DSSF-7.

A water slurry of 300 mL of Reillex™-HPQ resin in the nitrate form was vacuum filtered. The resin was transferred to a 1-L beaker and 300 mL of shrinking solution (6.0 M $NaNO_3$ and 2.0 M NaOH) were added. The resin was vacuum filtered, washed with 300 mL of water, and then washed into a 500 mL graduated cylinder. The resin volume had not changed; it was still 300 mL.

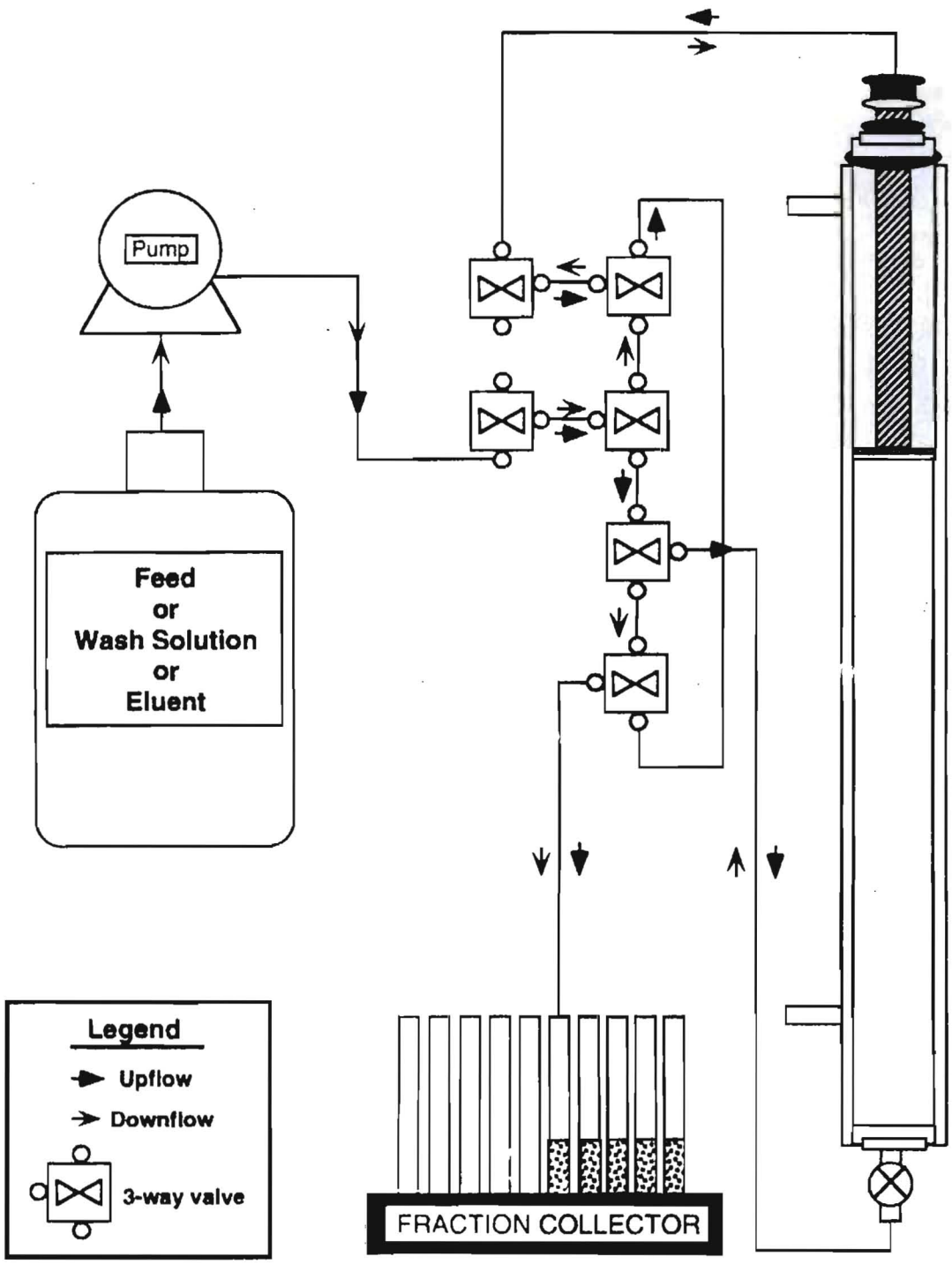


Figure 4. Experimental Column Set-up for Sustainability and Flow Studies.

Approximately 257 mL of treated Reillex™-HPQ resin were added to the column as a water slurry. After the resin had settled, it was backwashed with water. A packing reservoir attached to the top of the column was used to ensure enough volume for the resin and backwash liquid. The resin was well classified using this procedure. After the resin had settled, a flow adapter was placed in the column and adjusted so that there was no space between it and the top of the resin bed. Approximately two bed volumes (500 mL) of shrinking solution were then pumped through the column. After the resin shrank, the flow adapter was readjusted to fit against the top of the resin.

DSSF-5 simulant (1:1.4 dilution of DSSF-7) containing pertechnetate was pumped through the column. The usual procedure was to collect 240 mL in a 250 mL graduated cylinder. Then 10 mL was collected in a 10 mL graduated cylinder. Of this 10 mL, 4.00 mL were taken and counted. Occasionally, another method was used which collected a desired volume, mixed it , and then 4.00 mL were withdrawn for counting. The simulant was pumped through the column until the desired percent breakthrough had been achieved.

The column was then eluted. This part of the process differed from run to run, but always used an upflow elution of a solution comprised of 1.00 M NaOH, 1.00 M en, and $SnCl_2$. It should be noted that only BT-1 used 0.010 M $SnCl_2$ in the eluent solution, all the rest had 0.005 M $SnCl_2$. From each fraction, 4.00 mL were taken and counted. During some of the elutions, the activity of the column at various distances from the bottom of the column was measured with an hand held gamma counter. A 1/4" thick steel plate with an 1/4" hole drilled into its center was attached to the pancake detector in order to get a semi-quantitative reading from the region of the column of interest.

Repetitive or sustainability studies (BT-1 to BT-11) used the same resin bed for eleven cycles of loading and elution. The resin bed was not disturbed in any way in the initial six experiments. After the sixth and seventh experiment, BT-6 and BT-7, the resin bed needed to be reclassified with a backflow of water and then treated with several bed volumes of shrinking solution before placing the column back into service for the remaining four runs.

In the cases of the flow studies (F-1 to F-8), a new bed of resin was prepared for each experiment. F-7 and F-8 were intended to be full breakthrough experiments. Reillex™-HPQ was used in F-7 and Dowex™ AG MP-1 was used in F-8. The final breakthrough was 90% in both experiments.

13. Technetium K_d Values for 101-SY and 103-SY Samples

A weighed portion of resin, 0.2000 g, was placed into a polyethylene vial with 2.000 mL of the 101-SY or 103-SY waste solution. The sample was then contacted for 2 hours using a Burrell Wrist-Action Shaker at ≈ 25°C. At the end of the contact period, the resin/solution sample was poured into a Bio-Rad Econo-Column and the filtrate collected. A 0.200 mL aliquot of the filtrate and the original waste solution were analyzed by the method described in section 3. Smaller batch contact samples were treated in an analogous manner and always used a 10:1 ratio of sample:resin. Resin stability was measured by placing 0.2000 g of resin in 2.000 mL of waste solution and letting it sit in a sealed container for at least a month before doing the analytical work.

14. Oxidants of 103-SY Waste: Feed Adjustment Chemistry

Oxidation of the 103-SY solution was attempted with several oxidants. The amount of oxidant added to each sample was determined by the amount of 0.1 M $(NH_4)_2Ce(NO_3)_6$ required to maintain the ceric color in the analytical procedure described in section 3 above. This amount of ceric required for a 0.200 mL sample of 103-SY was 0.06 mmoles. An equivalent amount of each oxidant, plus 10% excess, was added to the waste sample for these experiments; the amounts were however prorated for the 2 mL of 103-SY waste used in this study.

The oxidants used for the first experiment were 0.14 mg $NaBrO_3$ (Allied Chemical, N.Y.), 0.031 mL of 30% H_2O_2 and 0.550 mL NaOCl. A fourth sample, a control, had no oxidant added. The $NaBrO_3$ and NaOCl samples were allowed to sit for 1 hour at ambient temperature. The H_2O_2 sample was placed in a water bath at 40°C for 1 hour. Each solution was then contacted for 2 hours with 0.2000g of Reillex™-HPQ resin using a wrist shaker. After phase

separation, the analytical procedure was performed on a 0.200 mL aliquot of each sample.

A second experiment was done using only NaOCl. Again, four 2 mL samples of 103-SY were taken. One and two had 0.550 and 1.100 mL of NaOCl, respectively, added to them. These sat for 1 hour @ ambient temperature. The third and fourth samples each had 0.550 mL of NaOCl added to them. These samples sat for 3 and 18 hours, respectively, @ ambient temperature. All samples were treated as described in the previously.

RESULTS AND DISCUSSION

1. Technetium Counting

Technetium partitioning schemes are being developed for the Hanford TWRS program for treating the DSSF waste tanks AP-105 and AW-101 and the DSS waste tank 241-AN-106. The average ^{99}Tc activities in these waste types are 69.8 μCi/L and 84.7 μCi/L, respectively.[31,32] These activities translate to the respective ^{99}Tc concentrations of 4.2×10^{-5} M and 4.92×10^{-5} M. In FY95 we received our first samples of Hanford waste. These solutions originated from tanks 101-SY and 103-SY but were diluted by factors of approximately 4 and 3, respectively, before we obtained them. The reported ^{99}Tc concentrations in these solutions were 1.7×10^{-5} M and 3.5×10^{-5} M. However, our analyses (vide infra) gave 5.9×10^{-5} M and 6.7×10^{-5} M, respectively. Based on the above information, we have set the ^{99}Tc concentration in the DSSF-7 and DSS simulants at 5×10^{-5} M using [$Li^{99}TcO_4$]. Dilutions of DSSF-7 had their ^{99}Tc concentration adjusted accordingly. Thus, the DSSF-5 simulant had a ^{99}Tc concentration of 3.5×10^{-5} M. Because of the uncertainty in the ^{99}Tc concentration in the real waste samples we have formulated our 101-SY and 103-SY simulants to also have 3.5×10^{-5} M [$Li^{99}TcO_4$].

Technetium-99 is a pure beta emitter with a half-life of 2.13×10^5 years and can be analyzed by liquid scintillation counting (LSC). The problem with LSC is that sample cocktail solutions need to be prepared with water and an organic scintillant. For a large number of samples this can be labor intensive, expensive, and require a significant amount of time to obtain reliable data. In addition, LSC produces a mixed waste stream that can be difficult and expensive to dispose of. For these reasons the analytical method for determining the technetium concentration in most of our samples was changed.

We are fortunate at LANL, and particularly, in CST-11, to have the medical radioisotopes group located adjacent to our laboratories. They routinely irradiate molybdenum targets with 800 MeV protons at the Los Alamos Meson Physics Facility. The spallation reactions produced in this target generate many isotopes including the gamma emitting technetium isotope, ^{95m}Tc. This isotope is separated from the dissolved target as a by-product of the medical isotope

production business; it is for sale and is the only significant source of the tracer in the United States.[34] Their proximity allows CST-11 to obtain the material at a reduced cost, with minimal administrative requirements. In addition, there has been a symbiotic relationship between our work and theirs. They are presently using Reillex™-HPQ in their anion exchange columns to effect the ^{95m}Tc separation from caustic molybdenum solutions.

Adding ^{95m}Tc tracer to simulant solutions containing a macro concentration of ^{99}Tc is a great advantage to this program because it allows samples to be gamma counted (204 keV). This technique is at least three times faster than LSC. This technetium tracer also allows solid phases to be counted, an option that was not possible using LSC. Because there are two technetium sources in the solutions being studied, it is imperative that the technetium isotopes be in the same oxidation state before adding them to the working solution, and that both technetium sources equilibrate with each other before performing experiments. These precautions are taken by first drying each of the isotopes down in HNO_3 three times and independently evaluating their K_d value between Reillex™-HPQ and DSSF-7 or DSS simulant. A technetium source that achieved a 1 hour K_d value of 250 ± 25 mL/g with DSSF-7 simulant or 330 ± 30 mL/g with DSS simulant qualified to be added to the working solution.[20,21] The isotopes were allowed to equilibrate in the solution for 24 hours before starting an experiment.

2. Simulants

Only chromate free DSS simulants were used in FY95. This mixed waste issue was discussed in last year's annual.[21] We have previously shown that chromate does not sorb onto Reillex™-HPQ resin to a significant extent in caustic media; K_d values were less than 6.0 in 1 M NaOH.[20] Experiments done with chromate deficient DSS simulant should not detract from the validity of the results. It is interesting that the recipe (Table 4) for preparing the DSSF-7 simulant does not contain any chromium even though the DSSF waste tank AP-105 contains 2.7×10^{-3} M CrO_4^{2-}.[31] However, we do feel that some larger column experiments will have to be run in the future to make sure that chromium is not a factor with long exposure to the resin. The concern with chromate under basic conditions is that it could oxidize the pyridinium functionality of the

Reillex™-HPQ resin to a pyridone.[35] It should also be noted that ferricyanide is a common oxidant used for the pyridone reaction. This oxidant is a component of Hanford waste. Clearly, further chemical stability studies on Reillex™-HPQ resin need to be made; work in this area was performed in FY95.

Characterization data for the DSSF-7 simulants 7A-E (Table 7) had a free OH^- titer of ≈1.15 M, significantly lower than the 1.67 M obtained by PNL for their DSSF-7 simulant.[30] The discrepancy between the results appears to be the result of substituting NaOH for some of the $NaNO_3$ in the PNL preparation. Other results for 7A-E are consistent with AP-105 characterization data. The data for the DSS simulants (Table 8) prepared in FY95 were similar to those prepared in prior years and were consistent with the actual characterization data for tank 241-AN-106. The high free hydroxide values (≈3.8 M, Table 9) for the 101-SY and 103-SY simulants are higher than the expected actual waste values of ≈2.0 M. Our higher values are due to formulating these simulants with NaOH to set the sodium concentration. The DSSF-5, 101-SY, and 103-SY simulants have densities similar to the DSS, ≈1.24 g/mL. We experienced problems (vide infra) running columns with the DSSF-7 simulant which has a density of 1.35 g/mL. Because the DSS and DSSF-5 performed well in column studies, the density of a waste stream may give the first indication as to whether it is amenable to processing by anion exchange without dilution.

Table 12 compares the molar concentrations of ions in the 5 waste simulants. The DSSF simulants are the most simple, being composed only of simple inorganic salts. The DSS has only one organic complexant while the SY simulants have transition metal salts and an oxalate complexant. Unless a technetium reductant is added, these complexants probably will have little effect on the sorption of technetium. On the other hand, the nitrate anion competes strongly against TcO_4^- for the Reillex™-HPQ resin's active site; thus the technetium K_d values should increase in the order DSSF-7 < DSSF-5 < DSS <103-SY < 101-SY.

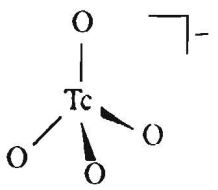
3. Justification for Using Rhenium as a Surrogate for Technetium

We are collaborating with Professor Kenneth Ashley from East Texas State University (ETSU) to develop certain aspects of this technetium partitioning

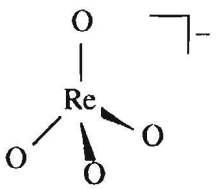
Table 12. Simulant Comparisons.

Species	DSS	DSSF-7	DSSF-5	101-SY	103-SY
Na^+	4.400	6.999	4.999	5.263	6.024
NO_3^-	1.498	3.521	2.515	0.885	1.130
Al^{3+}	0.486	0.721	0.515	0.548	0.623
K^+	0.014	0.945	0.675	0.036	0.041
OH^-	1.269	4.634	3.310	3.50	3.88
NO_2^-	0.857	1.512	1.080	-------	-------
CO_3^{-2}	0.385	0.147	-------	-------	-------
PO_4^{3-}	0.114	0.014	0.010	0.030	0.036
Cl^-	0.093	0.102	0.073	0.099	0.117
F^-	0.080	-------	-------	-------	-------
Ca^{2+}	0.002	-------	-------	0.001	0.001
Citrate	0.073	-------	-------	-------	-------
$C_2O_4^{2-}$	-------	-------	-------	0.067	0.012
SO_4^{2-}	0.031	0.008	0.006	0.022	0.023
CrO_4^{2-}	0.014	-------	-------	0.001	0.001
MoO_4^{2-}	-------	-------	-------	0.0005	0.003
Si	-------	-------	-------	0.005	0.003
TIC	-------	-------	-------	0.046	0.049
$Li^{99}TcO_4$	5×10^{-5}	5×10^{-5}	3.5×10^{-5}	3.5×10^{-5}	3.5×10^{-5}
^{95m}Tc	$< 10^{-9}$	$< 10^{-9}$	$< 10^{-9}$	$< 10^{-9}$	$< 10^{-9}$
Density	1.24	1.35	1.27	1.23	1.26
Ionic Strength (μ)	6.2	12.4	8.5	7.7	8.6

project. This collaboration increases the efficiency and reduces the cost of doing research for the TWRS program. Dr. Ashley has his own contingent of students who help with the research. While at their home campus, they are not allowed to work with radioactive materials such as technetium (there are no non-radioactive isotopes of this element). Thus, they are required to substitute rhenium for technetium. In the summer, Dr. Ashley is an affiliate researcher at LANL and is able to apply his research to technetium. It is important to establish the basis for substituting rhenium for technetium in order not to waste time and money developing a process that can not be applied to real technetium problems. Scenarios for processing nuclear waste streams generally assume that technetium will be present as pertechnetate (TcO_4^-) or that it can be set in that state. As TcO_4^-, it can be separated from waste streams by methods that rely on an ion pairing mechanism. Perrhenate (ReO_4^-) can be used as a chemical surrogate for pertechnetate when this mechanism is operable. The main reason for this is that both TcO_4^- and ReO_4^- are tetrahedral anions of about the same size (Figure 5) and have about the same free energy of hydration (ΔG_{hydr}).[36,37] Thus, similar anion exchange behavior is expected for the interaction of these anions with the cationic functional groups of anion resins. Only when redox chemistry becomes important will these species significantly differ.



TcO_4^-



ReO_4^-

bond length	(Tc–O) = 1.711(3)Å	(Re–O) = 1.719(5) Å
ΔG_{hydr}	-60 Kcal/mole	-56 Kcal/mole
reduction potential	TcO_4^-/TcO_2 E° = 0.74 V	ReO_4^-/ReO_2 E° = 0.51 V

Figure 5. Comparison of the Pertechnetate and Perrhenate Anions.

4. Calculation of Distribution Coefficients (K_d)

The caustic conditions of Hanford tank supernates will make only the strong base sites of Reillex™-HPQ active for pertechnetate anion exchange. Equation (2) represents the interaction of technetium with the nitrate form of the resin:

$$R^+NO_3^- + TcO_4^- \longrightarrow R^+TcO_4^- + NO_3^- \qquad (2)$$

The symbol R^+ represents the exchange site on the Reillex™-HPQ resin; $R^+NO_3^-$ represents the exchange site with nitrate as the counter ion; and $R^+TcO_4^-$ represents the exchange site with pertechnetate as the counter ion. The equilibrium constant (K_2) for Equation (2) can be defined by Equation (3):

$$K_2 = \frac{[R^+TcO_4^-]\ [NO_3^-]}{[R^+NO_3^-]\ [TcO_4^-]} \qquad (3)$$

In caustic solution, some of the resin will be converted to the hydroxide form by the reaction in Equation (4):

$$R^+NO_3^- + OH^- \longrightarrow R^+OH^- + NO_3^- \qquad (4)$$

where R^+OH^- represents the exchange site with hydroxide as the counter ion. The equilibrium constant (K_4) for Equation (4) can be defined by Equation (5):

$$K_4 = \frac{[R^+OH^-]\ [NO_3^-]}{[R^+NO_3^-]\ [OH^-]} \qquad (5)$$

Pertechnetate can also react with the hydroxide form of the resin by Equation (6):

$$R^+OH^- + TcO_4^- \longrightarrow R^+TcO_4^- + OH^- \qquad (6)$$

The equilibrium constant (K_6) for Equation (6) can be defined by Equation (7):

$$K_6 = \frac{[R^+TcO_4^-]}{[R^+OH^-]} \frac{[OH^-]}{[TcO_4^-]} \quad (7)$$

Rearranging Equation (3) gives an expression for the technetium distribution coefficient, K_d:

$$K_2 \frac{[R^+NO_3^-]}{[NO_3^-]} = \frac{[R^+TcO_4^-]}{[TcO_4^-]} = K_d \quad (8)$$

Distribution coefficients obtained in hydroxide/nitrate media will measure the partitioning of technetium between all resin active sites and the solution matrix. Equation (9) gives an expression for the total concentration of resin active sites, R_t.

$$R_t = [R^+NO_3^-] + [R^+OH^-] \quad (9)$$

Equation (5) can be rearranged to give an expression for the ratio of these active sites:

$$K_4 \frac{[OH^-]}{[NO_3^-]} = \frac{[R^+OH^-]}{[R^+NO_3^-]} \quad (10)$$

Adding 1 to both sides of Equation (10) and inverting yields Equation (11):

$$\frac{[NO_3^-]}{K_4[OH^-] + [NO_3^-]} = \frac{[R^+NO_3^-]}{[R^+OH^-] + [R^+NO_3^-]} \quad (11)$$

Substituting from Equation (9) and rearranging gives:

$$\frac{[NO_3^-]\,R_t}{\{K_4[OH^-] + [NO_3^-]\}} = [R^+NO_3^-] \quad (12)$$

Substituting for $[R^+NO_3^-]$ in Equation (8) gives:

$$\frac{K_2 R_t}{\{K_4 [OH^-] + [NO_3^-]\}} = K_d \qquad (13)$$

Theoretically, Equation (13) states that technetium distribution coefficients should vary directly with the total resin active sites and inversely with the nitrate and hydroxide concentrations. The experimental technetium distribution coefficient is described by Equation (14):

$$K_d = \frac{\dfrac{(\text{mmoles } TcO_4^-)_{resin}}{\text{mass of dry resin}}}{\dfrac{(\text{mmoles } TcO_4^-)_{sol}}{\text{mL of solution}}} = \frac{\dfrac{\{(TcO_4^-)_{total} - [TcO_4^-]_{sol} \times V_{sol}\}}{\text{mass of dry resin}}}{\dfrac{[TcO_4^-]_{sol} \times V_{sol}}{V_{sol}}} \qquad (14)$$

If pertechnetate is the only technetium species present, then the quantity $(TcO_4^-)_{total}$ is the total number of mmoles of technetium in the sample. The quantity $[TcO_4^-]_{sol}$ is the concentration of TcO_4^- in moles per liter in V_{sol} mL of solution after contact with the resin. Using LSC or gamma counting, the experimental distribution coefficient can be defined by Equation (15):

$$K_d = \frac{\{(cpm)_{total} - (cpm)_{sol}\} \text{ per gram of resin}}{(cpm)_{sol} \text{ per mL of solution}} \qquad (15)$$

where the quantity $(cpm)_{total}$ is the number of counts per minute attributable to ^{99}Tc or ^{95m}Tc in the sample before contact. The quantity $(cpm)_{sol}$ is the number of counts per minute in solution attributable to ^{99}Tc or ^{95m}Tc after contacting the resin. Except where noted, the experimental distribution coefficients have an estimated error of ±10%.

