Removal of Technetium from Alkaline Nuclear-Waste Media by a Solvent-Extraction Process Using Crown Ethers*

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ABSTRACT

Crown ethers dissolved in suitably modified aliphatic kerosene diluents can be employed to extract technetium as pertechnetate anion (TcO_4^-) with good extraction ratios from realistic simulants of radioactive alkaline nitrate waste. The modifiers utilized are non-halogenated and non-volatile, and the technetium can be removed from the solvent by stripping using water. The crown ethers bis-4,4'(5')[(*tert*-butyl)cyclohexano]-18-crown-6 (di-t-BuCH18C6) and dicyclohexano-18-crown-6 (DCH18C6) provide stronger TcO_4^- extraction than dicyclohexano-21-crown-7 and 4-*tert*-butylcyclohexano-15-crown-5. Whereas DCH18C6 provides somewhat higher TcO_4^- extraction ratios than the more lipophilic di-t-BuCH18C6 derivative, the latter was selected for further study owing to its lower distribution to the aqueous phase. Particularly good extraction and stripping results were obtained with di-t-BuCH18C6 at 0.02 M in a 2:1 vol/vol blend of tributyl phosphate and Isopar® M. Using this solvent, 98.9 % of the technetium contained (at 6 x 10^{-5} M) in a Double-Shell Slurry Feed (DSSF) Hanford tank waste simulant was removed following two cross-current extraction contacts. Two cross-current stripping contacts with deionized water afforded removal of 99.1 % of the technetium from the organic solvent.

INTRODUCTION

Technetium-99, a uranium fission product with a low-energy beta emission and a half-life of 2.13 x 10^5 years, is thought to be present in alkaline nuclear-waste media mainly in the +7 oxidation state as the environmentally mobile oxo-anion, pertechnetate (TcO_4^-). Standard high-temperature vitrification procedures employed to immobilize other radionuclides present in the waste for geologic disposal lead to difficulties when used for technetium, due to the volatility of Tc(VII) oxides. Thus, separation of pertechnetate from alkaline nuclear-waste media prior to vitrification is currently being considered as part of waste-cleanup and environmental-restoration efforts. Removal of pertechnetate from the complex waste mixture poses a challenging problem, primarily due to the presence of nitrate (NO_3^-), which competes with pertechnetate in extractive processes and is often present in the waste at concentrations 10^4-10^7 times that of pertechnetate. Methods for extracting pertechnetate under these conditions exist but have been considered unsuitable for a large-scale process due to one or more shortcomings, necessitating the development of a new technology. Some of the existing methods for the extraction of pertechnetate from alkaline media have included the use of cyclohexanone,[1] tetraphenylarsonium chloride,[2] tetraalkylammonium halides,[3] and polyethylene glycols.[4] Whereas adequate extraction of pertechnetate from alkaline media was demonstrated by each method, undesirable characteristics include the use of hazardous chemicals as defined by the Resource Conservation and Recovery Act (RCRA), or difficulty in the regeneration of the extractant.

We describe here the results of our research efforts aimed at developing an efficient solvent-extraction process that seeks to avoid many of the problems of the previous methods. The process utilizes crown ethers for the direct extraction of pertechnetate from high-nitrate-containing alkaline nuclear-waste media, such as that comprising the tank wastes at Hanford, Washington, and at other DOE locations such as Oak Ridge. The tank wastes are typically strongly alkaline and contain Tc, actinides, and other radioactive contaminants. These contaminants may be found in the aqueous supernates under certain conditions, or they may be solubilized from the sludge during washing or leaching operations. Many such

waste streams contain high concentrations of salts such as sodium nitrate and thus pose special problems for current extraction technology. We have been investigating[5] crown ethers as potential solvent-extraction reagents for Tc removal because the high-salt condition actually promotes Tc extraction and because an inexpensive water wash effects stripping of the Tc from the solvent. Figure 1 depicts the conceptual process. The mechanism of extraction and stripping can most easily be described by a reversible equilibrium involving complexation of an alkali metal ion by a crown ether. The high alkali metal concentration in the aqueous phase during the extraction portion of the cycle drives the equilibrium toward formation of the crown ether-alkali metal complex. It is important to note that this is different from the usual "salting out" enhancement of extraction by increasing the activity of the entity to be extracted, with little or no effect on the extractant; aside from the possible presence of salting effects, here the enhancement results primarily from the conversion of the ineffective neutral crown ether to the effective cationic crown ether-alkali metal complex. An anion is necessary to conserve charge neutrality, and in this way the pertechnetate anion is also extracted:

$$Na^+ + TcO_4^- + \overline{CE} \rightleftharpoons \overline{(CE)NaTcO_4} \tag{1}$$

where CE is the crown ether, and the overbar designates organic-phase species. Stripping is accomplished by simply reversing this equilibrium. The organic solvent containing the crown ether-alkali metal-pertechnetate complex is contacted with deionized water, promoting dissociation of the complex to free alkali metal pertechnetate in the aqueous phase and free crown ether in the organic phase. As will be discussed further below, the extracted cation need not be Na^+ but can also advantageously include other cations from the waste. We note that equation 1 represents at present only a postulated model. Detailed equilibrium studies are in process to test this model as well as to reveal other equilibria that may occur, especially the competing extraction of sodium nitrate.