5. Technetium Batch Distribution Coefficients Between Reillex™-HPQ and AG®MP-1 Resins from Hanford Simulants

Because of problems associated with running columns with DSSF-7 simulant (vide infra), most of the work in FY95 used the DSSF-5 simulant. The kinetics for the sorption of TcO_4^- onto Reillex™-HPQ from DSSF-5 simulant as a function of time at 25°C were studied. For comparison, the same experiment was done with the Dowex type resin AG®MP-1. These experiments were performed in batch mode using a 10:1 ratio of simulant to resin. Table 13 contains the

Table 13. Pertechnetate K_d Values as a Function of Time Between Reillex™-HPQ and AG®MP-1 Resins and DSSF-5 Simulant.

Reillex™-HPQ		AG®MP-1	
minutes	K_d	minutes	K_d
5	129	5	31
5.8	141	5.75	64
---	---	7.5 [a]	87
11	171	11	91
---	---	15.5 [a]	147
20	229	20	157
---	---	30	124
---	---	35 [a]	205
40	240	40	105
---	---	50	144
60	261	60	203
---	---	80 [a]	196
120	267	120	235
120	263	120	215
120	252	120	215
		120	222

[a] These K_d values were determined using a wrist shaker.

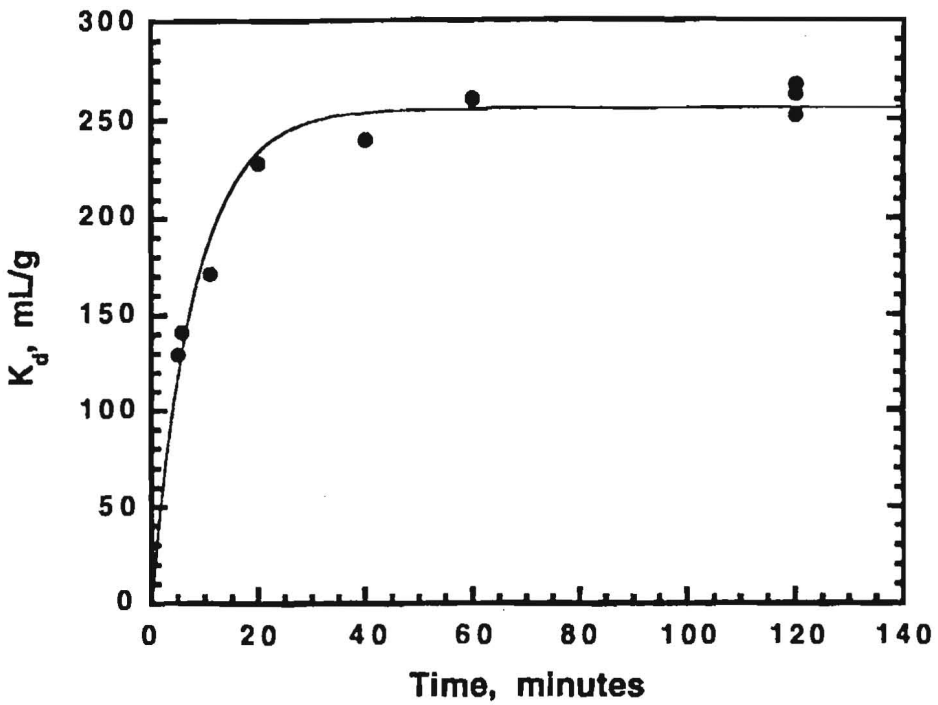


Figure 6. Batch K_d Values for Technetium Between Reillex™-HPQ and DSSF-5 Simulant. The line is resulting least-squares fit of the data to the equation $K_d = {}^fK_d - {}^fK_d e^{-kt}$ with ${}^fK_d$ = 256 (±5) mL/g and k = 0.123 (± 0.011) s^{-1}.

distribution data acquired. Figures 6 and 7 are plots of the data for the Reillex™-HPQ and AG®MP-1 resins, respectively. Note the difference in the data for the wrist-shaker versus the orbital-shaker for the AG®MP-1. We ascribe the poorly reproducible data for the orbital shaker to be due to ineffective water/resin contact. This type of effect has not been observed for the Reillex™-HPQ resin. Since the resins have approximately the same density, the difference in behavior may be attributed to lower wetting of the AG®MP-1 resin by the DSSF-5 simulant. The lines in the figures are the least-squares fits of the data to the equation $K_d = {}^fK_d - {}^fK_d e^{-kt}$, where ${}^fK_d$ is the final K_d value and k is the time constant for sorption. The time constant for Reillex™-HPQ is

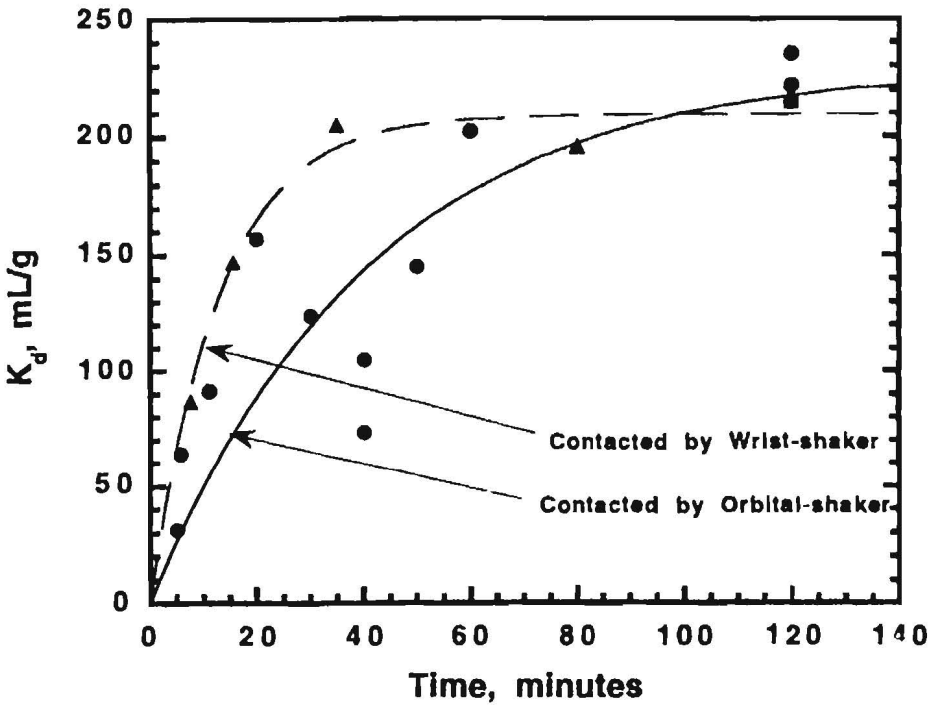


Figure 7. Batch K_d Values for Technetium Between AG®MP-1 and DSSF-5 Simulant. The lines are the least-squares fits of the data to the equation $K_d = {}^fK_d - {}^fK_d e^{-kt}$. For the wrist-shaker, ${}^fK_d$ = 209 (± 7) mL/g and k = 0.078 (± 0.009) s^{-1} and for the orbital-shaker ${}^fK_d$ = 229 (± 28) mL/g and k = 0.025 (± 0.008) s^{-1}.

0.123 (± 0.011) s^{-1}, which is 1.5 time larger than the AG®MP-1 constant 0.078 (± 0.009) s^{-1} indicating the faster kinetics of the Reillex™-HPQ resin.

The kinetics for the sorption of TcO_4^- onto Reillex™-HPQ from DSSF-7 simulant were reported previously and can be compared to the DSSF-5 simulant data. Figure 8 shows the K_d versus time plots at 25, 40, and 60°C for the DSSF-7 simulant. The time constant, k, at 25°C is 0.114 (± 0.018) s^{-1} which is slightly lower, as expected for this more highly salted solutions, than the DSSF-5 value. The distribution coefficients for the DSSF-7 and DSSF-5 simulants are >100 after 5 minutes and within ~80% of their equilibrium value after 20 minutes. The

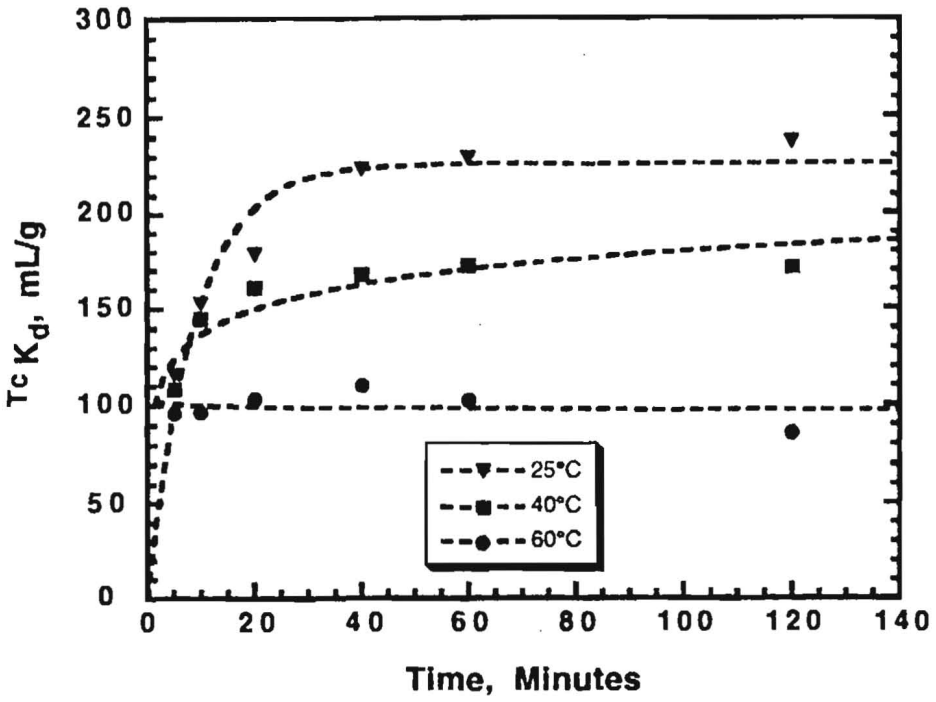


Figure 8. Batch K_d Values for Technetium Between Reillex™-HPQ and DSSF-7 Simulant. The curve for the 25°C data is the resulting least-squares fit of the data to the equation $K_d = {}^fK_d - {}^fK_d e^{-kt}$ with ${}^fK_d$ = 226 (± 9) mL/g and k = 0.114 (± 0.018) s^{-1}.

distribution coefficients for DSSF-5 are 10-15% higher than the DSSF-7 simulant at corresponding times and temperatures. The DSSF-7 data also show that equilibrium is obtained faster at higher temperatures but the K_d decreases. These effects are similar to the DSS and 1:3 diluted DSS simulant results.[19] However, the overall K_d values for the DSSF simulants are 30-50% lower due to the higher nitrate concentration in these simulants.

The kinetics for the sorption of TcO_4^- onto Reillex™-HPQ from 101-SY and 103-SY simulant as a function of time at 25°C were studied. These experiments were performed in batch mode using a 10:1 ratio of simulant to resin. Table 14

Table 14. Pertechnetate K_d Values as a Function of Time Between Reillex™-HPQ and 101-SY and 103-SY Simulants.

101-SY		103-SY	
minutes	K_d	minutes	K_d
7	421	5	160
11	609	10	384
15.5	674	15	459
30	832	30	437
60	1105	60	850
120	1060	120	860

contains the data acquired. Figure 9 show the K_d versus time plots for the 101-SY and 103-SY simulants. The distribution coefficients are >100 after 5 minutes and at the equilibrium value after 60 minutes for both simulants. The time constants the 101-SY and 103-SY systems are 0.0670 (± 0.0082) s^{-1} and 0.0406 (± 0.012) s^{-1}, respectively.

6. Modeling Technetium Sorption in Caustic Nitrate Solutions

Nitrate and hydroxide are the major anionic constituents in Hanford tank waste supernates (Table 12). Nitrate has been shown to be a major competitor against technetium for Reillex™-HPQ resin's active sites while hydroxide has considerably little affinity for the resin. Figure 10 illustrates the dependence of technetium distribution coefficients on the nitrate concentration in NaOH solutions. It has previously been shown that in 1 M NaOH, and using the nitrate form of Reillex™-HPQ, that the K_d dependence (lowest curve in Figure 10) fits Equation (13) derived in section 4:[20]

$$K_d = \frac{K_2 R_t}{\{K_4 [OH^-] + [NO_3^-]\}} \qquad (13)$$

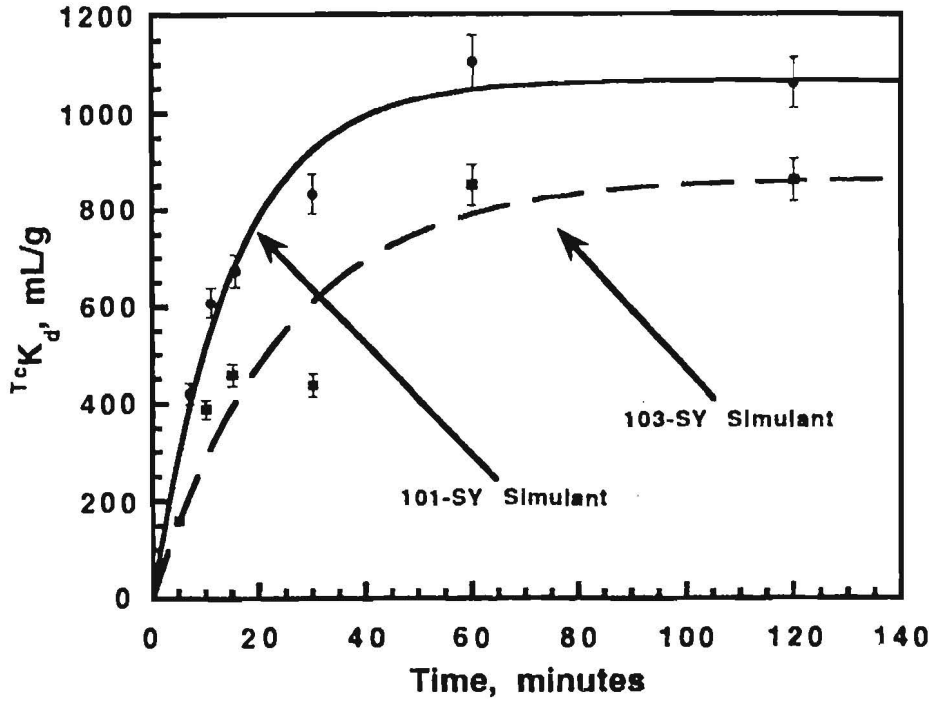


Figure 9. Batch K_d Values for Technetium Between Reillex™-HPQ and 101-SY and 103-SY Simulants. The lines are resulting least-squares fit of the data to the equation $K_d = {}^fK_d - {}^fK_d e^{-kt}$ For 101-SY, ${}^fK_d$ = 1066 (± 45) mL/g and k = 0.0670 (± 0.0082) s^{-1} and for 103-SY ${}^fK_d$ = 865 (± 100) mL/g and k = 0.0406 (± 0.012) s^{-1}.

The $K_2 R_t$ factor is equal to 391 ± 19 meq/g dry resin. Since the resin capacity, R_t, is 3.34 ± 0.10 meq/g dry resin, the value of K_2 is 117 ± 7. The equilibrium constant for the exchange of hydroxide for nitrate in the resin, K_4, was found to be 0.389 ± 0.022. This constant, being less than one, verifies the low affinity of hydroxide for the nitrate form of the resin. The weak affinity of hydroxide for the resin is further illustrated by the two other curves presented in Figure 10. In 0.1 M NaOH (middle curve in Figure 10) the technetium K_d values are significantly higher at the lower nitrate concentrations (<0.1 M) compared to the 1 M NaOH

system. The K_d values in the 0.1 M NaOH system are actually suppressed by nitrate ion released into the system when the resin is put into basic solution (i.e.

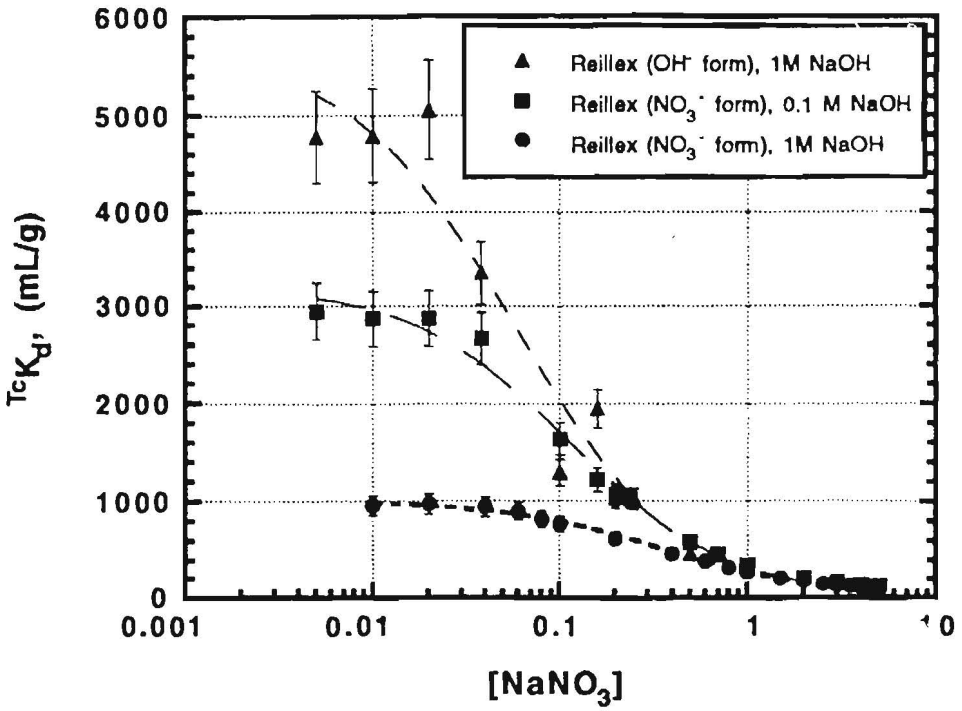


Figure 10. Technetium K_d Values as a Function of [NO_3^-].

the pyridinium [-$C_5H_4NH^+NO_3^-$] weak base exchange sites become neutralized and release NO_3^- to the solution phase). If this source of nitrate is also eliminated by using the hydroxide form of the resin, then the technetium K_d values are even higher at the low nitrate concentrations (top curve in Figure 10). All the curves converge at nitrate concentrations >1 M; in this region the strong affinity of nitrate swamps any competitive effect by hydroxide and the K_d values become inversely dependent on the nitrate concentration.

The three sets of data fit the general form of Equation (13); the fit is generally good with respective correlation coefficients of 0.997, 0.996 and 0.967. The measured K_d values in the convergent portion of Figure 10 are slightly higher

than those predicted by Equation (13).[19] At high salt concentrations lower Donnan potentials allow sodium ions to enter the resin phase which effectively increases the number of exchange sites in the resin phase. Thus the experimental K_d values are greater than theoretical at high external solution concentrations. The effect is usually small, especially in this particular case where NO_3^- and TcO_4^-, which have similar affinities for anionic sites, are the competing ions.

Figure 11 shows the technetium distribution coefficient as a function of the hydroxide concentration at various constant nitrate concentrations. It has been shown that the curve at 1.0 M [NO_3^-] follows the behavior predicted by Equation (13) at low hydroxide concentrations; the K_d values are decreasing from 0.01 M to 0.4 M [OH^-].[20] Above 0.4 M [OH^-] the curve deviates from the predicted behavior. In this region the K_d values increase, almost doubling their value between 1 and 5 M NaOH. This trend is observed for the other systems in Figure 11. The bottom two curves were generated at 1.5 and 3.5 M [NO_3^-], which are the nitrate concentrations found in the DSS and DSSF simulants, respectively. These solutions also show an approximate doubling of their K_d values between 1 and 5 M NaOH. Many Hanford tank supernates are in the regime depicted by the bottom three curves.

The dramatic increase in the experimental K_d values above 1.0 M NaOH can be attributed to the lower Donnan potential in these highly salted solutions. The effect is greater in Figure 11 compared to Figure 10 because the highly hydrated hydroxide ion concentration is increasing in these systems. Selectivity in aqueous anion exchange is influenced by the degree of hydration of the resin, ion-water interactions and the effect of the anion on the water structure.[38] The free energies of hydration, ΔG_{hydr}, for OH^-, NO_3^- and TcO_4^- are -90, -67, and -60 Kcal/g-ion, respectively.[36] At high concentrations, the small, highly-hydrated, hydroxide ion ties up a significant portion of the aqueous phase. The resin phase, which also contains water, is also dehydrated making it more selective for unsolvated anions like TcO_4^-. In addition, hydroxide hydrogen bonds to water further decrease the amount of free water available to other anions. Based on the ΔG_{hydr} values, the shortage of free water with increasing [OH^-] will have a greater effect on TcO_4^- compared to NO_3^-. Sodium ion pairing also becomes important as the amount of free water decreases; the relative size

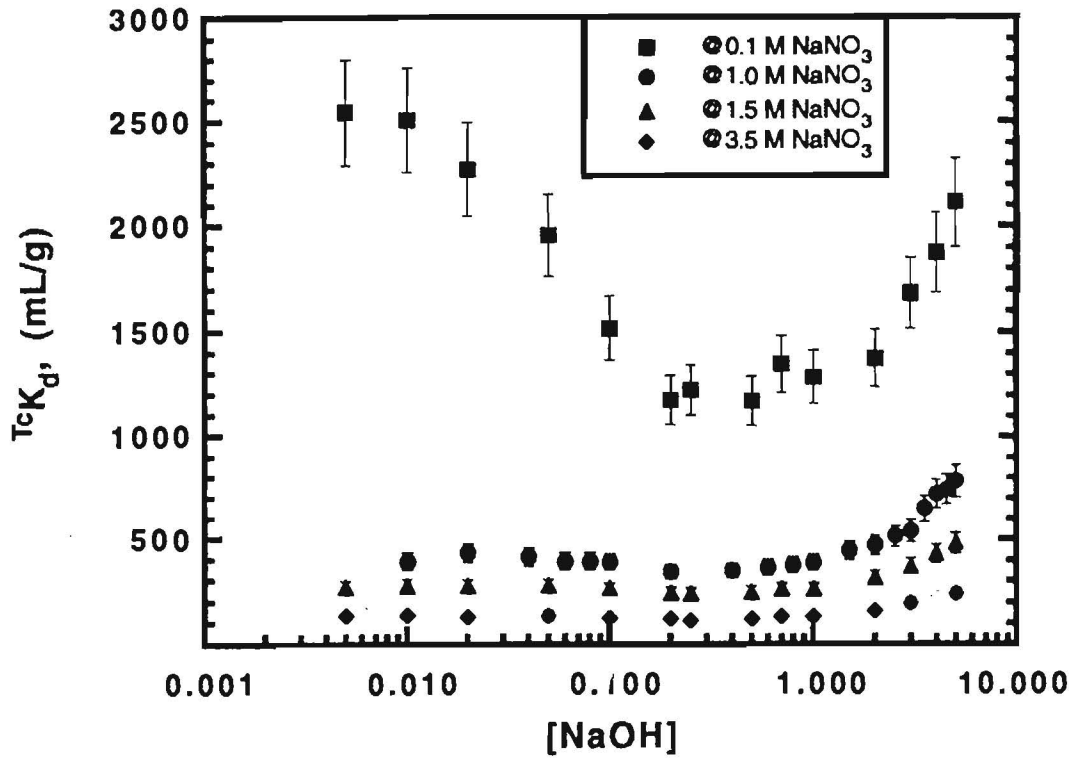


Figure 11. Technetium K_d Values as a Function of [NaOH].

of the ions favors the Na^+/OH^- and Na^+/NO_3^- ion pairs over the Na^+/TcO_4^- ion pair. An important consequence of these interactions is that the NO_3^- ion's retention by the external aqueous phase increases and therefore it becomes less competitive relative to TcO_4^- for the resin sites. The net effect is that TcO_4^- anions, having been squeezed from the external aqueous phase into the hydrophobic resin phase, can form energetically favorable ion pairs with the large quaternary amine cations with reduced competition from NO_3^-.

The information in Figure 10 and 11 can help predict the behavior of pertechnetate with Reillex™-HPQ resin in matrixes that may be encountered at Hanford. The distribution coefficients of technetium from DSS (K_d = 330) and DSSF-7 waste simulants (vide infra), which are 1.5 M and 3.5 M [NO_3^-]

respectively, are consistent with the convergent region of Figure 10. Uptake of pertechnetate by the resin from tank supernates containing even higher nitrate concentration than the DSSF simulant would also be predicted by this region of the graph. Dilution of Hanford tank supernates with water to lower the nitrate concentration can be used to improve the performance of the resin. Technetium separation from sludge washing streams should also be an efficient process. These wash use 2 M NaOH and the resultant solutions may contain a higher concentration of hydroxide than nitrate. Figure 11 shows that technetium sorption onto Reillex™-HPQ should improve with each successive wash cycle. Figure 11 also predicts the performance of Reillex™-HPQ with the 101-SY and 103-SY simulants. These simulants contain more hydroxide than nitrate. At 3.5-3.9 M hydroxide and ≈ 1 M nitrate, this figure predicts technetium K_d values of 700 mL/g. This compares to experimental values of 1060 and 860 mL/ g for these simulants, respectively.

7. Distribution Coefficients for Reillex™ Resins

A number of resins that are derivatives of the standard Reillex™-HP resin have been obtained. A description of the resins is given in the experimental section and summarized in Table 10. We have measured the technetium distribution coefficients with these reins as part of our effort to characterize the sorption characteristics of Reillex™-HPQ. Table 15 lists the technetium K_d values obtained from 60 minute contacts at 25°C in DSS and DSSF-7 simulants. All the resins had higher technetium K_d values in the DSS simulant compared to the DSSF-7. This is predicted based on the lower nitrate concentration in the DDS simulant. The surprising result is the K_d value for Reillex™-HP. This resin has no strong base sites and should therefore be inactive in these matrixes. Apparently the pyridine functional group in this resin is acting like pyridine when it serves as an extractant for pertechnetate.[39] A paper on the sorption properties of Reillex™-HP resin is included in Appendix C of this report. The first four resins in Table 15 are all pyridinium resins with methyl, butyl, hexyl and octyl substitutions on the pyridine nitrogen, respectively. The maximum K_d occurs with the butyl substituted resin. These results are similar to those presented in Table 2 for 101-SY simulant.

Table 15. Technetium K_d Values for Reillex Resins.

RESIN	K_d DSS	K_d DSSF-7
Reillex™-HPQ	410	250
N-Butyl-HP	721	426
N-Hexyl-HP	330	141
N-Octyl-HP	277	103
Reillex-4632-15	400	257
Reillex-4632-17	326	212
Reillex™-HP	268	130

8. Resin Stability Studies

The exchange capacity of the batch of Reillex™-HPQ resin used in this study was measured to be to be 3.54 ± 0.05 milliequivalents per gram of dry resin (meq/g). Samples of Reillex™-HPQ in the nitrate form were contacted with 2.00 M NaOH at 50°C for 28 days. Table 16 shows the chloride capacity of the resin as a function of contact time. There was a small change in the capacity within the first 48 hours. However, after this time there appeared to be a single-stepped drop in capacity. The average capacity from 72 through 669 hours was 2.46 ± 0.24 meq/g. This represents a 30.5 % decrease in the capacity of the resin. Technetium batch K_d values obtained on the 532 and 669 hour sample with DSSF-7 simulant were 141 and 133, respectively. These distribution coefficients are 36% lower than the uncontacted resin used in this study which had a $^{Tc}K_d$ of 209.

A similar study at 25°C indicated there was no decrease in capacity after 7 days. These results are suspect because of uncertainty in the method of determination of the capacity of the resin at the time of the experiment. However, we have alternative data from our repetitive (sustainability) column

studies that show that the capacity decreases slowly over 50 days and then levels off.

The exchange capacity for the nitrate form of Reillex™-HP resin has been determined to be 3.45 ± 0.01 meq/g. The capacity of this resin did not change in 2.0 M NaOH at 50°C after 300 hours. The difference in the results between the Reillex™-HP and Reillex™-HPQ resins suggest that the alkylation of the Reillex™-HP resin to make the Reillex™-HPQ resin may have caused degradation or fractionating of the polymer backbone. These lighter molecular weight fractions are possibly leaching from the resin during the caustic solution contact. The observation that the capacity levels off suggests that this is the case because a continuous attack by base on the pyridinium functionality would show a continuous and steady decrease in capacity with time.

The capacities of N-Butyl-HP, Amberlyst A-26 and A-27 resins were also studied in base as a function of time. The measured capacities of the Amberlyst resins are 3.853 ± 0.040 and 2.372 ± 0.030 meq/g, respectively. After 90 days in 2.00 M NaOH at 50°C the capacities are 3.781± 0.030 and 2.242± 0.160 meq/g. Thus, these two strong base quaternary amine resins are stable in caustic media. The N-Butyl-HP form has an initial capacity of 4.18± 0.26 meq/g. Over 12 days in 2.00 M NaOH at 50°C the capacity decreases and then remains constant at 3.44 ± 0.12 meq/g for up to 33 days. It appears that this the butyl form of Reillex™-HP is also washing out a lower molecular weight fraction but at a much slower rate. The lower rate might be expected because this resin with its larger alkyl group may not wet as well as the Reillex™-HPQ resin.

Anion exchange resins are not infinitely stable. A major degradation mechanism involves attack at the quaternary nitrogen to effect the loss of strong base capacity. [40,41] This can be caused by dissolved oxygen or strong oxidants including chromate, hypochlorite and hydrogen peroxide. In addition, strong oxidants including chromate, hypochlorite and hydrogen peroxide may also attack the polymer backbone. Common transition metals can catalyze both mechanisms. Common anion exchange resins have been shown to lose 10-17% of their capacity on contacting 5% peroxide; capacity losses were less with more highly cross-linked resins. The resins in Table 17 were contacted for 24 hours with a 5% peroxide solution at 30°C. The technetium Kd values were

Table 16. The Chloride Capacity of Reillex™-HPQ Resin After Contact with 2.00 M NaOH at 50°C.

Hours	meq/g
0	3.54
48	3.45
72	2.59
124	3.04
193	2.37
269	2.27
294	2.16
321	2.33
336	2.34
367	2.48
508	2.71
532	2.41
669	2.40

Table 17. Stability of Resins in 5% H_2O_2 at 30°C.

Resin	$^{Tc}K_d$ Before	$^{Tc}K_d$ After
Reillex™-HPQ	258	266
Reillex™-HPQ 4632-15	231	245
Reillex™-HPQ 4632-17	203	234
N-Butyl-HP (43%)	509	553
N-Butyl-HP (89%)	417	433
Reillex™-HP	211	197
Ionac™SR-6	103	----[a]
Purolite™A-520-E	453	432
Amberlite IRA-900	163	169
Amberlite IRA-904	346	331
Amberlyst A-26	200	201
AG 1-X8	242	253

[a] Lost sample.

measured in DSSF-7 simulant before and after the peroxide treatment. Since the $^{Tc}K_d$ values are within 10% of each other before and after this treatment, it appears that there was no effect on any of the resins. Quite possibly the pretreatment of the resins by the methods described in the experimental may have substantially lowered the traces of transition metals in the resins to limit any oxidation. However, it should be noted that Ionac™SR-6, Purolite™A-520-E, and AG 1-X8 had significant gas production relative to all the other resins.

9. Elution of Technetium from Anion Exchange Resins

Sorbing technetium onto a resin is the first step of a technetium partitioning process. Other aspects include eluting technetium, recovering the element and, especially for process development, recycling the reagents. Mechanistically, Reillex™-HPQ anion exchange resin bases its separation on ion pairing between the resin's pyridinium cationic functional group and the pertechnetate anion. Reversing this association can take three approaches. These include 1) elution with anions that have a strong affinity for the resin, 2) reduction of pertechnetate to a form that is not sorbed, and 3) reduction coupled with complexation to form a soluble complexed technetium species, preferably a cation.

Method 1, using the standard 8 M HNO_3 reagent, presents several problems. Large scale processing with an oxidizing acid in contact with organic resin is potentially explosive.[42] This issue has been familiar to Hanford for thirty years; a conceptual redesign of "B-Plant", done in 1965, to institute a technetium recovery process concluded that contacting anion exchange resin with nitric acid may be unstable.[43] In addition, significant secondary wastes are generated by the large volume of acid required to elute technetium. Other specific problems are the slow elution rate for anion exchange and the recovery of technetium from the nitric acid. Method 2 deposits reduced technetium, TcO_2, onto or in the resin. Even though there is no electrostatic attraction, our experience is that this is a very difficult material to remove from the resin.

In FY 94 we were successful in developing method 3. The reduction and complexation option for eluting technetium is based on research in the medical

radioisotope field. The general reaction to form a reduced ^{99}Tc complex is given by Equation (16)

$$^{99}TcO_4^- + \text{Reductant} + \text{ligand} \rightleftharpoons [\text{product complex}]^z \qquad (16)$$

The ligand type will determine the charge (z) of the technetium complex. A cationic complex was desired because it would be electrostatically rejected by the resin. Because the waste streams we are working on are caustic it was desirable that the cationic complex form in basic media. In addition, the reaction had to be fast and produce a single product. The stannous ion is the most common reductant for the synthesis in equation (16) because of its rapid kinetics to give Tc(V).[44] Further reduction by stannous to Tc(IV) is slower. Having the ligand present during the reduction traps the Tc(V) state and stabilizes it. The geometry of the complex is dependent ligand type; oxygen and sulfur ligands yield a square pyramid geometry with a technetyl, TcO^{3+}, core while nitrogen ligands favor an octahedral complex with a TcO_2^+ core with the oxygens trans to each other.[45] The significance of this is that neutral nitrogen ligands will produce cationic complexes.

For eluting technetium, the chemistry has to work between the aqueous and resin phases. In addition, all the reagents and the reaction products need to be soluble in the aqueous phase, stable in caustic and, lastly, the whole process should have the potential of recycling the reagents. Based on the above information, an eluent system that generated a simple cationic amine Tc (V) complex would be desirable. These types of complexes have been discussed in the literature and the most desirable species to try to form during elution was the *trans* -$[O_2(en)_2Tc^V]^+$ complex[45], where en = ethylenediamine.

The most successful eluent systems found were Sn(II)/en/NaOH mixtures where the base and the en concentrations ranged between 0.1 and 1.0 M and the Sn(II) concentration ranged from 0.005 to 0.016 M. All these solutions contained a small amount of mossy tin to minimize the oxidation of Sn(II) to Sn(IV). In general, this eluent system was found to quantitatively remove technetium from a column that had been loaded with technetium from a DSS simulant. The elution was efficient, >99% of the technetium removed by three

column volumes. Most work in FY 95 was with DSSF simulant. Before starting large column experiments, it was necessary to test the eluent with this simulant. In addition, we had previously shown that the eluent system is effective for removing technetium sorbed onto other anion resins.[46] We have extended this study to other Reillex resins. Figure 12 shows the elution of technetium from these resins after loading them with technetium from either DSSF-7 or DSS simulant. All the elutions removed >99% of the technetium with < 4 bed volumes of eluent.

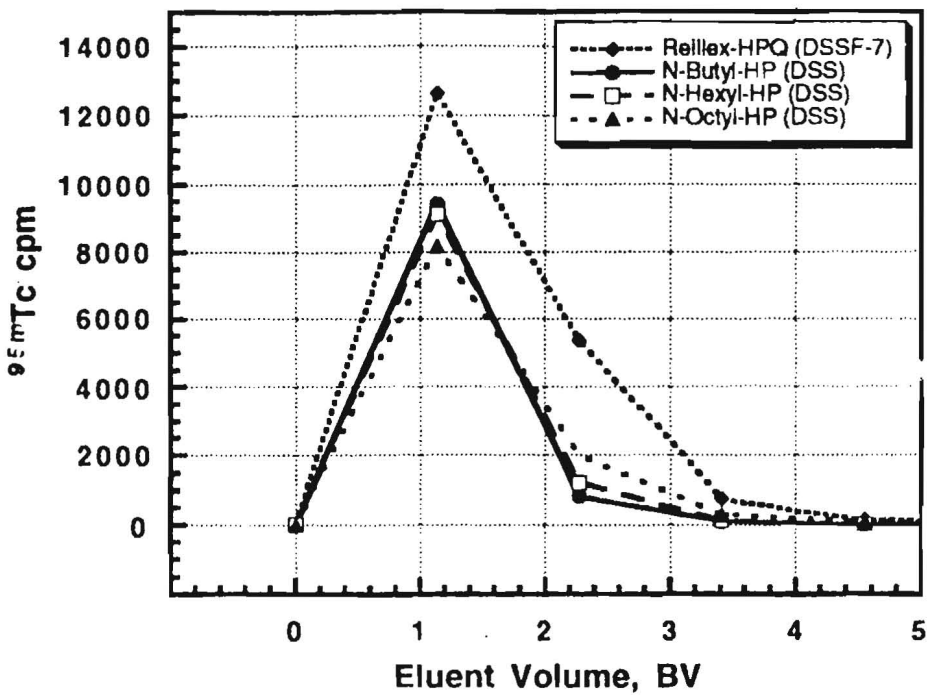


Figure 12. Elution of Technetium from Reillex Resins.

Application of the eluent for Hanford Processing will depend on the acceptability of tin to the processing streams and its effect on the performance criteria of the LLW or HLW glass. We are trying to minimize the amount of tin used and to recycle as much of the tin as possible. In our large column studies we have maintained a Sn(II) concentration of 0.005 M. Based on this

concentration and assuming a technetium concentration of 5 x 10^{-5} M in the waste we have calculated the amount of tin that needs to be recycled so as not to load the waste form more that 1% by weight with tin. In this calculation we assume that 1 L of DSSF-7, which is 60% salt (assume it is all $NaNO_3$) is mixed 1:3 by weight with glass frit and vitrified to produce 868 g of glass/L of DSSF-7. A 1% tin loading limits the tin to 8.7 g. Based on the stoichiometry in equation (16) and the column performance data previously observed for eluting technetium from a saturated column, we estimate that 81.4 grams of tin are required for the elution. Thus 72.7g or 90% of the tin needs to be recycled.

We have taken the combined tin effluents from our Flow 7 column experiment (vide infra) and recovered the tin from this solution by precipitating the stannic oxide by neutralizing the solution with HNO_3. Tin begins to precipitate at pH 9.7. The solution was taken to pH 7 and centrifuged to collect the tin oxide. A 97% recovery of the tin was obtained, while 94% of the technetium stayed with the supernate.

10. Repetitive Breakthrough Experiments with a Reillex™-HPQ Anion Exchange Column (2.54 x 50 cm) and DSSF-5 Simulant

In FY94 we ran 1 x 20 cm columns with the DSS simulant. Eleven cycles of loading technetium from DSS simulant and eluting with stannous/en/NaOH solution were performed. The 1% breakthrough volume for TcO_4^- decreased from 57.7 to 23.5 bed volumes over the experiment. At that time we attributed the breakthrough decrease to column bleeding and to operational problems that occurred during the experiment to alter the resin bed characteristics. In addition, wall effects may have given lower than expected breakthrough volumes. In FY95 we have used 2.54 x 50 cm columns. This column diameter is greater than 20 resin bead diameters which should negate wall effects. We have replumbed our column apparatus (Figure 4) to allow us to elute the column using an upflow mode. This was done to eliminate column bleed. Unfortunately, we were requested to work with DSSF simulant in FY95 so the direct consequences of these changes were not measured with the DSS simulant.

Table 12 shows the concentration of the various ions in the DSSF-7 simulant. The ionic strength and the total salt concentration are twice that of the DSS simulant. Even more important, as far as technetium distribution coefficients are concerned, the nitrate concentration of DSSF-7 is 2.3 times that of the DSS simulant. Even so, the 1 hr $^{Tc}K_d$ for the for DSSF-7 is 250 mL/g and $^{Tc}K_d > 100$ is obtained in 5 minutes, a time that is expected to be less than the residence time of feed to a processing column. Our initial experiments with DSSF-7 simulant started with 1 x 20 cm columns. These experiments were wrought with problems. We were loading this simulant directly onto a resin bed that had been packed in water and conditioned with 1 M NaOH. Abnormal breakthrough curves were obtained characterized by earlier than expected breakthroughs (< 7 BV) and curves that had a decreasing slope shortly after achieving breakthrough. Column performance did improve as the column runs proceeded or as the feed flow rates increased. What was striking about these initial runs was the shrinkage of the resin bed after contacting the DSSF-7 simulant, ~ 8%. Conditioning the column with a 4 M $NaNO_3$ solution preshrunk the resin bed slightly and improved the column performance. However, it was apparent that resin bed instability was going to continue to be a problem. At this point we switched to the 2.54 cm diameter columns with the expectation that the wider column would not serve as a crutch to support an unstable resin bed; the resin bed would naturally settle to a well packed state.

The initial 2.54 cm column run with DSSF-7 was as poor as any of the 1 cm runs. Preshrinking the resin bed with "cold" DSSF-7 simulant tremendously improved the column performance. Preconditioning columns with solutions as complex as simulants is not a remedy for a potential processing operation. Two options were available to solve this problem; dilute the simulant enough to give good column performance and/or preshrink the resin with a simple solution. Two dilutions of DSSF-7, 1:6 and 1:2, gave good column performance. This is not unexpected since the 1:2 dilution is about equivalent to the DSS simulant which never gave us these types of problems. However, guidance from the TWRS program indicated that the maximum dilution allowed would be to 5 M $[Na^+]$, thus we were limited to a 1:1.4 dilution (DSS-5). Fortunately we were able to find a shrinking solution consisting of 6 M $NaNO_3$ and 2 M NaOH that could precondition the resin bed to match the expected shrinkage by the DSSF-5 solution. Concentrations greater than DSSF-5 will be difficult to process

because shrinking solutions with higher nitrate and hydroxide concentrations are almost at their limit of solubility.

Three types of column experiments were performed with the DSSF-5 simulant. These were 1) a repetitive column loading and elution study, 2) a flow-rate study to determine the optimum flow-rate, and 3) full breakthrough studies. The purpose of the repetitive column loading and elution experiments was to establish the viability of recycling a 2.54 x 50 cm Reillex™-HPQ column that is used to remove TcO_4^- from a DSSF-5 simulant. The viability of the column was indicated by the 1.0% breakthrough volume measured in bed volumes (BV); the larger the number the better the performance. The 2.54 x 50 cm column was prepared, conditioned with a solution containing 6.0 M $NaNO_3$ and 2.0 M NaOH (μ = 8.0), loaded with technetium from the DSSF-5 (μ = 8.6) simulant until at least 1% breakthrough occurred, and then eluted with the reducing/complexing reagent (1.0 M NaOH/1.0 M en/5mM Sn^{2+}). After regeneration with a solution containing 6.0 M $NaNO_3$ and 2.0 M NaOH, the column was put into service for

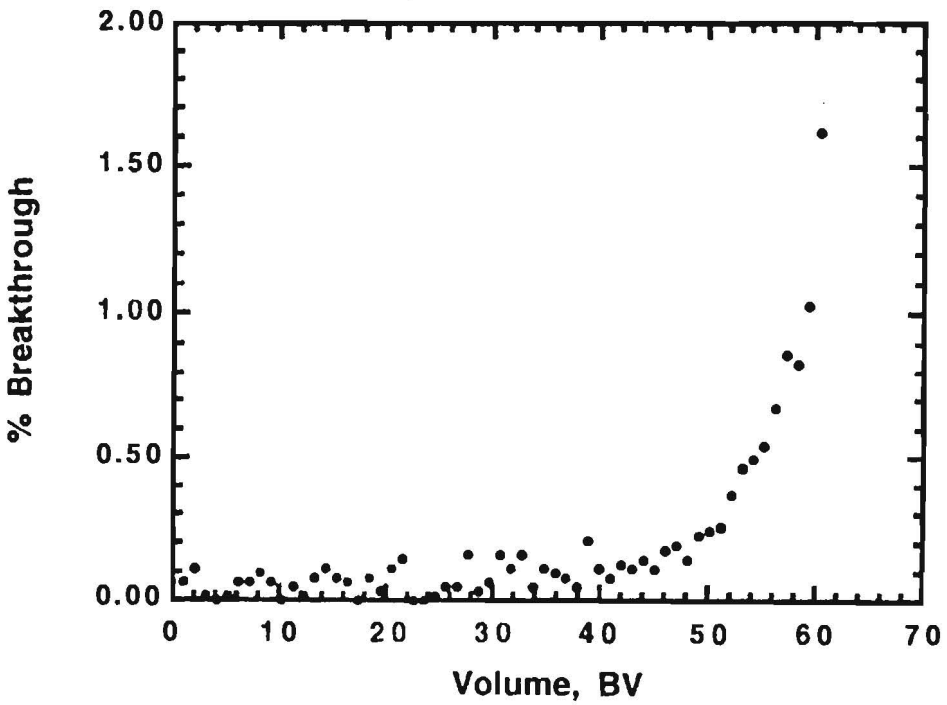


Figure 13. Breakthrough Curve for the BT-1 Column Experiment.

another loading and elution cycle. The feed solutions were passed through the column in the down-flow direction at 3 cm/min while the elution was in an upflow direction. A total of 11 cycles were run which kept the column in service and in contact with caustic solution for 94 days. Figures 13, 14, and 15 are breakthrough curves for the first, seventh, and eleventh runs (BT-1, BT-7 and BT-11). Summaries of the individual experiments are given in Appendix A. Mechanical problems occurred after runs BT-6 and BT-7 that required that the resin bed be repacked after these runs. This was accomplished with an up-flow of water through the column to remove air and reclassify the resin bed. No further mechanical problems were encountered for the remaining runs. The 1% breakthrough point for the BT-1 run occurred at 50 bed volumes (BV). The breakthrough curves of runs 2 through 11 were effected by "activity bleeding" from the column as a result of incomplete removal of technetium by the previous run's elution. Thus the 1% breakthrough volumes (BV) are reported at a particular percent. For example the 1% breakthrough point for BT-7 is at 1.55% because activity bleeding from the column creates a baseline at 0.55%.