Experimental efforts are presently focused on evaluating the most effective combination of solvent components, including crown ether, diluent, and modifier. Jalhoom[6] and Korpusov[7] both described the use of crown ethers for extraction of pertechnetate from basic solutions, and our work largely builds upon their results. Specifically, we have developed good alternatives to halogenated diluents and have demonstrated a complete solvent cycle incorporating stripping with water. Further, we have tailored the chemistry for efficient waste processing and have characterized process-related aspects, such as the competing effect of sodium and potassium nitrate extraction.

EXPERIMENTAL
Crown Ethers and Diluents

The crown ether bis-4,4'(5')[(*tert*-butyl)cyclohexano]-18-crown-6 (abbreviated di-t-BuCH18C6) was used as received from either Parish Chemical or Eichrom Industries, Inc. It should be cautioned that the isomer ratios, and hence extraction performance, for this crown can vary from lot to lot;[8] hence it is important to use the same lot, or lots of equivalent performance, when making comparisons. The crown ethers 4-*tert*-butylcyclohexano-15-crown-5, dicyclohexano-18-crown-6 (~1:1 ratio of *cis-syn-cis* and *cis-anti-cis* isomers), and dicyclohexano-21-crown-7 (abbreviated 4-t-BuCH15C5, DCH18C6, and DCH21C7, respectively) were used as received from Parish Chemical. Isopar® M (a completely aliphatic isoparaffinic kerosene) was obtained from Exxon Chemical Company, Houston, Texas. Deionized water was obtained from a Barnstead Nanopure filtering system (resistivity 18 MΩ). All other diluents, modifiers, and reagents were used as received without further purification. All diluent blends are prepared on a volume basis unless otherwise noted. Beta liquid scintillation counting of ^{99}Tc was performed using a Packard Tricarb® Model 4530 counter and Packard Ultima Gold™ XR scintillation cocktail.

Waste Simulants

The compositions of the waste simulants used in these experiments are shown in Table 1. Melton Valley Storage Tank W-29 (MVST W-29) simulant was formulated and prepared based on an analysis
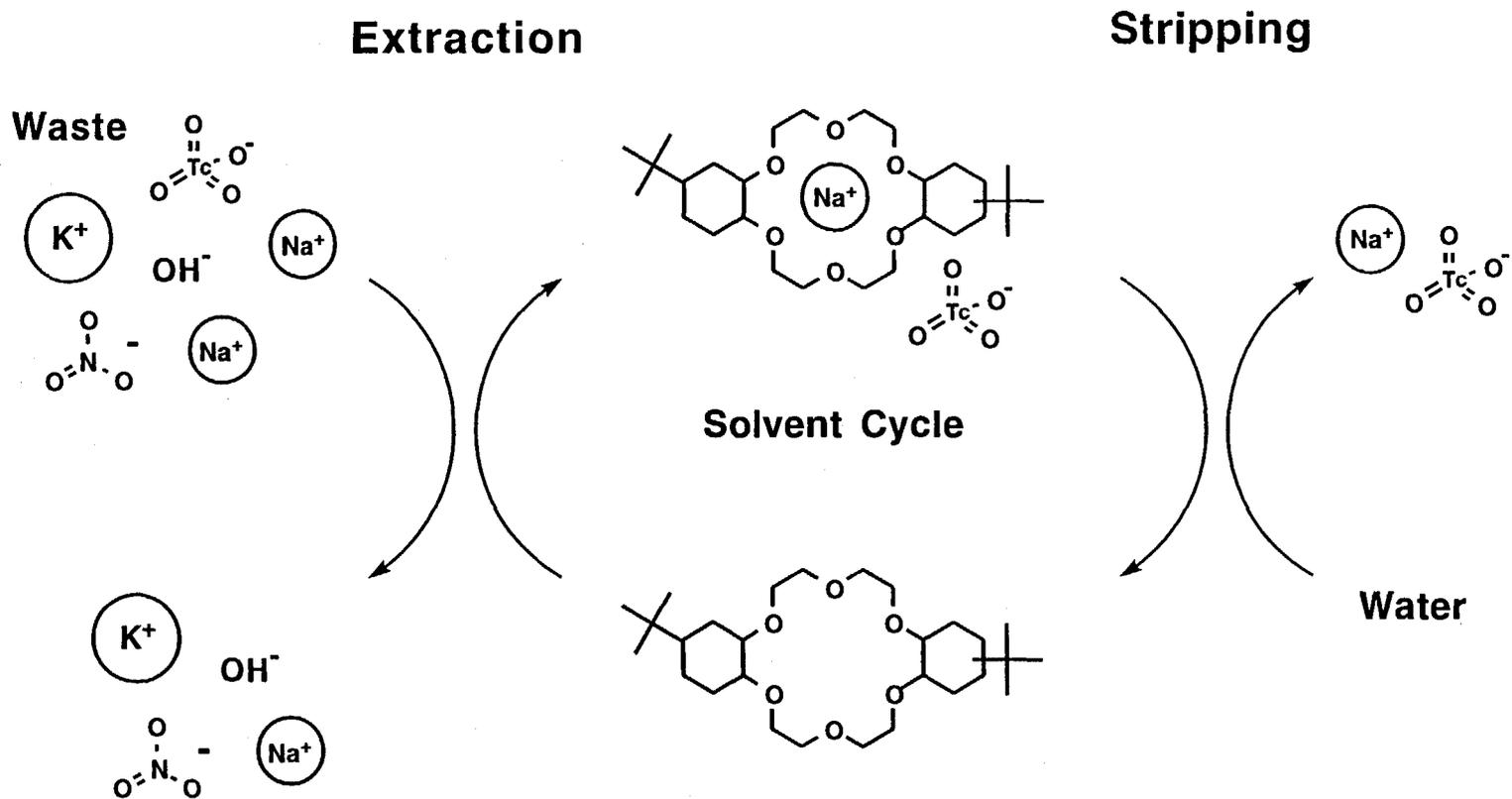
Figure 1.   Mechanism of extraction of pertechnetate by a crown ether from a waste stream containing alkali metal ions, and stripping with water.

Table 1. Comparison of different waste simulants used in this study.

Species	Concentration (M)		
	MVST W-29[a]	NCAW[b]	DSSF-7[c]
Na^+	4.59	4.99	7.00
K^+	2.90×10^{-1}	1.20×10^{-1}	9.45×10^{-1}
Rb^+	not added	5.0×10^{-5}	not added
Cs^+	4.3×10^{-6}	5.0×10^{-4}	7.0×10^{-5}
Ca^{2+}	8.7×10^{-5}	not added	not added
Sr^{2+}	1.1×10^{-5}	not added	not added
Al^{3+}	1.65×10^{-5}	4.30×10^{-1}	7.21×10^{-1}
OH^- (total)	1.58×10^{-1}	3.40	4.63
OH^- (free)	1.58×10^{-1}	1.68	1.75
Theoretical pH	13.2	14.52	14.56
F^-	not added	1.7×10^{-2}	not added
Cl^-	8.5×10^{-2}	not added	1.02×10^{-1}
Br^-	6.3×10^{-4}	not added	not added
NO_2^-	not added	4.30×10^{-1}	1.51
NO_3^-	4.52	1.67	3.52
CrO_4^{2-}	4.2×10^{-5}	not added	not added
SO_4^{2-}	7.0×10^{-3}	1.50×10^{-1}	8.0×10^{-3}
CO_3^{2-}	1.0×10^{-1}	2.30×10^{-1}	1.47×10^{-1}
PO_4^{3-}	not added	2.5×10^{-2}	1.4×10^{-1}
$^{99}TcO_4^-$	6.0×10^{-5}	6.0×10^{-5}	6.0×10^{-5}

[a]MVST W-29 simulant approximates the supernatant liquid in Melton Valley Storage Tank W-29 (Oak Ridge).
[b]NCAW approximates Hanford tank 241-AZ-101 Neutralized Current Acid Waste.
[c]DSSF-7 approximates Hanford tank 101-AW Double-Shell Slurry Feed.
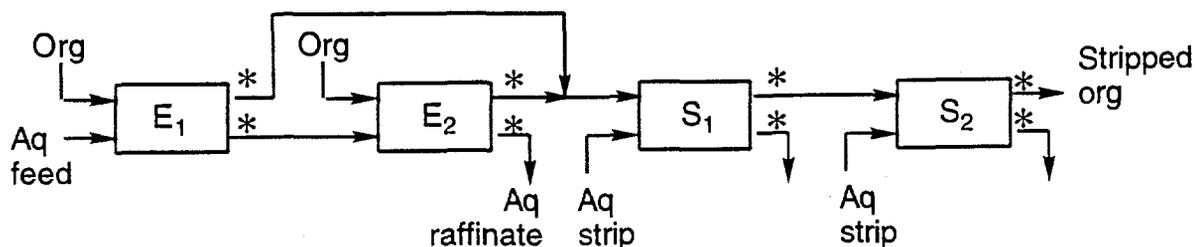
Scheme 1. Cross-current two-extraction two-strip contacting procedure (1:1 volume ratios) used for tests in this work. The asterisk (*) denotes when samples were taken for analysis. (Note: this is not meant to represent a process flowsheet).

obtained at Oak Ridge on the supernatant solution. Simulants which approximate Hanford tank 241-AZ-101 Neutralized Current Acid Waste (NCAW) and Hanford tank 101-AW Double-Shell Slurry Feed (DSSF-7) were prepared following recommendations obtained from Pacific Northwest Laboratories. Technetium-99 was added to the waste simulants during the last stage of preparation by spiking the simulant with the appropriate amount of 3.0 mM $NH_4{}^{99}TcO_4$ (NIST Traceable $NH_4{}^{99}TcO_4$, Isotope Products Laboratories, Burbank, CA) to give the desired concentration of 6 x 10^{-5} M. This Tc concentration was selected as a representative concentration for Tc in most Hanford tanks, though Melton Valley supernatant waste probably contains much lower concentrations.