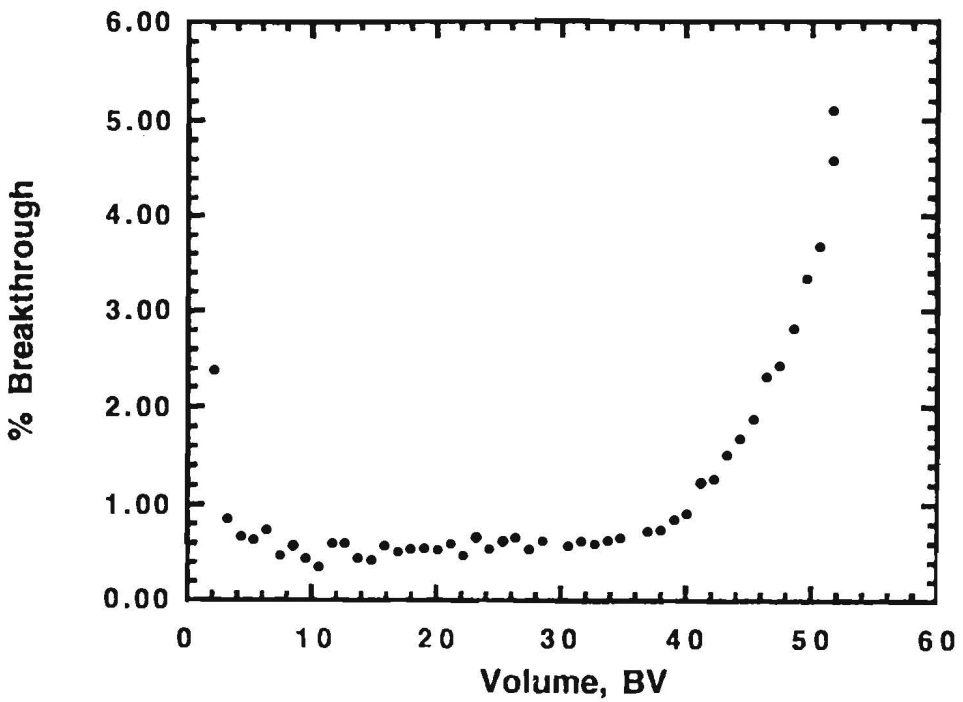


Figure 14. Breakthrough Curve for the BT-7 Column Experiment.

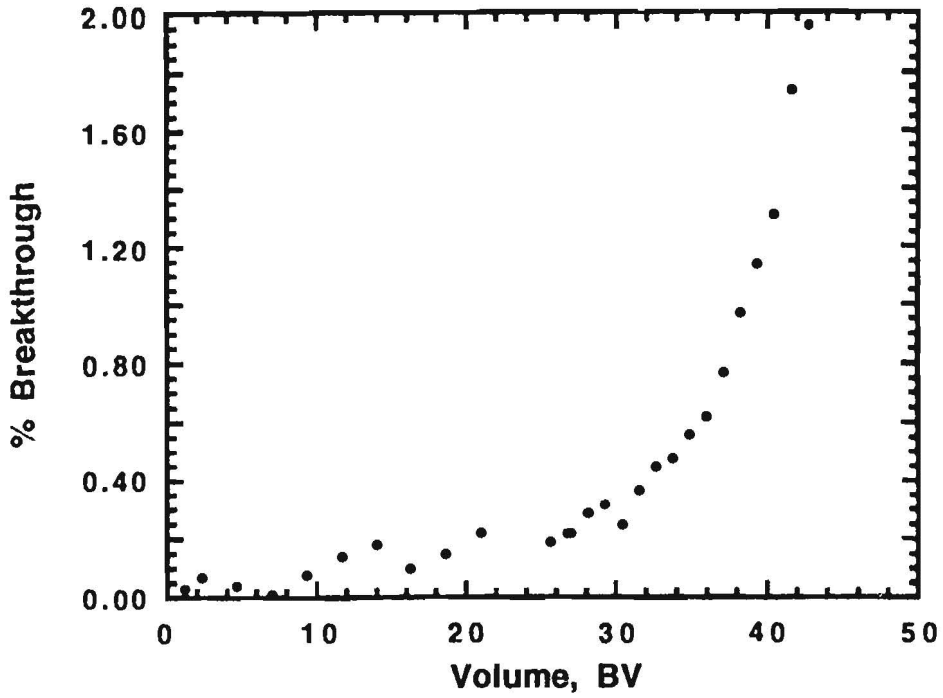


Figure 15. Breakthrough Curve for the BT-11 Column Experiment.

Table 18 contains the summary of the 1% breakthrough volumes for each run along with the time that the resin had been in contact with the caustic medium. Figure 16 is the plot of the 1% breakthrough volumes for the BT-1 through BT-11 runs as a function of time. This breakthrough volumes have an initial plateau for the first four runs, decreasing values for runs five through seven, and then another plateau for the remaining runs. The 1% breakthrough point has decreased from 60 bed volumes (BV) in the initial run to about 40 BV in runs 8 to 11; a 33% change. The loss in performance was predicted by the Reillex™-HPQ resin stability study performed in 2 M NaOH at 50°C. That study also showed an initially stable period of 2 days then a 30% decrease in the resin's capacity over the next three days and finally a stable period out to at least 27 days. The higher temperature in this experiment explains the accelerated rate compared to the column runs.

Table 18. Summary of the 1% Breakthrough Volume Data.

Run	time, days	1% breakthrough volume, BV
BT-1	2	59.1
BT-2	7	58.7
BT-3	15	57.9
BT-4	21	58.4
BT-5	37	53.2
BT-6	43	51.0
BT-7	50	43.8
BT-8	58	40.0
BT-9	70	44.2
BT-10	80	39.8
BT-11	94	39.3

Table 19. Summary of Bed Volumes of Sn(II) Eluent Required to Elute Technetium from the BT Column Runs.

Run	BV Eluent	% Elution
BT-1	2.03	90.94
BT-2	3.66	98.93
BT-3	4.08	96.22
BT-4	4.34	95.82
BT-5	3.25	83.45
BT-6	4.14	97.78
BT-7	3.77	100.70
B7-8	3.72	103.09
BT-9	4.37	101.82
BT-10	4.50	104.19
BT-11	4.50	98.59
Average	**3.85**	**97.41**

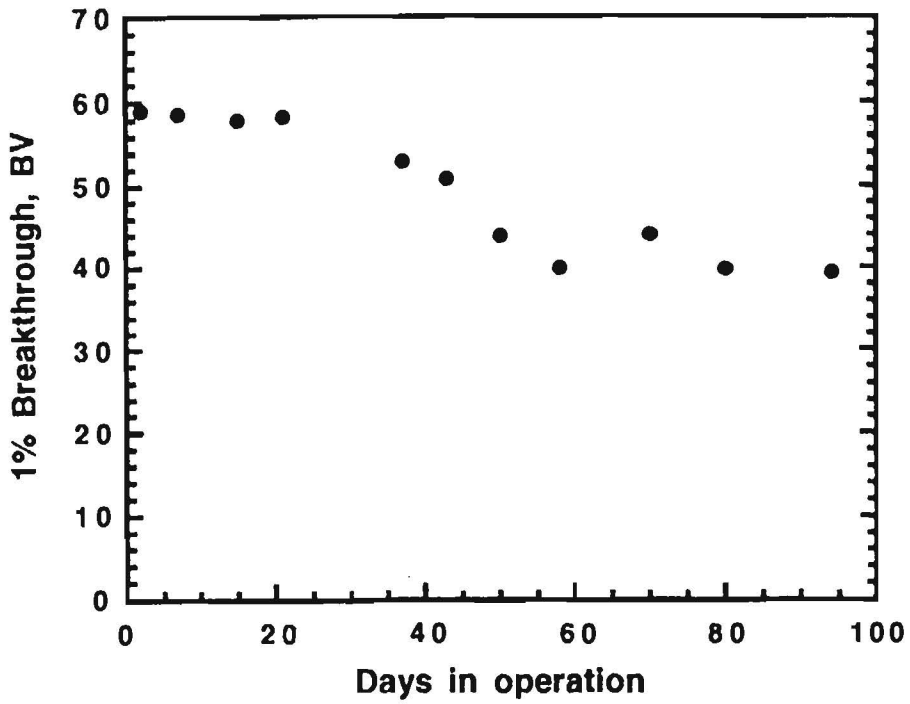


Figure 16. The 1% Breakthrough Volumes for BT-1 through BT-11 as a Function of Time.

Table 19 shows the bed volumes of the Sn(II)/NaOH/en eluent used to remove technetium from the column for each run. The BT-1 elution was efficient in the sense that it removed technetium with 2 bed volumes of solution but relatively in efficient in that it left 10% of the technetium on the column. We suspect that the reason for this inefficiency is that transition metal impurities in the simulant were deposited in the resin bed during the loading phase and that during the elution they became reduced and therefore capable of sorbing reduced technetium species. Reduced transition metals, especially iron, are capable of such behavior.[47] To prevent this, all subsequent tin elutions were preceded by a 1 M NaOH/1 M en upflow wash of the column. Except for BT-5, this seemed to rectify this problem. The bed volumes of eluent listed in Table 19 do not reflect the real efficiency of this eluent. Figure 17 shows the elution curve for the BT-8 experiment; this clearly shows that < 1.5 bed volumes of eluent are required to technetium.

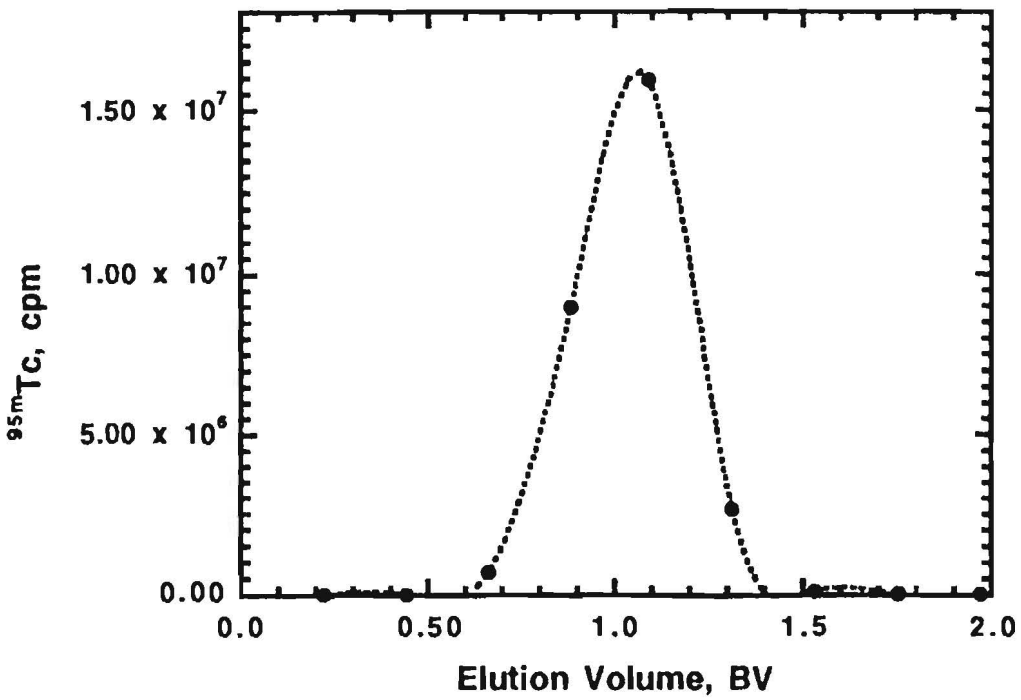


Figure 17. Elution Curve for the BT-8 Breakthrough Experiment.

Table 20 is an inventory of the ^{99}Tc activity for BT-1 through BT-11 experiments. The last column is a running percentage of the technetium remaining on the column. The poor elutions at BT-1 and BT-5 are recovered by subsequent elutions. Overall 2.91% of the technetium was not recovered from this experiment which spanned nearly 100 days. Some of the unrecovered technetium may have been lost to radioactive decay.

11. Flow Experiments with Reillex™-HPQ Anion Exchange Columns and Hanford Double-Shell Tank Simulant (DSSF-5)

We performed a flow-rate study at 5, 15, 25, 35, 45, 55, 60, and 65 mL/min corresponding to linear flow-rates of 1, 3, 5, 7, 9, 11, 12, and 13 cm/min, respectively. The purpose of this series of experiments was to establish the 1%

Table 20. Inventory of the ^{99}Tc Activity for BT-1 Through BT-11 Column Runs.

CPM Added	CPM Removed	CPM Remaining	Stepwise % remaining	Overall % remaining
BT-1				
23,046,000	20,958,803	2,087,197	9.06	9.06
BT-2				
22,977,000	22,731,080	245,920	1.07	5.06
BT-3				
23,285,913	22,404,625	881,288	3.78	4.64
BT-4				
23,175,600	22,012,050	1,163,550	4.18	4.52
BT-5				
25,328,875	21,137,588	4,191,287	16.64	7.11
BT-6				
23,325,222	22,811,395	513,827	2.22	6.30
BT-7				
20,114,825	20,255,507	-140,682	-0.70	5.42
BT-8				
28,975,050	29,870,689	-895,639	-3.09	4.13
BT-9				
21,084,000	21,468,314	-384,314	-1.82	2.86
BT-10				
14,841,375	15,462,733	-621,358	-4.19	2.34
BT-11				
17,339,875	17,094,540	245,335	1.41	2.27
Total				
243,493,734	236,401,819	7,091,915	----	2.91

breakthrough volume as a function of flow rate of DSSF-5 feed for 2.54 x 50 cm Reillex™-HPQ columns. A fresh resin bed was packed and classified for each run. Feed solutions were passed through the column in the down-flow direction while the elution was done in an upflow direction and at the same rate as the loading. Details of each run are given in Appendix B. Table 21 summarizes the flow rate experiments. Figure 18 shows a linear relationship between the 1% breakthrough volume and the flow rate for flows ranging from 15 to 65 mL/min. The run at 5 mL/min had a 1% breakthrough at 11 BV; much less than the expected value of 65 BV. It is possible that this result was due to a poor column packing. However, a more fundamental explanation is that this low a flow rate does not maintain enough pressure on the resin bed to maintain a stable bed. This experiment needs to be repeated.

The elutions for all flow rate experiments were preceded by a 1 M NaOH/1 M en upflow wash prior to the Sn(II) elution. It is interesting that the elutions, which were performed at the same flow rate as the loading, had very decent technetium recoveries. There does not appear to be a trend with flow rate.

Table 21. The 1% Breakthrough Volumes and Percent Technetium Eluted as a Function of Flow Rate.

Flow Rate mL/min	1% Breakthrough BV	% Eluted
15	59.1	90.9
25	55.0	94.1
35	40.8	106.0
45	45.3	91.9
55	35.2	98.5
60	27.9	98.5
65	31.0	84.7
Average		**94.94**

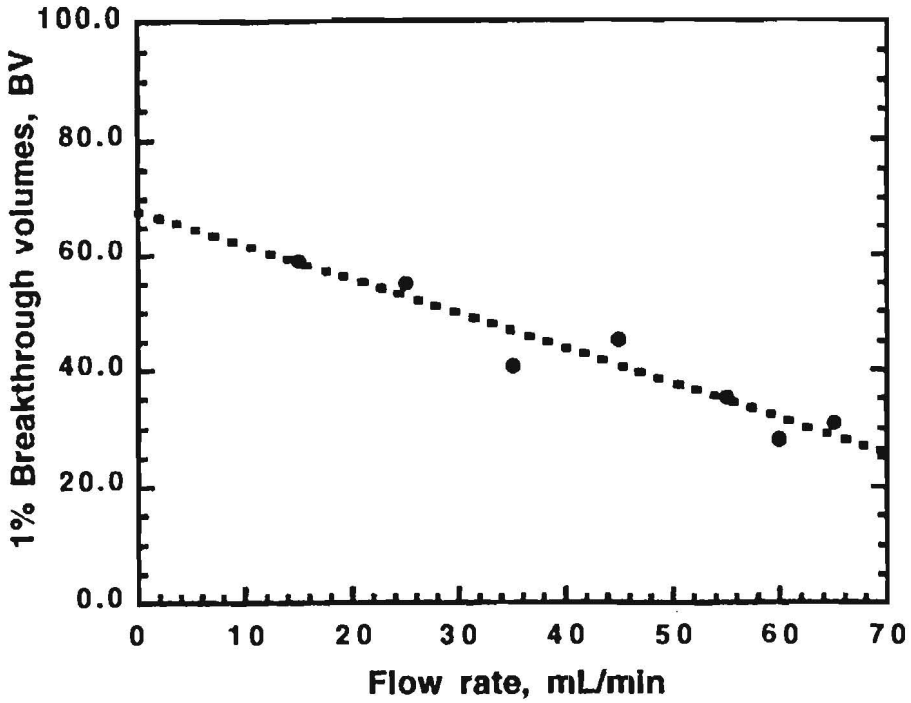


Figure 18. The 1% Breakthrough Volume as a Function of Flow Rate. The straight line is the least-squares fit of the data which results in the equation: Breakthrough volume = (67.8 ± 4.0)BV - (0.600 ± 0.87)(BV min/mL)(Flow rate)(mL/min).

Full breakthrough experiments were run at 60 mL/min for Reillex™-HPQ and a Dowex type resin (AG®MP-1). The Reillex™-HPQ experiment was run first. Unfortunately, the reservoir of DSSF-5 feed was exhausted at the 50% breakthrough point. After 45 hours, additional feed was available and the run was continued to 90% breakthrough. After a period of five days, the resin was eluted at 60 mL/min with the reducing/complexing reagent. (5mM Sn(II)/1.0 M NaOH/1.0 M en). Only 80% of the technetium was recovered, this is significantly lower than the 98.5% (Table 21) recovered in the 60 mL/min flow experiment which eluted technetium immediately after the loading. It is not possible at this point to say that the delay in elution is a true effect or just a poor elution.

For comparison, the experiment was repeated with Bio-Rad AG®MP-1 (20-50 mesh) resin. The run included a 45 hour interruption of the flow at the 50% breakthrough point and a five day delay in the elution. Technetium elution was quantitative in this experiment. Figure 19 shows the breakthrough curves for these two experiments and Table 22 summarizes the breakthrough volumes at various percent pertechnetate retained points by the AG®MP-1 and Reillex™-HPQ resins. The figure illustrates that the Reillex™-HPQ resin was more efficient than the AG®MP-1 resin. Not only is the 1% breakthroughs point three times longer, 27.9 vs. 10.2 BV, the overall retention was of technetium was 40% higher than the AG®MP-1 resin, 70% vs. 52%.

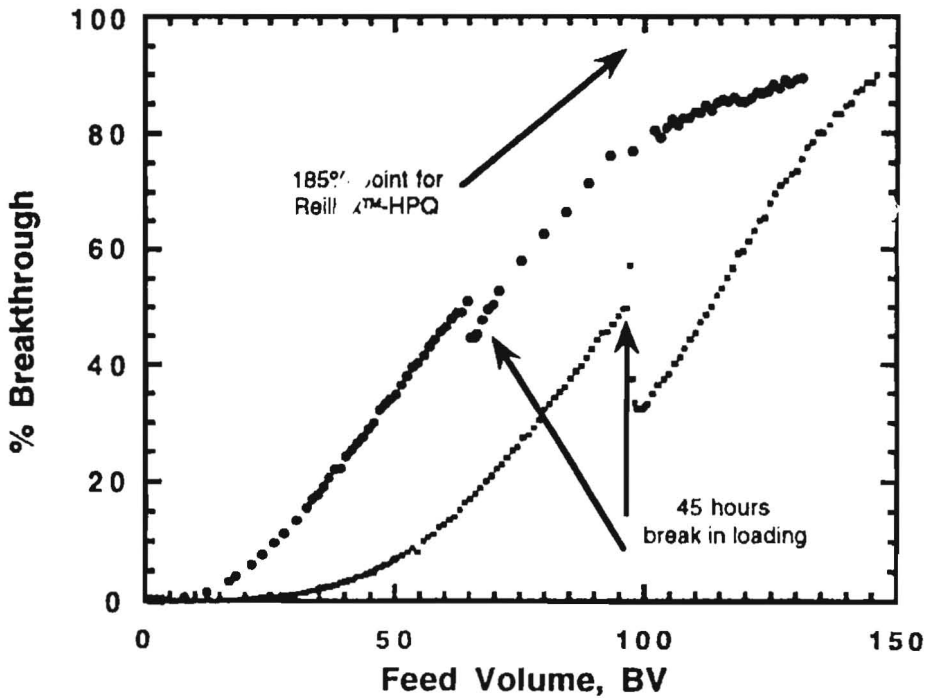


Figure 19. Full Breakthrough Curves for Reillex™-HPQ and AG®MP-1 Resins at 60 mL/min.

The break in the elutions curves at the 50% breakthrough points are interesting. At the restart of the loading procedure both curves have a lower % breakthrough value than before the 45 hour break; and the decrease is three times greater for the Reillex™-HPQ resin. Diffusion of technetium into the

interior of the bead may account for this effect and it may occur faster for the Reillex™-HPQ resin. The shape of the curves is also important. If the offset in the % breakthrough is removed, the curves are continuous. This suggests that the aqueous phase is controlling the rate of sorption.[48]

Table 22. The Breakthrough Volumes and Percent TcO_4^- Retention for the AG®MP-1 and Reillex™-HPQ Resins at 60 mL/min Flow.