General Two-Extraction/Two-Strip Procedure.

In a typical test, a synthetic waste solution containing $^{99}TcO_4{}^-$ at 6.0 x 10^{-5} M was gently contacted with an equal volume of solvent (crown ether plus diluent) for 1 hour at 25 °C in sealed borosilicate vials by end-over-end rotation at ~40 RPM using a Glass-Col® laboratory rotator. This contacting procedure ensures achievement of equilibrium, though kinetic tests show that 95% or more of the Tc is extracted within the first 5 minutes. After the phases were allowed to coalesce (either on their own or assisted by centrifugation as necessary), the aqueous and organic phases were subsampled and the ^{99}Tc activity in each phase determined using standard beta liquid scintillation counting techniques. An aliquot of the aqueous phase from the first contact was subsequently contacted with an equal volume of fresh extractant solution in the manner described above and the phases subsampled to determine the ^{99}Tc activity. In the stripping tests, aliquots of the organic phases from the first and second contacts were combined and contacted with an equal volume of deionized water in the manner described above. After the phases were subsampled, the organic phase from this first stripping operation was contacted with a second equal volume of water, comprising the second strip, and the phases were again subsampled to determine the ^{99}Tc activity. The entire cross-current two-extraction, two-strip procedure is shown diagramatically in scheme 1. All tests were run in duplicate, and the technetium extraction ratios ($[Tc]_{org}/[Tc]_{aq}$) are reported as the average of those obtained in the two stages E_1 and E_2. In general, the value of E_2 differed insignificantly from E_1.

RESULTS AND DISCUSSION
Technetium Extraction and Stripping as a Function of Crown Ether Structure

Representative extraction results for four commercial crown ethers (all 0.04 M in a 2:1 vol/vol blend of 2-octanone/Isopar® M) from NCAW and DSSF-7 are presented in Figure 2. The extraction ratio is the average of duplicate runs of the first and second contacts. Generally, the agreement in the extraction ratios E_1 and E_2 is excellent, though some variability was observed for DCH18C6, and to a lesser degree, di-t-BuCH18C6 during extraction from the DSSF-7 simulant. As can be seen, the best extraction results were obtained using DCH18C6, followed by di-t-BuCH18C6. The increase in the technetium extraction ratio observed for these two crown ethers on progressing from the NCAW to the DSSF-7 simulant can likely be attributed to the higher potassium concentration in the DSSF-7 simulant (0.945 M as opposed to 0.120 M in NCAW) and the fact that the 18-crown-6 family of crown ethers has a higher affinity for potassium than sodium.[9] In two contacts, it was possible to extract 98.4% and 97.6% of the pertechnetate present in the NCAW simulant with DCH18C6 and di-t-BuCH18C6, respectively. Similarly, 99.7% and 99.3% of the pertechnetate present in the DSSF-7 simulant could respectively be removed. It is worth noting that these high efficiencies for Tc extraction occur despite nitrate/pertechnetate concentration ratios of ~27,800 to 1 for the NCAW simulant, and ~58,700 to 1 for the DSSF-7 simulant.

Contacting the pertechnetate-containing organic phases twice with deionized water in effect removes nearly all of the technetium and regenerates the extractant. Figure 3 shows the total percent technetium removed from the Tc loaded organic phase following two cross-current stripping contacts with deionized water. In general (but not always), it was noted by comparison with Figure 2 that for a given crown ether stripping efficiency varied inversely with extraction efficiency.