	AG®MP-1		Reillex™-HPQ	
% Breakthrough	**BV**	**% Retention**	**BV**	**% Retention**
1	10.2	-	27.9	-
50	63.1	80.2	95.9	86.1
90	132.9	52.3	145.7	69.9
Percent TcO_4^- recovered by elution		**101.7**		**84.7**

12. Analytical Determination of Technetium in 101-SY and 103-SY Tank Waste Samples

The two samples derived from tanks 101-SY and 103-SY were analyzed for ^{99}Tc. Table 23 summarizes the analytical results. The average concentrations are 5.92 (± 0.88) x 10^{-5} and 6.57 (± 0.64) x 10^{-5} M, respectively. The analytical methods used to determine these concentration values varied from relatively simple sample preparations to elaborate methods that included a sulfide precipitation. There did not seem to be any difference in the results. What appears to be important in these procedures is to make the sample acidic with HNO_3, and thoroughly oxidize the sample with ceric. However, these results are significantly different from those obtained by Hanford/PNL; 1.7 x 10^{-5} and 3.5 x 10^{-5}, respectively. In our hands the PNL procedure (PNL-ALO-432), which uses a Cr(VI) oxidation of the sample (in caustic media), gave 7.6 x 10^{-6} and 2.1

x 10^{-5} M, respectively. The absence of good oxidizing conditions may explain these discrepancies.

Table 23. Technetium Concentrations in 101-SY and 103-SY Waste Samples.

Sample #	101-SY	103-SY
1	6.71 x 10^{-5}	7.60 x 10^{-5}
2	4.98 x 10^{-5}	6.64 x 10^{-5}
3	4.67 x 10^{-5}	6.26 x 10^{-5}
4	6.51 x 10^{-5}	5.77 x 10^{-5}
5	6.53 x 10^{-5}	7.02 x 10^{-5}
6	6.10 x 10^{-5}	6.96 x 10^{-5}
Average	**5.92 ± (0.88) x 10^{-5}**	**6.71 ± (0.64) x 10^{-5}**

13. Technetium K_d values from 101-SY and 103-SY Waste Samples

The average batch $^{Tc}K_d$ values measured on the 101-SY and 103-SY samples are 3.99 ± (0.19) and 5.16 ± (0.44) mL/g, respectively. These distribution coefficients, shown in Table 24, are much lower than the expected values of 1050 and 850 mL/g obtained from 101-SY and 103-SY simulant studies (Figure 9). These results indicate that approximately 65% of the technetium was not present as pertechnetate. We have obtained independent measurement of the pertechnetate concentrations in the 101-SY and 103-SY waste samples by ^{99}Tc NMR. Figure 20 shows a spectrum of $^{99}TcO_4^-$ in the as received 103-SY sample. These concentrations measured were 1.57 ± (0.46) x 10^{-5} and 2.30 ± (0.58) x 10^{-5} M, respectively. Completely oxidized waste samples, however, contained 4.19 ± (1.22) x 10^{-5} and 7.70 ± (1.96) x 10^{-5} M pertechnetate. These values are consistent with the radiochemical concentrations in Table 23. These

data indicate that only 37% and 30% of the technetium, respectively, is available for sorbing as pertechnetate from the waste samples. The NMR data is consistent with our radiochemical data. Based on the available pertechnetate concentrations the NMR data predicts $^{Tc}K_d$ values of 6.0 ± (1.3) and 4.0 ± (2.0) mL/g, for the 101-SY and 103-SY waste samples, respectively.

The batch $^{Tc}K_d$ values measured are not true distribution coefficients since the technetium species do not appear to be in equilibrium. The technetium fraction that does not sorb is intractable. When the supernate from the batch K_d measurement is contacted again with fresh resin no technetium sorbs.

14. Feed Adjustment Chemistry

Oxidation of the 103-SY waste was tried with bromate, hydrogen peroxide at 40°C, and bleach. Results are shown in Table 25. A 10% excess of oxidant was used in each case; the amount of oxidant required was based on ceric titrations under acidic conditions. Batch contacts after 2 hours reaction time gave $^{Tc}K_d$ of 5.96 and 4.84 for the first two oxidants indicating little or no oxidation. Bleach was more effective yielding a $^{Tc}K_d$ of 30.24. Increasing the reaction time or the ratio of bleach:technetium improved the $^{Tc}K_d$ values. Even so 20-25% of the technetium is still not pertechnetate. More rigorous "Feed Adjustment Chemistry" needs to be tried to bring technetium up to pertechnetate, the form needed to sorb onto an anion exchange resin, an extractant like Aliquat 336, or any other technetium partitioning method that relies on the pertechnetate anion being present!

Table 24. Technetium Distribution Coefficients Between Reillex™-HPQ and 101-SY and 103-SY Waste Samples.

Sample #	101-SY	103-SY
1	4.06	5.61
2	3.79	5.22
3	4.15	4.55
4		5.25
Average	**3.99 ± (0.19)**	**5.16 ± (0.44)**

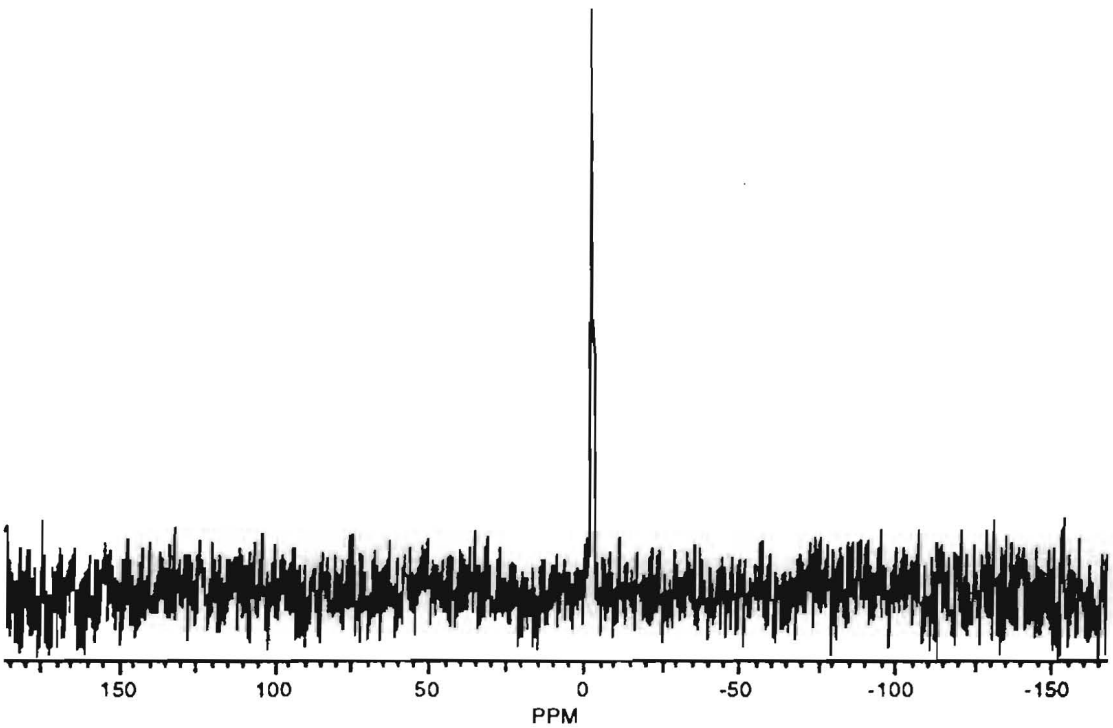


Figure 20. Technetium-99 NMR Spectrum of the 103-SY Waste Sample.

Table 25. Effect of Oxidants on the $^{Tc}K_d$ Values for 103-SY.

Oxidant	[Ox]/[Tc]	(Hrs)	$^{Tc}K_d$	% Not TcO_4^-
BrO_3^-	1	1	5.96	62.6
H_2O_2	1	1	4.84	70.4
NaOCl	1	1	30.24	29.7
NaOCl	1	3	38.76	24.8
NaOCl	1	24	45.45	21.9
NaOCl	2	1	44.36	25.9

15. Radiolytic Stability of Reillex™-HPQ in 101-SY and 103-SY Matrixes

Reillex™-HPQ was placed in each of the waste solutions for 9 weeks. The K_d values measured at the end of this period were essentially the same as the values obtained with only 2 hours of contact. The recovered resins though, after cleaning up, gave K_d values that were an order of magnitude lower than expected when contacted with the corresponding simulant. Results are shown in Table 26.

Table 26. Radiolytic Stability $^{Tc}K_d$ Values.

Matrix	9 Weeks $^{Tc}K_d$	2 Hours $^{Tc}K_d$
103-SY	5	5
101-SY	4	4
103-SY Sim	110	850
101-SY Sim	110	1000

CONCLUSIONS

This work has resulted in a number of conclusions, which are outlined below.

1. Reillex™-HPQ anion exchange resin continues to show good performance as a technology for partitioning technetium from Hanford waste streams.

2. Addition of ^{95m}Tc tracer to simulants containing macro concentrations of ^{99}Tc improves the efficiency of this research.

3. Reillex™-HPQ anion exchange resin efficiently sorbs technetium from DSSF-5 101-SY and 103-SY simulants; distribution coefficients are >200 from these matrixes. The rate of technetium sorption from these simulants follows the order DSSF-5 > 101-SY > 103-SY

4. Reillex™-HPQ sorbs technetium faster from DSSF-5 simulants than AG™MP-1 resin. The AG™MP-1 resin appears not to wet as well as Reillex™-HPQ.

5. The fundamental behavior of pertechnetate with Reillex™-HPQ resin is understood in caustic nitrate solutions. This behavior is described by the relationship $K_d = K_2 \bullet R_t / \{K_4 \bullet [OH^-] + [NO_3^-]\}$ where K_2 and K_4 are the equilibrium constants, respectively, for the exchange of TcO_4^- and OH^- with the nitrate form of Reillex™-HPQ, and R_t is the total concentration of resin sites in either the nitrate or hydroxide form. This information can be used at Hanford to estimate the sorption of pertechnetate onto Reillex™-HPQ resin from tank supernates, and sludge washing and leaching solutions.

6. Perrhenate behaves like pertechnetate with Reillex™-HPQ resin. Developmental work using perrhenate can be used to predict the behavior of pertechnetate; university collaborators working with rhenium can produce data that is applicable to pertechnetate.

7. Alkyl derivatives of Reillex™-HP resin appear to show a maximum technetium sorption when the alkyl substituent is butyl.

8. Sn(II)/en/NaOH solutions are effective eluents for removing technetium from Reillex™-HPQ, many alkyl derivatives of Reillex™-HP resin, and other strong base resins; the eluent appears to be generic.

9. Reillex™-HPQ resin loses ≈ 30% of its capacity in 2 M NaOH. This apparently due to low molecular weight polymers washing from the resin bead. These are possibly formed during the alkylation process since Reillex™-HP, the parent resin, does not lose capacity in base.

10. A 2.54 x 50 cm Reillex™-HPQ resin column can be used repetitively over a 100 day service period. Recovery of technetium over this period service is nearly quantitative.

11. Flow rate studies with 2.54 x 50 cm Reillex™-HPQ resin columns shows that the 1% breakthrough point varies inversely and linearly with the flow rate.

12. Full breakthrough experiments shows that Reillex™-HPQ columns are more efficient than AG™MP-1 columns.

13. Technetium K_d values, radiochemical analyses and 99Tc NMR data show that ≈ 70% of the technetium in the 101-SY and 103-SY waste samples is not pertechnetate. Oxidation of these non-pertechnetate forms is not readily achieved.

FUTURE WORK

A major result of our FY95 work was the discovery that a large fraction of technetium in the waste samples that we received was not pertechnetate. This problem is significant because it may effect the feasibility of separating technetium from tank waste. DOE is spending a significant amount of money developing methods (including anion exchange, extractions using Aliquat, crown ethers, PEG, etc.) to partition pertechnetate from the waste. If technetium is not pertechnetate, or not readily converted to pertechnetate, these methods may fail. Failure to address this problem may result in a greater financial loss by building a plant that is incapable of processing the waste. This would be a

major embarrassment to DOE and its contractors and further erode the public's confidence in our ability to solve nuclear waste problems.

Future work to resolve this problem:

- If the technetium results for the 101-SY and 103-SY derived samples continue to show higher than expected technetium concentrations and low technetium distribution coefficients, then we should obtain, analyze, and measure the $^{Tc}K_d$ values for the unaltered 101-SY and 103-SY samples
- If the results for the 101-SY and 103-SY unaltered samples are positive, then a suite of ten samples representing 10 waste types from the Hanford tanks should be tested for total technetium and their technetium K_d values measured. This will determine if the problem is generic.
- Characterize or determine the technetium species in the tanks. Determine their physical and chemical properties in order to develop the feed adjustment chemistry for the waste stream.
- Develop feed adjustment chemistry. Possible solutions would involve examining oxidizing agents for the feed matrices, electrolytic oxidation, or destroying the matrix with hydrothermal treatment.
- The ^{99}Tc NMR method should be developed further to help determine ^{99}Tc chemical speciation. This is a non-destructive analytical method which uses < 1.5 mL of sample. It would be useful for developing the feed adjustment chemistry because we could follow the oxidation non-pertechnetate species to $^{99}TcO_4^-$.
- Reillex™-HPQ studies with the adjusted feed should be performed to verify its performance relative to what is expected from simulant work. Since we have developed a fundamental understanding of pertechnetate with this resin we should be able to verify the success of the feed adjustment.

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Appendix A

2.54 x 50 cm Column Experiments
Experimental and Result Summaries for Sustainability Studies

BT-1:

Amount of resin used:	257.4 mL
Bed Volume After Water Classification (Gravity Settling):	257.4 mL
Bed Volume After 2 BV of Shrinking Solution run through column:	249.8 mL
Bed Volume of Resin after Breakthrough:	244.2 mL
Percent Shrinkage of Column:	5.13%
Counts per 4 mL of DSSF Simulant	6249.7 CPM
1% breakthrough volume @ 1.00%, Bed Volume	59.1 BV

Loading

Solution	Direction, mL/min	# Fractions	Total Volume, L	Total CPM Through column
DSSF-5	Downflow, 15	59	14.75	38,878

Elution

Solution	Direction, mL/min	# Fractions	Total Volume; mL, (BV)	Total CPM
1.0 M NaOH	Downflow, 15	3	750, (3.07)	20,875
A	Upflow, 1.5	66	495, (2.03)	20,606,462
C	Upflow, 1.5	80	615, (2.52)	157,659
B	Upflow, 1.5	1	1353, (5.54)	9,606
1.0 M NaOH	Downflow, 0.33	2	1363, (5.58)	103,010
D	Downflow, 15	1	750, (3.07)	22,313

Inventory

Added, CPM	Bleed, CPM	Total Eluted, CPM	% Eluted	Amount left on Column, CPM
23,046,000	38,878	20,958,803	90.94	2,087,197

A: Solution is 1.0 M NaOH, 1.0 M ethylenediamine, and 0.010 M $SnCl_2 \cdot 2\ H_2O$.
B: Solution is 1.0 M NaOH and 1.0 M ethylenediamine.
C: Solution is 1.0 M NaOH and 0.10 M ethylenediamine.
D: Solution is 2.0 M NaOH and 6.0 M $NaNO_3$.

BT-2:

Initial Bed Volume:	237.1 mL
Bed Volume of Resin after Breakthrough:	233.6 mL
Percent Shrinkage of Column:	1.48%
Counts per 4 mL of DSSF Simulant	6,360.4 CPM
1% breakthrough volume @ 4.17%, Bed Volume	58.7 BV

Loading

Solution	Direction, mL/min	# Fractions	Total Volume, L	Total CPM Through column
DSSF-5	Downflow, 15	65	14.45	812,650

Elution

Solution	Direction, mL/min	# Fractions	Total Volume; mL, (BV)	Total CPM
B	Upflow, 1.5	100	750, (3.21)	4,72[illegible]875
B	Upflow, 0.33	1	1000, (4.28)	5,755,500
B	Upflow, 0.33	4	40, (0.17)	664,174
A	Upflow, 1.5	69	522.0, (2.17)	10,630,726
A	Upflow, 0.22	45	225.0, (0.96)	42,793
A	Upflow, 1.5	12	88.4, (0.38)	5,777
B	Upflow, 1.5	80	600, (2.57)	29,387
1.0 M NaOH	Upflow, 0.33	10	45, (0.19)	5,823
B	Upflow, 0.33	3	2250, (9.63)	46,875
1.0 M NaOH	Upflow, 15	2	2000, (8.56)	250
C	Upflow, 15	1	1000, (4.28)	12,250

Inventory

Added, CPM	Bleed, CPM	Total Eluted, CPM	% Eluted	Amount left on Column, CPM
22,977,000	812,650	22,731,080	98.93	245,920

A: Solution is 1.0 M NaOH, 1.0 M ethylenediamine, and 0.005 M $SnCl_2 \cdot 2\ H_2O$.
B: Solution is 1.0 M NaOH and 1.0 M ethylenediamine.
C: Solution is 2.0 M NaOH and 6.0 M $NaNO_3$.

BT-3:

Initial Bed Volume:	233.6 mL
Bed Volume of Resin after Breakthrough:	232.71 mL
Percent Shrinkage of Column:	0.38%
Counts per 4 mL of DSSF Simulant	6,423.7 CPM
1% breakthrough volume @ 3.40%, Bed Volume	57.9 BV

Loading

Solution	Direction, mL/min	# Fractions	Total Volume, L	Total CPM Through column
DSSF-5	Downflow, 15	58	14.5	561,438

Elution

Solution	Direction, mL/min	# Fractions	Total Volume; mL, (BV)	Total CPM
B	Upflow, 15	15	750, (3.22)	935 988
A	Upflow, 15	21	950, (4.08)	20,907,200

Inventory

Added, CPM	Bleed, CPM	Total Eluted, CPM	% Eluted	Amount left on Column, CPM
23,285,913	561,438	22,404,625	96.22	881,288

A: Solution is 1.0 M NaOH, 1.0 M ethylenediamine, and 0.005 M $SnCl_2 \cdot 2\ H_2O$.
B: Solution is 1.0 M NaOH and 1.0 M ethylenediamine.

BT-4:

Initial Bed Volume:	232.71 mL
Bed Volume of Resin after Breakthrough:	230.55 mL
Percent Shrinkage of Column:	0.93%
Counts per 4 mL of DSSF Simulant	6,621.6 CPM
1% breakthrough volume @ 1.36%, Bed Volume	58.4 BV

Loading

Solution	Direction, mL/min	# Fractions	Total Volume, L	Total CPM Through column
DSSF-5	Downflow, 15	56	14.00	122,938

Elution

Solution	Direction, mL/min	# Fractions	Total Volume; mL, (BV)	Total CPM
C	Downflow, 15	15	750, (3.25)	272,625
B	Upflow, 15	15	750, (3.25)	159,038
A	Upflow, 15	16	1000, (4.34)	21,651,944

Inventory

Added, CPM	Bleed, CPM	Total Eluted, CPM	% Eluted	Amount left on Column, CPM
23,175,600	122,938	22,206,545	95.82	969,055

A: Solution is 1.0 M NaOH, 1.0 M ethylenediamine, and 0.005 M $SnCl_2 \cdot 2\ H_2O$.
B: Solution is 1.0 M NaOH and 1.0 M ethylenediamine.
C: Solution is 2.0 M NaOH and 6.0 M $NaNO_3$.

BT-5:

Initial Bed Volume:	230.55 mL
Bed Volume of Resin after Breakthrough:	230.55 mL
Percent Shrinkage of Column:	0 %
Counts per 4 mL of DSSF Simulant	7368.4 CPM
1% breakthrough volume @ 1.29%, Bed Volume	53.2 BV

Loading

Solution	Direction, mL/min	# Fractions	Total Volume, L	Total CPM Through column
DSSF-5	Downflow, 15	15	13.750	133,875

Elution

Solution	Direction, mL/min	# Fractions	Total Volume; mL, (BV)	Total CPM
B	Downflow, 15	3	750, (3.25)	221,313
A	Upflow, 15	15	750, (3.25)	20,782,400

Inventory

Added, CPM	Bleed, CPM	Total Eluted, CPM	% Eluted	Amount left on Column, CPM
25,328,875	133,875	21,137,588	83.45	4,191,287

A: Solution is 1.0 M NaOH, 1.0 M ethylenediamine, and 0.005 M $SnCl_2 \cdot 2\ H_2O$.
B: Solution is 2.0 M NaOH and 6.0 M $NaNO_3$.

BT-6:

Initial Bed Volume:	230.55 mL
Bed Volume of Resin after Breakthrough:	230.55 mL
Percent Shrinkage of Column:	0 %
Counts per 4 mL of DSSF Simulant	7457.6 CPM
1% breakthrough volume @ 1.40%, Bed Volume	51.0 BV

Loading

Solution	Direction, mL/min	# Fractions	Total Volume, L	Total CPM Through column
DSSF-5	Downflow, 15	44	12.53	148,268

Elution

Solution	Direction, mL/min	# Fractions	Total Volume; mL, (BV)	Total CPM
C	Downflow, 15	1	250, (1.08)	126,188
B	Upflow, 16.5	1	250, (1.08)	298,313
A	Upflow, 15	19	954, (4.14)	22,207,251
B	Upflow, 0.30	1	250,(1.08)	31,375

Inventory

Added, CPM	Bleed, CPM	Total Eluted, CPM	% Eluted	Amount left on Column, CPM
23,325,322	148,268	22,811,395	97. 78	513,827

A: Solution is 1.0 M NaOH, 1.0 M ethylenediamine, and 0.005 M $SnCl_2 \cdot 2\ H_2O$.
B: Solution is 1.0 M NaOH and 1.0 M ethylenediamine.
C: Solution is 2.0 M NaOH and 6.0 M $NaNO_3$.

The column was repacked and reclassified by backwashing with water after this experiment. The increase in resin volume is due to this, and not to a change in the The column was repacked and reclassified by backwashing with water after this resin itself.

BT-7:

Initial Bed Volume:	238.6 mL
Bed Volume of Resin after Breakthrough:	238.6 mL
Percent Shrinkage of Column:	0 %
Counts per 4 mL of DSSF Simulant	6847.6 CPM
1% breakthrough volume @ 1.55%, Bed Volume	43.8 BV

Loading

Solution	Direction, mL/min	# Fractions	Total Volume, L	Total CPM Through column
DSSF-5	Downflow, 15	48	11.750	249,488

Elution

Solution	Direction, mL/min	# Fractions	Total Volume; mL, (BV)	Total CPM
C	Downflow, 15	1	250, (1.08)	139,138
B	Upflow, 15	4	822, (3.45)	441,556
A	Upflow, 15	4	900, (3.77)	19,394,400
B	Upflow, 1.5	2	500, (2.10)	30,625

Inventory

Added, CPM	Bleed, CPM	Total Eluted, CPM	% Eluted	Amount left on Column, CPM
20,114,825	249,488	20,255,507	100.70	0

A: Solution is 1.0 M NaOH, 1.0 M ethylenediamine, and 0.005 M $SnCl_2 \cdot 2\ H_2O$.
B: Solution is 1.0 M NaOH and 1.0 M ethylenediamine.
C: Solution is 2.0 M NaOH and 6.0 M $NaNO_3$.