The proof-of-principle having been demonstrated, it was next necessary to focus on selecting the most effective combination of crown ether, diluent, and modifier with regard to process economics and
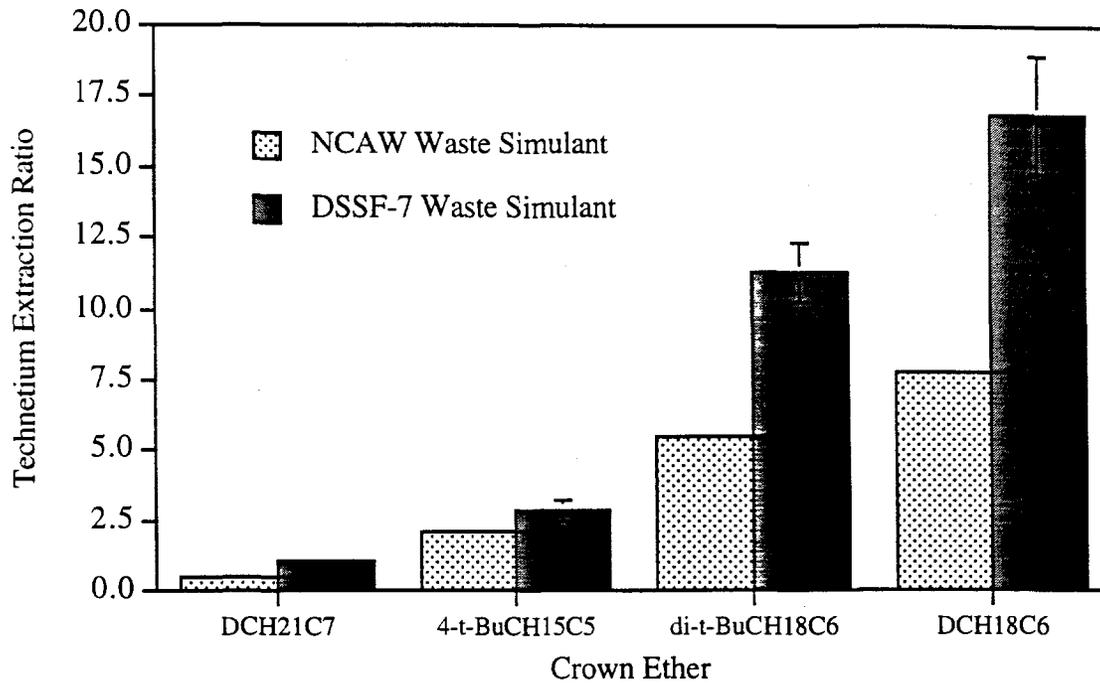
Figure 2. Extraction of pertechnetate from NCAW and DSSF-7 simulants by selected crown ethers (0.04 M in 2:1 vol/vol 2-octanone/Isopar® M). The extraction ratio is the average of the first and second contacts in the duplicate runs. In most cases the error bars are too small to be seen.
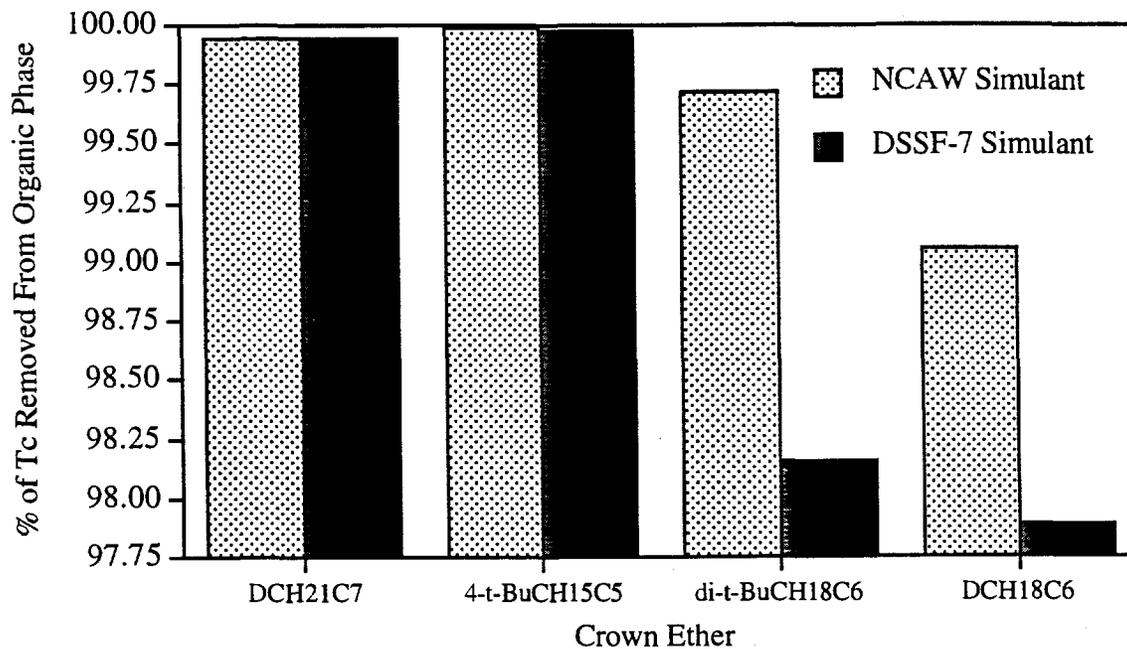

Figure 3. Total percentage of Tc removed from Tc laden 2:1 vol/vol 2-octanone/Isopar® M solutions shown in Figure 2 following two cross-current stripping contacts with deionized water.

performance. Bis-4,4'(5')[(*tert*-butyl)cyclohexano]-18-crown-6 (di-t-BuCH18C6) was selected as the crown ether worthy of further evaluation on the basis of its high degree of lipophilicity (and thus low degree of loss to the aqueous phase), its ability to strongly bind both sodium and potassium (which are both present in many tank wastes), and the fact that this crown ether is currently being considered for a process for the removal of strontium from acidic waste media.[8]

Effect of the Diluent and the Crown Ether Concentration

The nature of the diluent has a profound effect on both the Tc extraction and stripping efficiencies. In general, but not always, polar diluents that provide high extraction ratios do not strip well. Thus, diluent properties need to be carefully balanced so that both good extraction and stripping performance can be obtained. Additionally, there are certain requirements that an ideal diluent (or modified diluent) should meet to be suitable for a process. These include low volatility and flash point ≥ 60 °C (the threshold below which solvents are deemed ignitable and thus RCRA hazardous), low toxicity, low solubility in water, high chemical stability, high radiation stability, good phase-disengagement behavior with low emulsion tendency, and good capability to solvate and extract the desired species. With regard to chemical and radiation stability, the breakdown products should be minimal, should not interfere with the process, and should not impart any hazards. Aliphatic kerosenes such as those comprising the Isopar® line (Exxon Chemical) generally meet the above requirements, and are excellent and economical diluents. However, due to their extremely low polarity they are often incapable of solvating the crown ether-alkali metal-pertechnetate complex, let alone the crown ether extractant itself. Addition of a suitable modifier possessing some degree of polarity improves extraction power and promotes solubility without imparting undesirable properties to the system.

There is literature precedent for using ketones,[10] trialkyl phosphates,[10] and pyridines[10,11] as extractants for pertechnetate, and this formed a starting point for the selection of candidate modifiers to the base aliphatic kerosene diluent. Some of the modifiers that we have examined include 2-octanone, tributyl phosphate[12] (TBP), and 4-(1-butylpentyl)pyridine (4-BPP).[13] These modifiers all possess the desirable properties mentioned above. In addition, TBP has enjoyed a long history in solvent extraction in the nuclear industry,[14] and 4-(1-butylpentyl)pyridine, while a bit exotic, has been investigated fairly extensively in Pakistan as an extractant for a variety of metals,[15] including technetium.[13]

In selecting appropriate diluents for the solvent extraction and stripping cycle, we screened for diluents and modified diluents that would provide the best extraction and stripping efficiency, while still being suitable for a process. Table 2 lists the extraction and stripping results obtained using di-t-BuCH18C6 at 0.02 M in Isopar® M modified with equal volumes of 4-BPP, 2-octanone, or TBP. (The molar concentrations of 4-BPP, 2-octanone, and TBP are respectively 2.2, 3.2, and 1.8 M.) The extraction and stripping performance obtained using the modifier 2-octanone was very slightly better than that obtained using 4-BPP. The extraction performance obtained using TBP at 50 vol% in Isopar® M was markedly better, and stripping, while slightly less efficient, was still over 99%. Excellent coalescence on both extraction and stripping was observed for all systems, but particularly for the TBP/Isopar® M system.

As TBP appeared to be an excellent modifier, more detailed extraction and stripping tests employing it were performed. Experiments were conducted in which the crown ether concentration was varied at constant TBP concentration, and in which the TBP concentration was varied at a constant crown ether concentration of 0.02 M. Figure 4 shows the relationship between the technetium extraction ratio and the first stripping ratio for extraction from MVST W-29 and DSSF-7 simulants by 0.01, 0.02, and 0.04 M di-t-BuCH18C6 in 1:1 vol/vol TBP/Isopar® M, whereas Figure 5 shows this relationship for 0.02, M di-t-BuCH18C6 in Isopar® M containing 25, 50, or 67 vol% TBP. In both cases it can be seen that extraction and stripping performance vary inversely and that increasing either the crown ether concentration or the vol% TBP increases extraction but decreases stripping. Extraction of Tc from the DSSF simulant exceeds that from the MVST simulant due likely to the higher sodium and potassium content (leading to higher alkali metal loading of the crown ether) and the lower nitrate content (leading to less competition for pertechnetate). It can be seen that essentially the same level of extraction and stripping

Table 2.   Extraction of Pertechnetate from DSSF-7 Waste Simulant by di-t-BuCH18C6 at 0.02 M in Selected Diluents. Stripping by Back-Extraction with Water.[a]

Diluent	E_{Tc}[b]	% Extracted[c]	% Stripped[c]
1:1 4-BPP / Isopar® M	2.04 ± 0.02	89.21	99.97
1:1 2-octanone / Isopar® M	2.33 ± 0.23	90.95	99.99
1:1 TBP / Isopar® M	4.77 ± 0.01	97.00	99.79

[a]25 °C, 1:1 phase ratio, 1 h contacts. [b]E_{Tc} is the average of the technetium extraction ratios ($[Tc]_{org}/[Tc]_{aq}$) obtained in the two stages E_1 and E_2. [c]Total % extracted and total % stripped, respectively, after two cross-current extraction steps and two stripping steps.