BT-8:

Initial Bed Volume:	230.6 mL
Bed Volume of Resin after Breakthrough:	228.5 mL
Percent Shrinkage of Column:	0.91%
Counts per 4 mL of DSSF Simulant	11,411 CPM
1% breakthrough volume @ 1.39%, Bed Volume	40.0 BV

Loading

Solution	Direction, mL/min	# Fractions	Total Volume, L	Total CPM Through column
DSSF-5	Downflow, 15	29	10.400	235,163

Elution

Solution	Direction, mL/min	# Fractions	Total Volume; mL, (BV)	Total CPM
C	Downflow, 15	1	250, (1.09)	163438
B	Upflow, 15	3	750, (3.28)	661,188
A	Upflow, 15	17	850, (3.72)	28,536,775
B	Upflow, 1.5	6	9,250, (40.48)	274,125

Inventory

Added, CPM	Bleed, CPM	Total Eluted, CPM	% Eluted	Amount left on Column, CPM
28,975,050	235,163	29,870,689	103.09	0.00

A: Solution is 1.0 M NaOH, 1.0 M ethylenediamine, and 0.005 M $SnCl_2 \cdot 2\ H_2O$.
B: Solution is 1.0 M NaOH and 1.0 M ethylenediamine.
C: Solution is 2.0 M NaOH and 6.0 M $NaNO_3$.

BT-9:

Amount of resin used:	222.4 mL
Bed Volume of Resin after Breakthrough:	222.2 mL
Percent Shrinkage of Column:	0.00%
Counts per 4 mL of DSSF Simulant	8032 CPM
1% breakthrough volume @ 1.00%, Bed Volume	44.1 BV

Loading

Solution	Direction, mL/min	# Fractions	Total Volume, L	Total CPM Through column
DSSF-5	Downflow, 15	31	10.50	82625

Elution

Solution	Direction, mL/min	# Fractions	Total Volume; mL, (BV)	Total CPM
C	Downflow, 15	1	250, (1.09)	32,063
B	Upflow, 15	2	500, (2.19)	326,500
A	Upflow, 15	15	750, (3.28)	20,943,188
A	Upflow, 1.5	1	250, (1.09)	17,938
C	Upflow, 0.33	4	7000, (30.64)	66,000

Inventory

Added, CPM	Bleed, CPM	Total Eluted, CPM	% Eluted	Amount left on Column, CPM
21,084,000	82,625	21,468,314	101.82	0.00

A: Solution is 1.0 M NaOH, 1.0 M ethylenediamine, and 0.005 M $SnCl_2 \cdot 2\ H_2O$.
B: Solution is 1.0 M NaOH and 1.0 M ethylenediamine.
C: Solution is 2.0 M NaOH and 6.0 M $NaNO_3$.

BT-10:

Initial Bed Volume:	222.4 mL
Bed Volume of Resin after Breakthrough:	222.4 mL
Percent Shrinkage of Column:	0.00%
Counts per 4 mL of DSSF Simulant	6249 CPM
1% breakthrough volume @ 1.15%, Bed Volume	39.8 BV

Loading

Solution	Direction, mL/min	# Fractions	Total Volume, L	Total CPM Through column
DSSF-5	Downflow, 15	28	9.500	59,023

Elution

Solution	Direction, mL/min	# Fractions	Total Volume; mL, (BV)	Total CPM
C	Downflow, 15	3	560, (2.52)	48,960
B	Upflow, 15	3	750, (3.37)	236,125
A	Upflow, 15	16	1000, (4.50)	15,059,375
B	Upflow, 1.5	4	9000, (40.46)	59,250

Inventory

Added, CPM	Bleed, CPM	Total Eluted, CPM	% Eluted	Amount left on Column, CPM
14,841,375	59,023	15,462,733	104.19	0.00

A: Solution is 1.0 M NaOH, 1.0 M ethylenediamine, and 0.005 M $SnCl_2 \cdot 2\ H_2O$.
B: Solution is 1.0 M NaOH and 1.0 M ethylenediamine.
C: Solution is 2.0 M NaOH and 6.0 M $NaNO_3$.

BT-11:

Initial Bed Volume:	214.8 mL
Bed Volume of Resin after Breakthrough:	214.8 mL
Percent Shrinkage of Column:	0.00%
Counts per 4 mL of DSSF Simulant	7301 CPM
1% breakthrough volume @ 1.10%, Bed Volume	39.3 BV

Loading

Solution	Direction, mL/min	# Fractions	Total Volume, L	Total CPM Through column
DSSF-5	Downflow, 15	27	9.500	65,866

Elution

Solution	Direction, mL/min	# Fractions	Total Volume; mL, (BV)	Total CPM
C	Downflow, 15	3	715, (3.24)	960,124
B	Upflow, 15	3	750, (3.37)	583,000
A	Upflow, 15	16	1000, (4.50)	15,485,550

Inventory

Added, CPM	Bleed, CPM	Total Eluted, CPM	% Eluted	Amount left on Column, CPM
17,339,875	65,866	17,094,540	98.59	1.41%

A: Solution is 1.0 M NaOH, 1.0 M ethylenediamine, and 0.005 M $SnCl_2 \cdot 2\,H_2O$.
B: Solution is 1.0 M NaOH and 1.0 M ethylenediamine.
C: Solution is 2.0 M NaOH and 6.0 M $NaNO_3$.

Appendix B

2.54 x 50 cm Column Experiments
Experimental and Result Summaries for Column Flow Rate Studies

Flow 1:

Bed volume after Water Classification (Gravity Settling):	268.0 mL
Bed volume after water pumped through column:	257.4 mL
Bed volume after 1BV of Shrinking Solution through column:	249.8 mL
Percent shrinkage of column:	2.95%
Flow rate of Feed	25.0 mL/min
Breakthrough Volume (1%):	54.9 BV
Total Percent Recovery	97.9 %

Loading

Solution	Direction, mL/min	# Fractions	Total Volume, L	Total CPM Through column
DSSF-5	Downflow, 25	57	14.25	34,013

Elution

Solution	Direction, mL/min	# Fractions	Total Volume; mL, (BV)	Total CPM
B	Upflow, 25	15	750, (3.00)	1,060,175
A	Upflow, 25	14	975, (4.90)	22,142,644

Inventory

Added, CPM	Bleed, CPM	Total Eluted, CPM	% Eluted	Amount left on Column, CPM
24,704,513	34,013	23,236,831	94.1	907,773

A: Solution is 1.0 M NaOH, 1.0 M ethylenediamine, and 0.005 M $SnCl_2 \cdot 2\ H_2O$.

B: Solution is 1.0 M NaOH and 1.0 M ethylenediamine.

Flow 2:

Bed volume after Water Classification (Gravity Settling):	267.8 mL
Bed volume after water pumped through column:	257.4 mL
Bed volume after 1BV of Shrinking Solution through column:	246.3 mL
Bed volume after DSSF Solution through column:	246.0 mL
Percent shrinkage of column:	4.45%
Flow rate of Feed	35.0 mL/min
Breakthrough Volume (1%):	41.3 BV
Total Percent Recovery	106.0 %

Loading

Solution	Direction, mL/min	# Fractions	Total Volume, L	Total CPM Through column
DSSF-5	Downflow, 35	50	12.5	103,000

Elution

Solution	Direction, mL/min	# Fractions	Total Volume; mL, (BV)	Total CPM
B	Upflow, 35	15	750, (3.05)	1,063,988
A	Upflow, 35	17	850, (3.46)	20,801,013

Inventory

Added, CPM	Bleed, CPM	Total Eluted, CPM	% Eluted	Amount left on Column, CPM
20,621,875	103,000	21,968,001	106.0	47,882*

A: Solution is 1.0 M NaOH, 1.0 M ethylenediamine, and 0.005 M $SnCl_2 \cdot 2\ H_2O$.

B: Solution is 1.0 M NaOH and 1.0 M ethylenediamine.

*This number is taken from counts of the resin itself, after the experiment was over.

Flow 3:

Bed volume after Water Classification (Gravity Settling):	274.6 mL
Bed volume after water pumped through column:	274.6 mL
Bed volume after 1BV of Shrinking Solution through column:	259.4 mL
Bed volume after beginning of flow	257.2 mL
Percent shrinkage of column:	0.85 %
Flow rate of Feed	45.0 mL/min
Breakthrough Volume (1%):	44.8 BV
Total Percent Recovery	91.9 %

Loading

Solution	Direction, mL/min	# Fractions	Total Volume, L	Total CPM Through column
DSSF-5	Downflow, 45	52	13.0	73,875

Elution

Solution	Direction, mL/min	# Fractions	Total Volume; mL, (BV)	Total CPM
B	Upflow, 45	1	250, (0.97)	12,625
A	Upflow, 45	19	940, (3.65)	22,884,475

Inventory

Added, CPM	Bleed, CPM	Total Eluted, CPM	% Eluted	Amount left on Column, CPM
24,991,850	73,875	22,970,975	91.9	52,408*

A: Solution is 1.0 M NaOH, 1.0 M ethylenediamine, and 0.005 M $SnCl_2 \cdot 2\ H_2O$.

B: Solution is 2.0 M NaOH and 6.0 M $NaNO_3$.

*This number is taken from counts of the resin itself, after the experiment was over.

Flow 4:

Bed volume after Water Classification (Gravity Settling):	265.5 mL
Bed volume after 1BV of Shrinking Solution through column:	251.6 mL
Percent shrinkage of column:	5.24%
Flow rate of Feed	55.0 mL/min
Breakthrough Volume (1%):	35.2 BV
Total Percent Recovery	98.5 %

Loading

Solution	Direction, mL/min	# Fractions	Total Volume, L	Total CPM Through column
DSSF-5	Downflow, 55	44	11.0	92,625

Elution

Solution	Direction, mL/min	# Fractions	Total Volume; mL, (BV)	Total CPM
B	Upflow, 55	5	250, (0.99)	12,200
A	Upflow, 55	18	900, (3.58)	15,0[illegible]2,263

Inventory

Added, CPM	Bleed, CPM	Total Eluted, CPM	% Eluted	Amount left on Column, CPM
15,385,700	92,625	15,157,088	98.5	174,613

A: Solution is 1.0 M NaOH, 1.0 M ethylenediamine, and 0.005 M $SnCl_2 \cdot 2\ H_2O$.

B: Solution is 2.0 M NaOH and 6.0 M $NaNO_3$.

Flow 5:

Bed volume after Water Classification (Gravity Settling):	274.6 mL
Bed volume after water pumped through column:	258.3 mL
Bed volume after 1BV of Shrinking Solution through column:	244.5 mL
Percent shrinkage of column:	10.96 %
Flow rate of Feed	65.0 mL/min
Breakthrough Volume (one per cent):	31.0 BV
Total Percent Recovery	98.5 %

Loading

Solution	Direction, mL/min	# Fractions	Total Volume, L	Total CPM Through column
DSSF-5	Downflow, 65	38	9.5	66,188

Elution

Solution	Direction, mL/min	# Fractions	Total Volume; mL, (BV)	Total CPM
B	Upflow, 65	5	250, (1.02)	10,513
A	Upflow, 65	15	750, (3.07)	12,738,950

Inventory

Added, CPM	Bleed, CPM	Total Eluted, CPM	% Eluted	Amount left on Column, CPM
13,008,663	66,188	12,815,561	98.5	31,421*

A: Solution is 1.0 M NaOH, 1.0 M ethylenediamine, and 0.005 M $SnCl_2 \cdot 2\ H_2O$.

B: Solution is 1.0 M NaOH and 1.0 M ethylenediamine.

*This number is taken from counts of the resin itself, after the experiment was over.

Flow 6:

Bed volume after Water Classification (Gravity Settling):	259.84 mL
Bed volume after 1BV of Shrinking Solution through column:	245.09 mL
Percent shrinkage of column:	5.68 %
Flow rate of Feed	5.0 mL/min
Breakthrough Volume (one per cent):	12 BV
Total Percent Recovery	64.2 %

Loading

Solution	Direction, mL/min	# Fractions	Total Volume. L	Total CPM Through column
DSSF-5	Downflow, 5	62	21.112	2,565,475

Elution

Solution	Direction, mL/min	# Fractions	Total Volume; mL, (BV)	Total CPM
A	Upflow, 5	10	1000,	19,681,850

Inventory

Added, CPM	Bleed, CPM	Total Eluted, CPM	% Eluted	Amount left on Column, CPM
34,635,292	2,565,475	22,247,325	64.2	12,387,967*

A: Solution is 1.0 M NaOH, 1.0 M ethylenediamine, and 0.005 M $SnCl_2 \cdot 2\ H_2O$.

B: Solution is 1.0 M NaOH and 1.0 M ethylenediamine.

*This number is derived from the amount of counts known to have been added and the number of counts eluted from the column.

**The data from this run are not trustworthy, nor are they indicative of the results one would obtain at this flow rate. The breakthrough curve from this experiment leads us to believe that the column was badly packed. Time constraints did not allow for a repetition of the experiment, though the necessity of doing so is acknowledged. A breakthrough experiment at this flow rate will be performed at a later time.

Flow 7:

Bed volume after 1BV of Shrinking Solution through column:	236.6 mL
Flow rate of Feed	60.0 mL/min
Breakthrough Volume (one per cent):	28.1 BV
Total Percent Recovery	84.7 %

Loading

Solution	Direction, mL/min	# Fractions	Total Volume, L	Total CPM Through column
1)DSSF-5	Downflow, 60	118	22.782	4,967,608
2)DSSF-5	Downflow, 60	53	11.706	12,188,831

The first part of the loading loaded the column to 49.79% of breakthrough. Loading was resumed 45 hours later. The column was then loaded to 90.01% of breakthrough.

Elution

Solution	Direction, mL/min	# Fractions	Total Volume; mL, (BV)	Total CPM
B	Upflow, 60	24	2733, (11.53)	27,032,323
A	Upflow, 60	3	750, (3.17)	64,376

Inventory

Added, CPM	Bleed, CPM	Total Eluted, CPM	% Eluted	Amount left on Column, CPM
55,244,603	17,156,439	44,253,138	84.7	10,991,467

A: Solution is 1.0 M NaOH, 1.0 M ethylenediamine, and 0.005 M $SnCl_2 \cdot 2\ H_2O$.

B: Solution is 1.0 M NaOH and 1.0 M ethylenediamine.

Flow 8:

Resin is AG®MP-1

Bed volume after Water Classification (Gravity Settling):	263.99 mL
Bed volume after 1BV of Shrinking Solution through column:	224.47 mL
Percent shrinkage of column:	14.97 %
Flow rate of Feed	60 mL/min
Breakthrough Volume (one per cent):	10.65 BV
Total Percent Recovery	101.7 %

Loading

Solution	Direction, mL/min	# Fractions	Total Volume, L	Total CPM Through column
1)DSSF-5	Upflow, 60	42	14.5	5,742,700
2)DSSF-5	Upflow, 60	40	14.9	22,253,513

The first part of the loading loaded the column to 51.0% of breakthrough. Loading was resumed 45 hours later. The column was then loaded to 89.4% of breakthrough.

Elution

Solution	Direction, mL/min	# Fractions	Total Volume; mL, (BV)	Total CPM
A	Upflow, 60	11	1100 (4.9)	31,692,150

Inventory

Added, CPM	Bleed, CPM	Total Eluted, CPM	% Eluted	Amount left on Column, CPM
58,677,825	27,996,213	59,688,363	101.7	0.0

A: Solution is 1.0 M NaOH, 1.0 M ethylenediamine, and 0.005 M $SnCl_2 \cdot 2\ H_2O$.

Appendix C

Copy of paper in press to *Solvent Extraction and Ion Exchange*

"Sorption Behavior of Perrhenate Ion on Reillex™-HP Anion Exchange Resin from Nitric Acid and Sodium Nitrate/Hydroxide Solutions"

SORPTION BEHAVIOR OF PERRHENATE ION ON REILLEX™-HP ANION EXCHANGE RESIN FROM NITRIC ACID AND SODIUM NITRATE/HYDROXIDE SOLUTIONS

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ABSTRACT

The distribution coefficients (K_d') are reported for perrhenate on the nitrate form of Reillex™-HP, a weak base anion exchange resin, as a function of nitric acid concentration from 0.100 to 10.0 M. Perrhenate K_d' values were determined in 1.00 M $NaNO_3$ from pH 2 to 13. The K_d' values were determined in solutions containing 1.35 M $NaNO_3$ and variable NaOH, 0.155 to 4.66 M, and in solutions containing 0.655 M NaOH and variable $NaNO_3$, 0.46 to 5.35 M. Maximum perrhenate loadings were <2.7% of theoretical capacity. The K_d' is defined by the following equation:

$$K_d' = \frac{Re_{total} - [Re]_{sol} \times V_{sol}}{\text{mass of dry resin}} \Big/ \frac{[Re]_{sol} \times V_{sol}}{V_{sol}} \quad \text{mL/g}$$

The total mmol of rhenium initially added is Re_{total} and $[Re]_{sol}$ is the analytical molarity of rhenium in V_{sol} mL of solution after a batch contact. At 1.0 M HNO_3 the value of K_d' is 73 mL/g. The behavior of the perrhenate system in acid can be described by assuming that perrhenic acid, $HReO_4$, is formed with a derived acid dissociation constant of about 6.5 M. In 1.00 M $NaNO_3$ from pH 2 to 13 the sorption behavior is initially what is expected for a weak base resin with an acid dissociation constant of 1.24×10^{-5} M. Thus, the K_d' value decreases with pH values above the pK_a value. However, instead of the value of K_d' decreasing to zero at higher pH values, it becomes constant at 15 mL/g. In a solution containing 1.00 M NaOH and 1.00 M $NaNO_3$, the value of K_d' is 25 mL/g. The unusual behavior of the Reillex™-HP anion exchange resin suggests that the resin's unprotonated pyridine functionality is solvating a $\left\{Na^+, ReO_4^-\right\}$ ion pair. The interaction of the perrhenate ion with Reillex™-HP is more involved than a simple ion exchange phenomenon and the presence of NaOH affects the resin-perrhenate interactions.

INTRODUCTION

Separation of technetium Low-Level Waste (LLW) stored at the Department of Energy (DOE) facility at Hanford, WA is a primary concern of the DOE.[1-4] We have been involved with this project for the past several years. Our interest has been in the removal of TcO_4^- from the waste stream. Recently, we reported the superior performance of Reillex™-HPQ as compared to Dowex™-1 for the sorption of TcO_4^-.[5] Our results with Dowex™-1 were consistent with those of Wheelwright, as well as a later report concerning this resin.[6, 7] In our continuing effort to characterize the anion exchange behavior of this resin, we recently reported the results of an investigation of the interaction of Reillex™-HPQ with potassium perrhenate and potassium dichromate in nitric acid solutions.[8] We have found that the behavior of ReO_4^- on Reillex™-HPQ is quantitatively very similar to that of TcO_4^-.[5, 8] Because of this similarity, we are able to use ReO_4^- as a surrogate for TcO_4^-. This allows us to scope-out important properties of these resins at facilities unable to accommodate radioactive materials; significant effects can then be explored with technetium at Los Alamos National Laboratory.

The reward of finding a selective anion exchange resin, such as Reillex™-HPQ, for TcO_4^- is followed by the punishment of devising a method of removing the anion from the resin. The generally used method involves large volumes of a concentrated eluent, i. e. 6-8 M HNO_3. Safety and waste minimization problems make this option unacceptable for large scale processing. A possible solution to this elution problem would be to use the weak base anion exchange resin Reillex™-HP. In principle the resin could be loaded in acidic solution and eluted by a weakly basic solution.

Reillex™-HP is a copolymer of 4-vinylpyridine and divinylbenzene (24% crosslinked) that functions as a weak base anion exchange resin when the pyridine nitrogen is protonated to give pyridinium sites.[9] A 4-vinylpyridine resin that is methylated (75%) at the pyridine nitrogen to give pyridinium strong base sites is commercially available as Reillex™-HPQ.[9] The pyridinium functionalities of Reillex™-HP and HPQ resins are unique; most other anion exchange resins contain alkyl amines and alkyl quaternary amines. Reillex™-HPQ has been reported to exhibit superior chemical and radiolytic stability and is especially-well suited for plutonium separations.[10-12]

Initial experiments with TcO_4^- and Reillex™-HP produced unexpected results. Because the TcO_4^- could not be eluted easily with base, we decided to begin an extended investigation of the interaction of ReO_4^- with this resin. Additionally, since Reillex™-HPQ contains 25% unmethylated pyridine, this study would give a better understanding of Reillex™-HPQ behavior. Herein we report the details of the sorption behavior of perrhenate anion on Reillex™-HP in sodium nitrate solutions ranging from 10.0 M nitric acid to 5.00 M NaOH.

EXPERIMENTAL

Reagents

Reagents were analytical grade. All water was deionized to 18 MΩ. Standard solutions of nitric acid were prepared from concentrated nitric acid and standardized against standard sodium hydroxide. Standard solutions of carbonate-free sodium hydroxide were prepared by diluting a 50% sodium hydroxide solution and standardizing these dilutions with potassium hydrogen phthalate. Standard solutions

of sodium nitrate were prepared by weighing the desired quantity of $NaNO_3$ (dried at 120 °C). The Reillex™-HP resin (Lot # 21227AA) was purchased from Reilly Industries (Indianapolis, IN) in the chloride form and 30-60 mesh size.[9] The potassium perrhenate ($KReO_4$) was purchased from Cleveland Refractory Metals (29855 Aurora Rd., Solon, OH 44139). The concentration units of molarity and normality are interchangeable in this report because only monocharged ions are considered.

Assay Techniques

Rhenium was analyzed by Atomic Absorption spectroscopy using a Perkin Elmer Model 2380 instrument with a rich nitrous oxide-acetylene flame. Standard rhenium solutions were prepared from potassium perrhenate that was assumed to be 100% pure. Potassium perrhenate was dried for 24 hours at 120 °C and used to prepare the 30.0 mM stock solution. For acidic solutions, standard curves were prepared by measuring the absorbances of three different concentrations of perrhenate (1.00, 5.00 and 10.0 mM ReO_4^-) at different nitric acid concentrations. As the acid concentration increased, the slopes of the linear standard curves decreased. Therefore, a single standard curve was unsatisfactory for all of the acid concentrations in the samples. As a result, standard curves were prepared at 10.00, 9.00, 8.00, 7.00, 6.00, 5.00, 4.00, 3.00, 2.00, 1.00, 0.500 and 0.100 M nitric acid. These standard curves were interpolated to obtain standard curves between these acidities. The interpolations were less than 10% of the extremes and the standard curves had zero intercepts within experimental error. Solutions in variable base or variable sodium nitrate followed the same procedure as in acid. Because all of the standard curves were linear, later rhenium determinations were performed by measuring the absorbances of the contacted solutions and non-contacted solutions and then calculating the distribution coefficients (K_d) directly from the values of the absorbances.