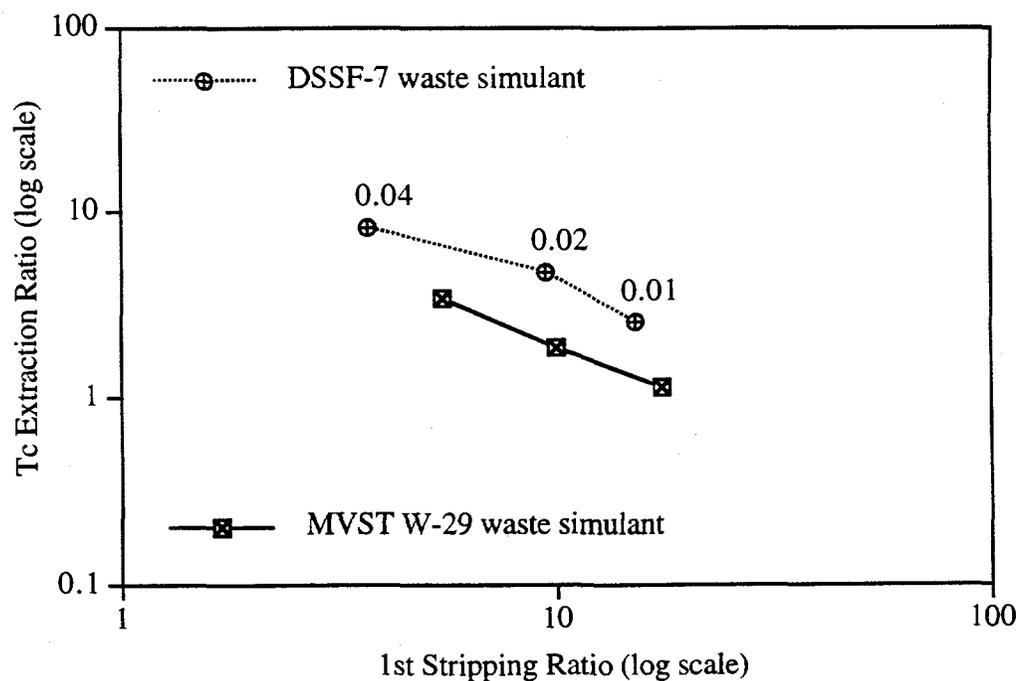Figure 4.   Tc extraction and stripping ratios for 1:1 vol/vol TBP/Isopar® M as a function of di-t-BuCH18C6 concentration (0.04, 0.02, and 0.01 M).
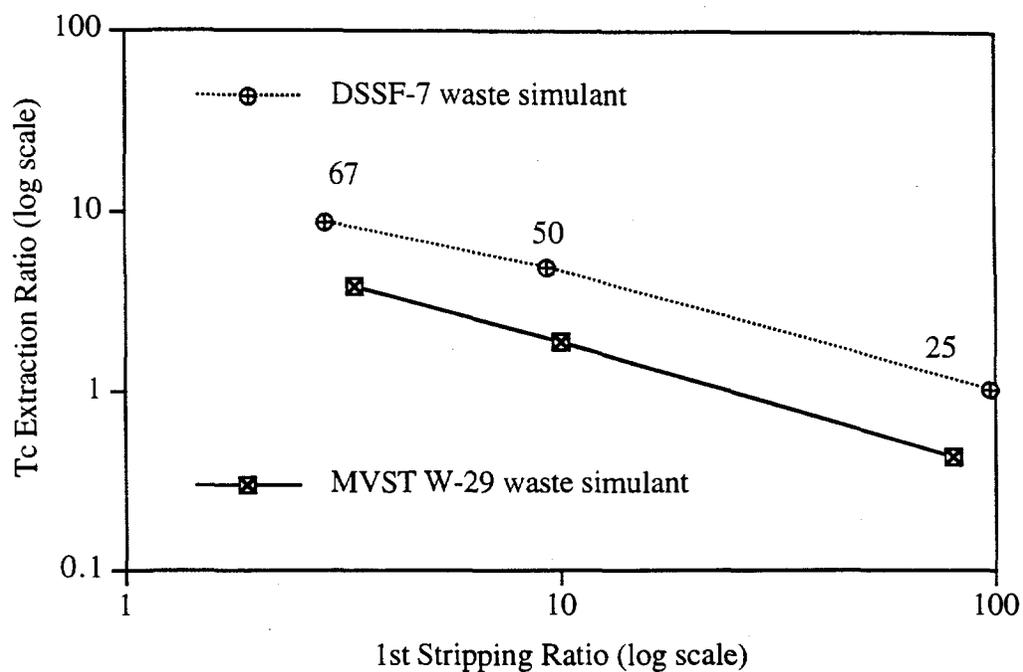
Figure 5.   Tc extraction and stripping ratios for 0.02 M di-t-BuCH18C6 in
TBP/Isopar® M blends as a function of vol% TBP (67, 50, and 25 vol%).
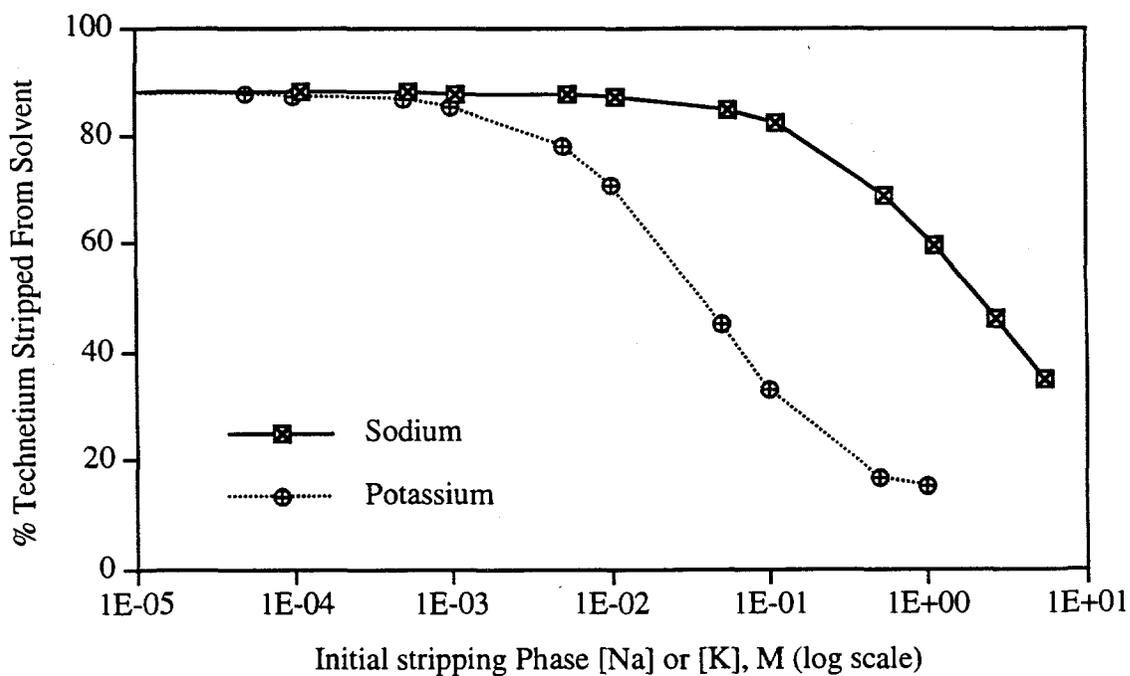