Resin Treatment

The Reillex™-HP anion exchange resin was washed in a beaker by decantation with 20 bed-volumes of water to remove the excess chloride and any floating resin beads. The washed resin was packed into a column and converted to the nitrate form by passing 20 bed-volumes of 2.0 M nitric acid through the resin. After conversion, the

resin was washed with 20 bed-volumes of water and stored in water. Before the resin was used it was dried at 60 °C for 48 hours and stored in a desiccator over silica gel to achieve constant resin mass.[13]

Distribution Coefficient Determinations (K_d')

Batch K_d' measurements were made by contacting Reillex™-HP resin with the selected potassium perrhenate solution. The rhenium concentrations in the solution before and after contacting the resin were determined and used to calculate the values of K_d' in mL/g. Equation (1) defines the experimental distribution coefficient K_d' for ReO_4^-.

$$K_d' = \frac{\frac{Re_{total} - [Re]_{sol} x V_{sol}}{\text{mass of dry resin}}}{\frac{[Re]_{sol} x V_{sol}}{V_{sol}}} \qquad (1)$$

The quantity Re_{total} is the total mmol of rhenium in the solution before resin contact. The quantity $[Re]_{sol}$ is the molar concentration of the rhenium species in V_{sol} mL of solution after contacting the Reillex™-HP resin. We assumed that there are no reduced rhenium species in solution; there was no evidence of any.

In the samples that were 0.100 to 10.0 M HNO_3 or 0.100 to 5.00 M NaOH, each sample was prepared by weighing 1.00 g of dried resin into a 30-mL Oak Ridge centrifuge tube. To each tube, we added 10.00 mL of 9.00 mM potassium perrhenate solution containing the selected amounts of $NaNO_3$ and HNO_3 or NaOH. Acidic and basic samples were contacted at room temperature for two hours and 30 minutes, respectively, based on separate experiments which confirmed that thirty minutes was sufficient time to reach a constant K_d' value. The contacted resin was separated from the solution by gravity filtration using Whatman #41 filter paper and the filtrates were analyzed for rhenium.

In the samples that were 1.00 M $NaNO_3$ and variable pH, we weighed 2.00 g of dried resin into a 30-mL Oak Ridge centrifuge tube. To each tube, we added 20.00 mL of a solution consisting of 9.00 mM potassium perrhenate and 1.00 M $NaNO_3$ at the desired pH. The solution was then adjusted to the desired pH with NaOH before adding the solution to the resin. After addition to the resin, the pH of the resin-solution sample was again measured using an Orion Model 940 pH meter with a glass electrode.

RESULTS AND DISCUSSION

Reillex™-HP is a weak base anion exchange resin with a pyridine nitrogen as the site that is protonated. The average pK_a for the active sites of the resin is 3.75 in 1.00 M $NaNO_3$.[14] The ion exchange capacity of this resin, as measured by the amount of NaOH needed to neutralize the resin in 1.00 M $NaNO_3$, is 4.02 ± 0.05 meq/g.[14] The chloride ion exchange capacity of this resin is 4.65 ± 0.49 meq/g dry resin.[15] The reported capacity is 4.6 meq/g dry resin.[9] The proton capacity of the Rellex™-HP is difficult to determine because the measurement is dependent upon the length of time taken to titrate the resin; less than 40 hours will not give equilibrium results.[14] A similar caveat applies to the weak-base capacity of Reillex™-HPQ; the difference in capacity between a 2-hour and 12-hour titration time can be almost 60%.[14]

Equation (2) represents the interaction of ReO_4^- with the resin. The symbol

$$RNH^+NO_3^- + ReO_4^- \rightleftharpoons RNH^+ReO_4^- + NO_3^- \qquad (2)$$

RNH^+ represents the protonated exchange site on the Reillex™-HP resin. Thus, $RNH^+NO_3^-$ represents the exchange site with nitrate as the counter ion and $RNH^+ReO_4^-$ represents the site with perrhenate as the counter ion. The heterogenous equilibrium constant, ${}^{ReO_4^-}_{NO_3^-}K'_{HP^+}$, for Eq. (2) is defined by Eq. (3). We include no activity coefficients in this equation.

$${}^{ReO_4^-}_{NO_3^-}K'_{HP^+} = \frac{\left(RNH^+ReO_4^-\right)\left[NO_3^-\right]}{\left(RNH^+NO_3^-\right)\left[ReO_4^-\right]} \qquad (3)$$

The maximum amount of ReO_4^- of 0.09 meq/4.65 meq resin would result in a maximum resin loading of 1.9%. Under such low ReO_4^- loadings, the exchange sites on the resin associated with NO_3^- instead of ReO_4^- are very close to the total number of exchange sites on the resin $\left(RNH^+_{total}\right)$. Above a proton concentration of 10^{-2} M, the resin is essentially protonated and RNH^+ is the predominant form.

Figure 1 is a plot of ReO_4^- K_d' values as a function of $[HNO_3]$. Based on the discussion so far, the data should be described by Eq. (4). That is, with

$$K_d' = \frac{\left(RNH^+ReO_4^-\right)}{\left[ReO_4^-\right]} = {}^{ReO_4^-}_{NO_3^-}K'_{HP^+}\frac{\left(RNH^+NO_3^-\right)}{\left[NO_3^-\right]} \tag{4}$$

$\left[HNO_3\right] = \left[NO_3^-\right]$ and $\left(RNH^+NO_3^-\right) = \left(RNH^+_{total}\right) = 4.65$ meq/g dry resin (capacity), a plot of K_d' versus ${}^{ReO_4^-}_{NO_3^-}K'_{HP^+}\left(RNH^+_{total}\right)\Big/\left[HNO_3\right]$ should result in a straight line. However, it does not. Note that the ordinate is plotted as a log scale for viewing convenience only. The dotted line in Figure 1 is the least-squares fit of the data to Eq. 4.[18] The derived value of ${}^{ReO_4^-}_{NO_3^-}K'_{HP^+}\left(RNH^+_{total}\right)$ was 68.0 ± 4.5 mL/g with a correlation coefficient (R^2) of 0.78202. This relatively poor fit suggests that an alternate model is required to explain the data.

Similar behavior has been reported for both TcO_4^- and ReO_4^- in nitric acid solutions.[5, 8] In these studies, ReO_4^- and TcO_4^- were assumed to be moderately strong acids. Reaction (5) and Eq. (6) show respectively the perrhenic acid dissociation reaction and its equilibrium constant expression.

$$HReO_4 \rightleftharpoons H^+ + ReO_4^- \tag{5}$$

$${}^{ReO_4^-}K_a = \frac{\left[H^+\right]\left[ReO_4^-\right]}{\left[HReO_4\right]} \tag{6}$$

Equation (7) represents the mass balance for the perrhenate in solution. Combining Eqs. (6) and (7) results in Eq. (8) which relates the total rhenium in solution, $[Re]_{sol}$, and the deprotonated perrhenate ion, ReO_4^-, in solution.

$$\left[Re\right]_{sol} = \left[HReO_4\right] + \left[ReO_4^-\right] \tag{7}$$

$$\frac{\left[ReO_4^-\right]}{\left[Re\right]_{sol}} = \frac{\left[ReO_4^-\right]}{\left[ReO_4^-\right] + \left[HReO_4\right]} = \frac{{}^{ReO_4^-}K_a'}{{}^{ReO_4^-}K_a + \left[H^+\right]} \tag{8}$$

Assuming that this additional equilibrium is operative, Eq. (9) should describe

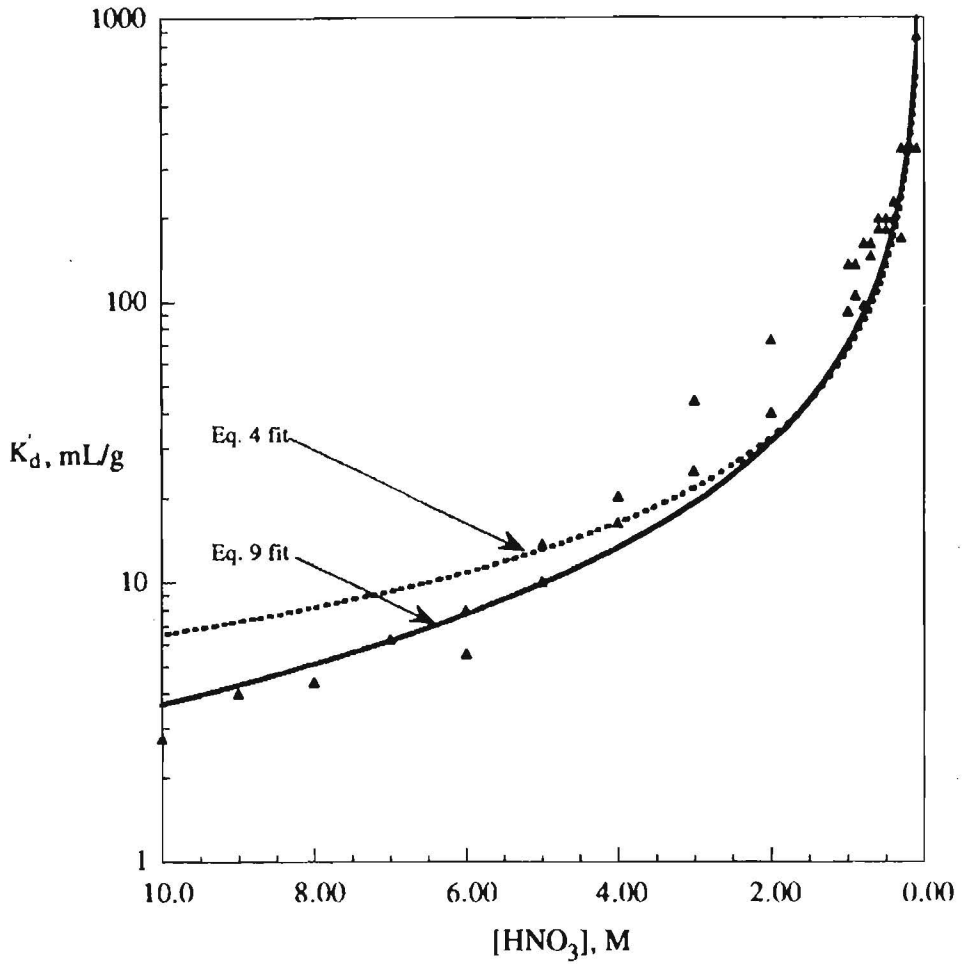

Figure 1. The values of K_d' for perrhenate as a function of $[HNO_3]$ for Reillex™-HP. The dotted line is the weighted least-squares fit of the data to Eq. 4 and the solid line is the weighted least-squares fit of the data to Eq. 9. The log scale of K_d' is for viewing convenience.

$$K_d' = \left\{ \frac{{}^{ReO_4^-}_{NO_3^-} K'_{HP^+} \left(RNH^+_{total} \right)}{\left[NO_3^- \right]} \right\} \left\{ \frac{{}^{ReO_4^-} K_a}{{}^{ReO_4^-} K_a + \left[H^+ \right]} \right\} \qquad (9)$$

the data. The solid line in Figure 1 is the least-squares fit of the data to Eq. (9), weighted as $\left(1/K_d'\right)^2$ and assuming that $\left[HNO_3\right] = \left[NO_3^-\right]$.[18] The linear correlation coefficient (R) was 0.99968. The value of ${}^{ReO_4^-}K_a$ was 9.16 ± 8.95 M and a value for ${}^{ReO_4^-}_{NO_3^-}K'_{HP^+}\left(RNH^+_{total}\right)$ of 76.2 ± 19.6 mmol/g was obtained.

The degree of dissociation (α) and the stoichiometric activity coefficients (y_s) are reported for solutions of nitric acid.[16] Hence, attempts to fit the nitric acid only data were made. The fit of $K_d^{'}$ to ${}^{ReO_4^-}_{NO_3^-}K^{'}_{HP^+}\left(RNH^+_{total}\right)\Big/\alpha\left[HNO_3\right]$ resulted in a value for ${}^{ReO_4^-}_{NO_3^-}K^{'}_{HP^+}\left(RNH^+_{total}\right)$ of 34.5 ± 7.5 with a correlation coefficient (R^2) of 0.99816. When $\alpha\left[HNO_3\right]$ was substituted for $\left[NO_3^-\right]$ and $\left[H^+\right]$ in Eq. 9, the value of ${}^{ReO_4^-}K_a$ was 2.83 ± 2.11 M and a value for ${}^{ReO_4^-}_{NO_3^-}K_{HP^+}\left(RNH^+_{total}\right)$ of 73.4 ± 22.2 mmol/g was obtained. The correlation coefficient (R^2) was 0.99902.

The fit of $K_d^{'}$ to ${}^{ReO_4^-}_{NO_3^-}K^{'}_{HP^+}\left(RNH^+_{total}\right)\Big/y_s\left[HNO_3\right]$ resulted in a value for ${}^{ReO_4^-}_{NO_3^-}K^{'}_{HP^+}\left(RNH^+_{total}\right)$ of 57.5 ± 10.7 with a correlation coefficient (R^2) of 0.99934. The fit to Eq. 9 when $y_s\left[HNO_3\right]$ was substituted for $\left[NO_3^-\right]$ and $\left[H^+\right]$ was unsuccessful.

A comparison of all of these resulting parameters for the data in HNO_3 solutions (no added $NaNO_3$) reveal that the data can be fit almost equally well by any of the equations and concentration parameters. Hence, no clear choice of a model can be made. We will choose the model represented by Eq. 9 to represent the data, i. e. the association of $HReO_4$. This is done because of the unavailability of the activity coefficients in the various solutions with sodium nitrate added. Activity coefficients for solutions of $HTcO_4$ and $HReO_4$ (no added salt) have been reported.[17] However, the activity coefficients are unavailable for the ions and water entrained in the resin. Thus, the activity effects are contained implicitly in the derived constants.

The sorption of the perrhenate ion at lower proton concentrations was also studied. However, in order to simplify the evaluation of the data, the nitrate ion concentration was kept high by the addition of 1.00 M $NaNO_3$ to all solutions. Figure 2 is a plot of $K_d^{'}$ as a function of $\log\left[HNO_3\right]$ or $\log\left[H^+\right]$. From 10.0 M to 0.0100 M HNO_3, the abscissa is the value of the $\log\left[HNO_3\right]$. The rest of the data in Figure 2 are from solutions prepared by adding NaOH solution to adjust the pH of the contact solutions. For this study, the relationship $pH = -\log\left[H^+\right]$ is used.

Because Reillex™-HP is a weak-base resin, we expected that the $K_d^{'}$ values would decrease to zero as the resin sites became completely deprotonated. Thus, we were surprised that the resin still had 20% of the exchange capacity at pH 10, five units above the $p\left({}^{HP}K_a\right)$ value of 4.91. We attribute this to another mode of sorption for ReO_4^- other than conventional anion exchange. An alternative mechanism would have a $\{Na^+, ReO_4^-\}$ ion pair being solvated by the resin's pyridine groups. The "solvating extractants," pyridine and picoline are known to extract

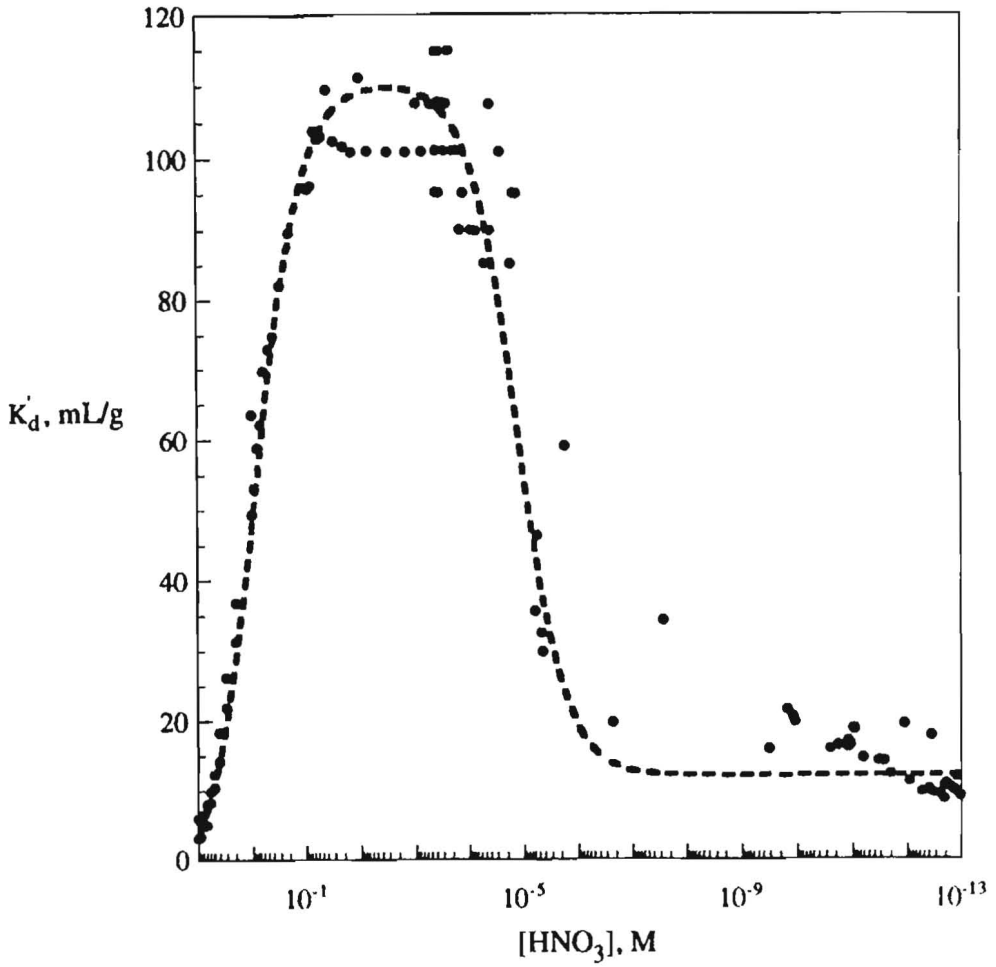

Figure 2. The values of K_d for perrhenate as a function of $[HNO_3]$ in 1.00 M $NaNO_3$ for Reillex™-HP. The line is the weighted least-squares fit of the data to Eq. 15. The log scale of $[HNO_3]$ is for viewing convenience only.

TcO_4^- and ReO_4^- from caustic solutions.[19] These extractions are strongly matrix dependent and are described by a "salting out" mechanism.[20]

The deprotonation-ion pair sorption reaction for the resin is represented by Eq. (10). The reaction is written to illustrate that the $RN\{Na^+, NO_3^-\}$ ion pair is sorbed by the deprotonated resin. The equilibrium expression representing this reaction is given by Eq. (11).

$$Na^+ + RNH^+NO_3^- \rightleftharpoons RN\{Na^+, NO_3^-\} + H^+ \qquad (10)$$

$$ {}^{HP}K_a = \frac{\left(RN\left\{Na^+, NO_3^-\right\}\right)\left[H^+\right]}{\left(RNH^+NO_3^-\right)\left[Na^+\right]} \qquad (11) $$

Because the resin was deprotonated, the standard anion exchange capacity is zero. Sorption of ReO_4^- at the higher pH values implies an ion pair sorption reaction as described in Eq. (12). The equilibrium expression is defined by Eq. (13).

$$ RN\left\{Na^+, NO_3^-\right\} + ReO_4^- \rightleftharpoons RN\left\{Na^+, ReO_4^-\right\} + NO_3^- \qquad (12) $$

$$ {}^{Na^+,ReO_4^-}_{Na^+,NO_3^-}K'_{HP} = \frac{\left(RN\left\{Na^+, ReO_4^-\right\}\right)\left[NO_3^-\right]}{\left(RN\left\{Na^+, NO_3^-\right\}\right)\left[ReO_4^-\right]} \qquad (13) $$

Assuming that both the protonated and the deprotonated Reillex™-HP can sorb ReO_4^-, the experimental distribution coefficient, K'_d, for ReO_4^- can be defined by Eq. (14). Equation (15) results from combining Eqs. 3, 7, 8 , 11, 13, and 14. This

$$ K'_d = \frac{\left(RNH^+ReO_4^-\right) + \left(RN\left\{Na^+, ReO_4^-\right\}\right)}{[Re]_{sol}} \qquad (14) $$

gives an expression that should describe the relationship between K'_d and $\left[H^+\right]$. The $\left(RN_{total}\right)$ term is the total amount of nitrate form resin, protonated plus deprotonated. For the sake of simplicity, we assumed that the ion pair sorption capacity of the resin is the same as its ion exchange capacity, which may not be valid.

$$ K'_d = \left\{ {}^{ReO_4^-}_{NO_3^-}K'_{HP^+}\left[H^+\right] + {}^{Na^+,ReO_4^-}_{Na^+,NO_3^-}K'_{HP}\,{}^{HP}K_a\left[Na^+\right] \right\} \qquad (15) $$

$$ \text{X} \quad \left\{ \frac{\left(RN_{total}\right)\Big/\left[NO_3^-\right]}{{}^{HP}K_a\left[Na^+\right] + \left[H^+\right]} \right\} \left\{ \frac{{}^{ReO_4^-}K_a}{{}^{ReO_4^-}K_a + \left[H^+\right]} \right\} $$

Above pH 7, Eq. (15) simplifies to Eq. (16) and $\left[NO_3^-\right]$ = (1.00 + 0.465)M.

$$K_d' = {}^{Na^+,ReO_4^-}_{Na^+,NO_3^-}K_{HP}'(RN_{total}) \Big/ \left[NO_3^-\right] \qquad (16)$$

The additional 0.465 M term is the result of nitrate ion being released from resin by its neutralization. The average value of K_d' in the pH range of 7 to 12 is 14.6 ± 5.4 mL/g, which results in a derived value of 21.3 ± 7.9 meq/g for the constant ${}^{Na^+,ReO_4^-}_{Na^+,NO_3^-}K_{HP}'(RN_{total})$. Below a pH of 2 and a $\left[H^+\right] > 0.01$ M, Eq. (15) simplifies to Eq. (17). Under these conditions, $\left[NO_3^-\right]$ = $\left(1.00 + \left[HNO_3\right]\right)$ M and the concentration of $\left[H^+\right]$ was taken as HNO_3 or 10^{-pH}.

$$K_d' = \left\{ {}^{ReO_4^-}_{NO_3^-}K_{HP^+}'(RN_{total}) \Big/ \left[NO_3^-\right] \right\} \left\{ \frac{{}^{ReO_4^-}K_a}{{}^{ReO_4^-}K_a + \left[H^+\right]} \right\} \qquad (17)$$

The weighted least-squares fit of the appropriate data to Eq. (17) gives a plot similar to the solid line in Figure 1. The value of ${}^{ReO_4^-}_{NO_3^-}K_{HP^+}'\left(RNH^+_{total}\right)$ is 124 ± 22 meq/g and the value of ${}^{ReO_4^-}K_a$ is 5.25 ± 3.05 M.

Between pH 2 and 7, Eq. (15) applies. The weighted least-squares fit of the data to Eq. (15), assuming that $\left[NO_3^-\right]$ = 1.00 M, gives the curve in Figure 2.[18] The resulting values of ${}^{ReO_4^-}_{NO_3^-}K_{HP^+}'(RN_{total})$, ${}^{ReO_4^-}K_a$, ${}^{HP}K_a$, and ${}^{Na^+,ReO_4^-}_{Na^+,NO_3^-}K_{HP}'(RN_{total})$ are (110 ± 17) meq/g, 6.45 ± 3.82 M, $(1.24 \pm 1.04)10^{-5}$ meq/mL, and 12.1 ± 2.2 meq/g .

Figure 3 is a plot of a series of K_d' determinations for solutions that contain 1.00 M NaOH and 0.100 to 5.00 M $NaNO_3$. The actual NaOH concentration (0.535 M) was corrected (decreased) for the amount of NaOH consumed by neutralization of 4.65 meq of resin $\left(RNH^+NO_3^-\right)$. The $NaNO_3$ concentrations (0.565 to 5.47 M) were calculated by adding the amount of $NaNO_3$ released when the resin was neutralized.

The data in Figure 3 could be described by an equation of the form of Eq. 18; the line in the figure is the least-squares fit of the data.[18] The form of this equation

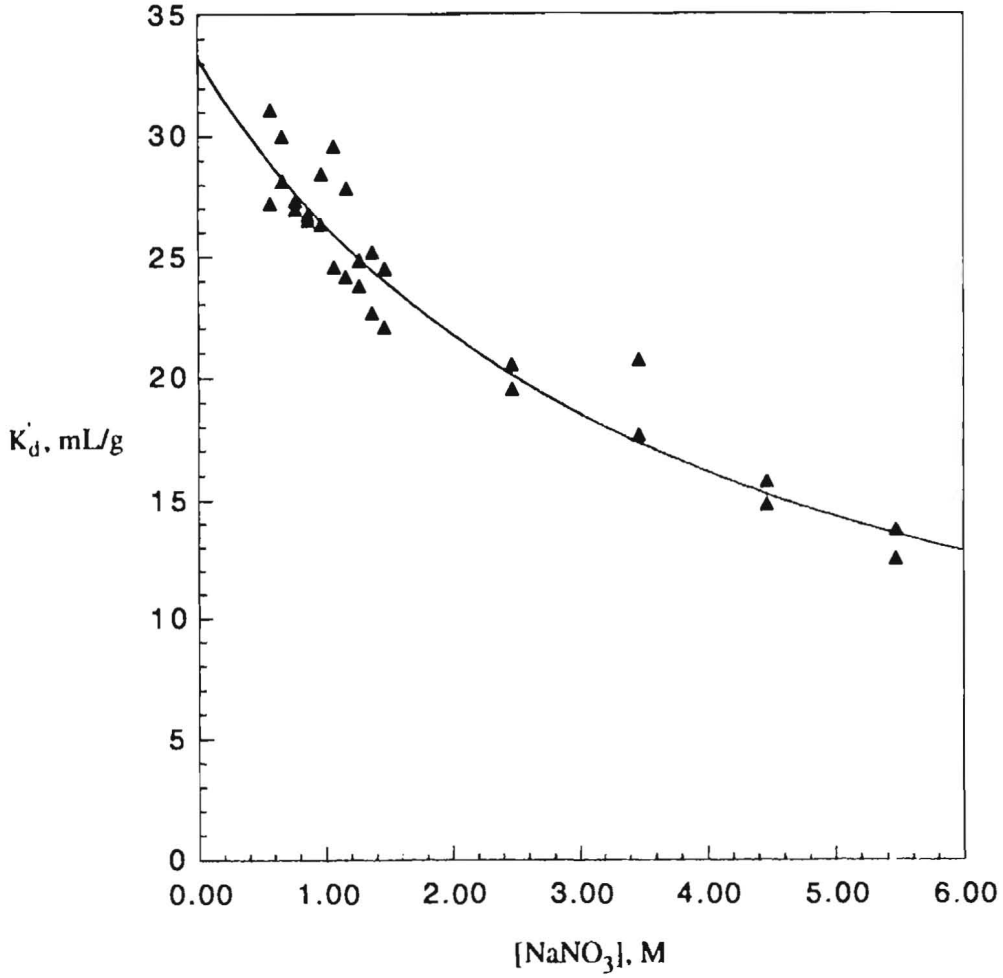

Figure 3. The plot of perrhenate $K_d^{'}$ versus $[NaNO_3]$ in solutions of constant 0.655 M NaOH for Reillex™-HP. The line is the weighted least-squares fit of the data to Eq. 18.

$$K_d^{'} = \frac{a}{(0.535 + b[NaNO_3])} \tag{18}$$

implies that NO_3^-, and possibly OH^-, are displaced from the resin as the ReO_4^- is sorbed. As before, it is assumed that the sites which are not associated with a $\{Na^+, ReO_4^-\}$ ion pair are associated with either a $\{Na^+, OH^-\}$ or a $\{Na^+, NO_3^-\}$ ion pair. To describe this, Eqs. (12), (19), and (20) are assumed to be operative. Equations (13), (21), and (22) define the equilibrium constants.

$$RN\left\{Na^+,OH^-\right\} + ReO_4^- \rightleftharpoons RN\left\{Na^+,ReO_4^-\right\} + OH^- \qquad (19)$$

$$RN\left\{Na^+,OH^-\right\} + NO_3^- \rightleftharpoons RN\left\{Na^+,NO_3^-\right\} + OH^- \qquad (20)$$

$$\underset{Na^+,OH^-}{^{Na^+,ReO_4^-}}K'_{HP} = \frac{\left(RN\left\{Na^+,ReO_4^-\right\}\right)\left[OH^-\right]}{\left(RN\left\{Na^+,OH^-\right\}\right)\left[ReO_4^-\right]} \qquad (21)$$

$$\underset{Na^+,OH^-}{^{Na^+,NO_3^-}}K'_{HP} = \frac{\left(RN\left\{Na^+,NO_3^-\right\}\right)\left[OH^-\right]}{\left(RN\left\{Na^+,OH^-\right\}\right)\left[NO_3^-\right]} \qquad (22)$$

Equation (23) is a mass balance statement that assumes a constant ion pair

$$\left(RN_{total}\right) = \left(RN\left\{Na^+,OH^-\right\}\right) + \left(RN\left\{Na^+,NO_3^-\right\}\right) \qquad (23)$$

sorption capacity, independent of the identity of the ion pair. Combining Eqs. (22) and (23) results in Eq. (24), the relationship of the total amount of resin associated with NO_3^-.

$$\frac{\left(RN\left\{Na^+,NO_3^-\right\}\right)}{\left(RN_{total}\right)} = \frac{\left(RN\left\{Na^+,NO_3^-\right\}\right)}{\left(RN\left\{Na^+,OH^-\right\}\right) + \left(RN\left\{Na^+,NO_3^-\right\}\right)} \qquad (24)$$

$$= \frac{\underset{Na^+,OH^-}{^{Na^+,NO_3^-}}K'_{HP}\left[NO_3^-\right]}{\left[OH^-\right] + \underset{Na^+,OH^-}{^{Na^+,NO_3^-}}K'_{HP}\left[NO_3^-\right]}$$

An expression for the perrhenate K'_d value, Eq. (25), can be obtained by substituting Eq. (24) into Eq. (13), using Eq. (14), and rearranging. Note that Eqs. (25) and (18) are of the same form.

$$K_d' = \frac{{}^{Na^+,ReO_4^-}_{Na^+,NO_3^-}K_{HP}' \; {}^{Na^+,NO_3^-}_{Na^+,OH^-}K_{HP}'(RN_{total})}{[OH^-] + {}^{Na^+,NO_3^-}_{Na^+,OH^-}K_{HP}'[NO_3^-]}$$

$$= \frac{{}^{Na^+,ReO_4^-}_{Na^+,OH^-}K_{HP}'(RN_{total})}{[OH^-] + {}^{Na^+,NO_3^-}_{Na^+,OH^-}K_{HP}'[NO_3^-]} \qquad (25)$$

The least-squares fit to the first equality of Eq. (25) gives a value for ${}^{Na^+,ReO_4^-}_{Na^+,NO_3^-}K_{HP}'(RN_{total})$ of 125 ± 54 meq/g and a value for ${}^{Na^+,NO_3^-}_{Na^+,OH^-}K_{HP}'$ of 0.17 ± 0.22. From the least-squares fit of the data to the second equality, ${}^{Na^+,ReO_4^-}_{Na^+,OH^-}K_{HP}'(RN_{total})$ is 17.8 ± 8.3 meq/g and ${}^{Na^+,NO_3^-}_{Na^+,OH^-}K_{HP}'$ is 0.14 ± 0.22. The correlation coefficient (R^2) is 0.95854 for both fits.

The behavior depicted in Figure 3 is also observed for both ReO_4^- and TcO_4^- with Reillex™-HPQ in alkaline solutions, which is not too surprising because Reillex™-HPQ includes about 25% weak-base sites.[21,22] However, the quantitative similarities are unknown at this time.

All the determined parameters are summarized in Table 1. The quantities (RNH^+_{total}) and (RN_{total}) are both 4.65 ± 0.49 meq/g. The (RNH^+_{total}) term is used to stress that the parameter was determined under conditions in which the protonated form of the resin predominated, whereas the term (RN_{total}) is used when the parameter is determined under conditions that include both forms or only the deprotonated form of the resin.

The parameter ${}^{ReO_4^-}_{NO_3^-}K_{HP^+}'(RNH^+_{total})$ has a value of 76.2 ± 19.6 meq/g in nitric acid solutions. The value in HNO_3 solutions that also contain 1.00 M $NaNO_3$ is 124 ± 22 meq/g. These numbers were obtained from fitting the data to Eqs. 9 and 17, respectively; these are the same equations. This apparent difference might simply be statistical or it could reflect activity effects because the value of 124 meq/g is derived from solutions that are 1.00 M in $NaNO_3$. The value of ${}^{ReO_4^-}_{NO_3^-}K_{HP^+}'(RN_{total})$ is 110 ± 17 meq/g, which was derived from Eq. 15. This is a remarkably good agreement with the first two values, considering the complexity of Eq. 15.

The value for ${}^{ReO_4^-}_{NO_3^-}K'_{HPQ^+}(RNCH_3^+{}_{total})$ for ReO_4^- with Reillex™-HPQ is 266 ± 55 mmol/mL.[8] The values of K'_d for ReO_4^- with Reillex™-HPQ in 10.0, 5.00, and 1.00 M HNO_3 are 5, 17, and 190 mL/g, respectively.[8] Equivalent values for Reillex™-HP (Eq. 15) are 4, 12, and 95 mL/g , respectively, which indicates that the methylated pyridinium resin is a better sorber for ReO_4^- than the protonated pyridinium resin in strong nitric acid solutions.

For a better comparison, consider the values of ${}^{ReO_4^-}_{NO_3^-}K'_{HPQ^+}$ and ${}^{ReO_4^-}_{NO_3^-}K'_{HP^+}$, which are 70 ± 14 and 16.4 ± 4.6.[15] However, even these numbers are not the best comparison because Reillex™-HPQ^+ contains about 25% weak-base sites. Taking this into account, we calculate the value for Reillex™-HPQ^+ for 100% strong base sites should be 90 ± 18. From these two observations it is interesting to speculate whether resins with larger alkyl substituents (i.e., ethyl, propyl, butyl, etc.) on the pyridine nitrogen might provide even higher ReO_4^- distribution coefficients. S. F. Marsh, Z. V. Svitra, and S. M. Bowen have reported on this effect for the sorption of TcO_4^- from *Simulated Hanford Double-Shell Slurry Feed (DSSF)*, an alkaline/nitrate solution.[23-25] They observed that the K'_d values for TcO_4^- increase with the size of the alkyl substituents on quaternary ammonium strong base anion resins (Sybron $(Et)_3N$, Sybron $(Pr)_3N$, and Ionac™ SR-6 (butyl)) and have reported the same trend for the ethyl, propyl, and n-butyl pyridinium derivatives of Reillex™-HP resins.[26, 27] Attempts are underway to obtain samples of ethyl, propyl, and n-butyl pyridinium Reillex™-HPQ resins and determine the values of K'_d for perrhenate ion.

The three separate values of ${}^{ReO_4^-}K_a$ determined in this work are in good agreement. They are also close to the value of 2.32 ± 0.81 determined in the ReO_4^--Reillex™-HPQ investigation.[8] Discussions of this parameter have been given.[5,8]

The value of ${}^{HP}K_a$ derived from the fit of Eq. (15) is $(1.24 \pm 1.04)10^{-5}$. This constant is defined as an exchange of a proton for a sodium ion in an ion pair species sorbed by the resin. The value of 1.8×10^{-4} (1.0 M $NaNO_3$) reported previously is in reasonable agreement.[14] This acid dissociation of the protonated Reillex™-HP is presently being studied in more detail.[28]

The observation that Reillex™-HP can also sorb perrhenate from basic solutions is very interesting. Between pH 7 and 12, the value of 21.3 ± 7.9 meq/g for ${}^{Na^+,ReO_4^-}_{Na^+,NO_3^-}K'_{HP}(RN_{total})$ is obtained from Eq. (16), a simplified form of Eq. (15). Applying Eq (15) to the data from 10.0 M HNO_3 to pH 12 gives a value of 12.1 ± 2.2 meq/g. Considering the complexity of Eq. (15), these two values agree well.

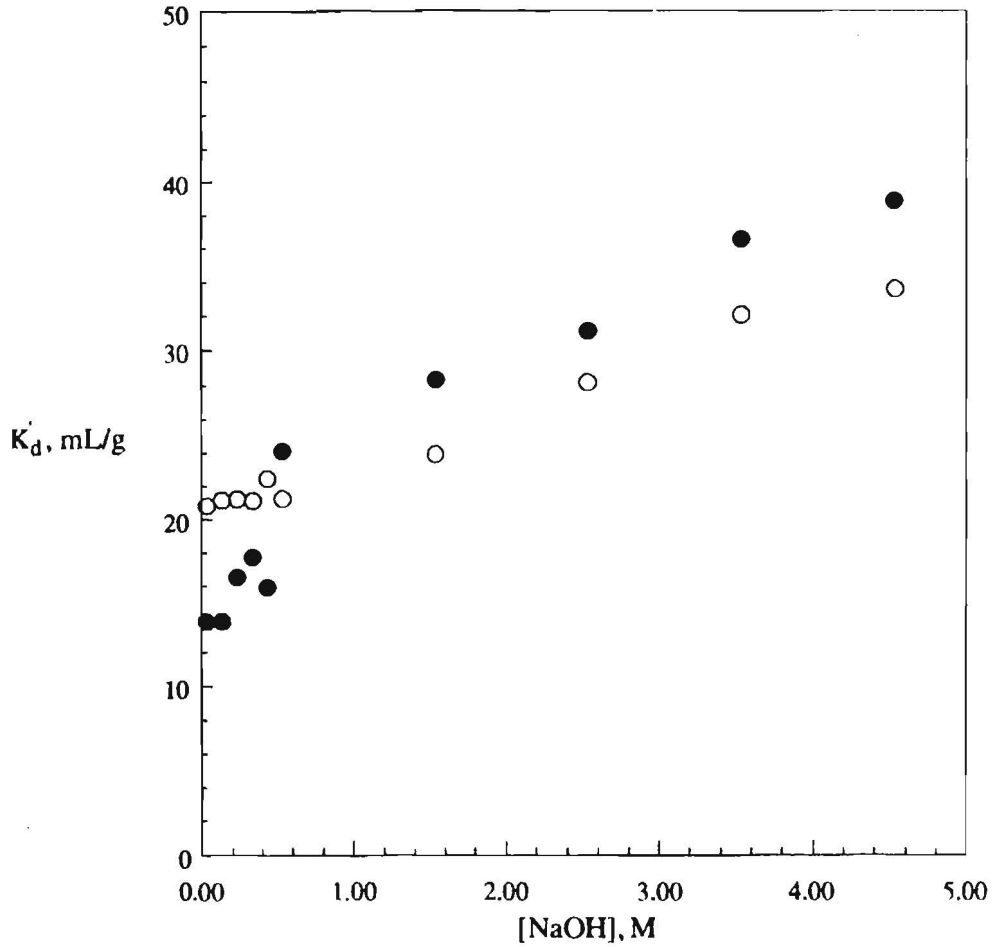

Figure 4. The plot of perrhenate K_d' versus [NaOH] in solutions of constant 1.35 M $NaNO_3$ for Reillex™-HP. The open and filled circles represent two different experiments.

In the solutions of 0.655 M NaOH with variable $NaNO_3$ concentration, the value of 125 ± 54 meq/g for ${}^{Na^+,ReO_4^-}_{Na^+,NO_3^-}K_{HP}'(RN_{total})$ is six times the value obtained below pH 12. Clearly the NaOH is affecting the resin in some manner. The value of the other parameter, ${}^{Na^+,NO_3^-}_{Na^+,OH^-}K_{HP}'$, in the first equality in Eq. (25) is 0.17 ± 0.22. The second equality in Eq. (25) gives a value of 18 meq/g for ${}^{Na^+,ReO_4^-}_{Na^+,OH^-}K_{HP}'(RN_{total})$ and 0.14 ± 0.22 for ${}^{Na^+,NO_3^-}_{Na^+,OH^-}K_{HP}'$. These values are all internally consistent.

Extending these K_d' measurements to solutions containing 1.00 M $NaNO_3$ and NaOH from 0.500 to 5.00 M yielded unexpected results. Figure 4 is a plot of K_d' versus [NaOH]. The NaOH concentrations (0.035 to 4.54 M) were corrected

(decreased) for the amount of NaOH consumed by neutralizing 4.65 meq of RNH^+. The total $NaNO_3$ concentration (1.47 M) was calculated by adding the amount of $NaNO_3$ that was released during the resin neutralization. The actual concentrations of the nitrate and hydroxide ions are uncertain because of the association of nitrate or hydroxide ion pairs with the resin (vide supra).

The behavior displayed in Figure 4 is very unusual. As the hydroxide ion concentration increases, the sorption of the $\left\{Na^+, ReO_4^-\right\}$ ion pair increases. This same behavior has been observed for both ReO_4^- and TcO_4^- with Reillex™-HPQ in alkaline solutions.[21,22]

Selectivity of ion exchange resins for specific ions is influenced by the ion-water interaction in the bulk solution as well as in the resin phase.[29] These same sorts of interactions also will be important for ion-pair selectivity. The Gibb's Free Energy of hydration, ΔG^o_{hyd}, of the exchanging ions can be linearly related to the extraction constants for a large number of systems.[30] Using the reported values of ΔG^o_{hyd} for OH^- (-433 kJ/mol), NO_3^- (-323 kJ/mol), and other simple ions, values of ΔG^o_{hyd} for ReO_4^- and TcO_4^- are -270 and -289 kJ/mol, respectively.

At high concentrations, the small, highly hydrated hydroxide ions con trains a significant portion of the aqueous phase. In addition, hydroxide ion bonding to water hydrogen further decreases the amount of available free water. Based on the ΔG^o_{hyd} values, the decreasing availability of free water with increasing OH^- concentration will dehydrate TcO_4^- and ReO_4^- most. This decreasing availability of water will have the net effect of increasing the ion pair formation constants for all species in the solution. Moreover, as the amount of available water decreases, the relative sizes of the ions favor the formation of the $\left\{Na^+, OH^-\right\}$ and $\left\{Na^+, NO_3^-\right\}$ ion pairs over the $\left\{Na^+, ReO_4^-\right\}$ ion pair which suggests that Reillex™-HP can more effectively sorb the $\left\{Na^+, ReO_4^-\right\}$ ion pair than other ion pairs. The net effect is that the $\left\{Na^+, ReO_4^-\right\}$ ion pair is "salted out" of the aqueous solution and into the resin. Hence, as the concentration of the hydroxide increases, the value of K_d' increases.

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Table 1. THE VALUES OF THE PARAMETERS FOR SORPTION OF ReO_4^- ONTO REILLEX-™HP.

Parameter	Value	Reference
${}^{ReO_4^-}_{NO_3^-}K'_{HP^+}\left(RNH^+_{total}\right)$	76.2 ± 19.6 mmol/g	Eq. (9)
${}^{ReO_4^-}_{NO_3^-}K'_{HP^+}$	16.4 ± 4.6	Eq. (9) and a
${}^{ReO_4^-}_{NO_3^-}K'_{HP^+}\left(RNH^+_{total}\right)$	110 ± 17 mmol/g	Eq. (15)
${}^{ReO_4^-}_{NO_3^-}K'_{HP^+}$	23.7 ± 4.43	Eq. (15) and a
${}^{ReO_4^-}_{NO_3^-}K'_{HP^+}\left(RNH^+_{total}\right)$	124 ± 22 mmol/g	Eq. (17)
${}^{ReO_4^-}_{NO_3^-}K'_{HP^+}$	26.7 ± 5.5	Eq. (17) and Ref. a
${}^{Na^+,ReO_4^-}_{Na^+,NO_3^-}K'_{HP}(RN_{total})$	12.1 ± 2.2 mmol/g	Eq. (15)
${}^{Na^+,ReO_4^-}_{Na^+,NO_3^-}K'_{HP}$	2.60 ± 0.55	Eq. (15) and Ref. a
${}^{Na^+,ReO_4^-}_{Na^+,OH^-}K'_{HP}(RN_{total})$	17.8 ± 8.3 mmol/g	Eq. (25)
${}^{Na^+,ReO_4^-}_{Na^+,NO_3^-}K'_{HP}(RN_{total})$	127 ± 208 mmol/g	Eq. (25)
${}^{Na^+,NO_3^-}_{Na^+,OH^-}K'_{HP}$	0.14 ± 0.22	Eq. (25)
${}^{ReO_4^-}K_a$	9.16 ± 8.95 mmol/mL	Eq (9)
${}^{ReO_4^-}K_a$	6.45 ± 3.82 mmol/mL	Eq. (15)
${}^{ReO_4^-}K_a$	5.25 ± 3.05 mmol/mL	Eq (17)
${}^{HP}K_a$	$(1.24 \pm 1.04)10^{-5}$ mmol/mL	Eq. (15)

[a]The chloride ion exchange capacity of the Reillex™-HP resin has been determined in this laboratory to be 4.65 ± 0.49 mmol/g.