Figure 6.   Technetium stripping efficiency from solvent as a function of the initial
stripping-phase sodium or potassium nitrate molarity. Solvent is 0.02 M
di-t-BuCH18C6 in 1:1 vol/vol TBP/Isopar® M. Stripping efficiency
is for one equal-volume contact at 25 °C for 1 hour.

performance can be obtained using di-t-BuCH18C6 at either 0.04 M in 1:1 TBP/Isopar® M or at 0.02 M in 2:1 TBP / Isopar® M (67 vol% TBP): the former system provides a Tc extraction ratio (from DSSF-7) of 8.46 ± 0.21 with 98.88 % extracted and 99.60 % stripped after two extraction and stripping contacts, whereas the latter system provides a Tc extraction ratio of 8.67 ± 0.27 with 98.93 % extracted and 99.08 % stripped . Due to the high cost of the crown ether relative to the cost of TBP, the latter system is more favorable economically.

Effect of Sodium and Potassium Concentration on Stripping Efficiency
　　　　The ability to economically remove (strip) the pertechnetate from the extractant and thus regenerate the solvent represents a major advantage of crown ethers in tank-waste remediation. In our routine experiments, we use a cross-current stripping procedure in which the loaded organic phase is stripped a first time by contact with deionized water, and then a second time by recontact of the organic phase with a fresh supply of deionized water. We have observed that the first stripping ratio is generally lower than the second, in large part because the concentration of dissolved salts (both complexed and uncomplexed by the crown ether) in the organic phase is higher prior to the first strip than the second. As was discussed above, the stripping reaction is simply a reversal of the equilibrium forces driving the crown ether to complex the alkali metal ion. During extraction, the very high concentration of alkali metal ions drives the reaction toward formation of the crown ether-alkali metal complex. To dissociate this complex, the stripping phase needs to be as low in concentration in cations that are strongly complexed as possible. Many solvent extraction contacting procedures are performed in a <u>counter-current</u> manner, and it is expected that the concentrations of sodium and potassium in the stripping solution will build up over time, thus suppressing overall stripping efficiency. It was therefore of interest to determine how the overall stripping efficiency would be affected by using stripping phases that contained sodium and potassium at various concentrations. A solvent consisting of 0.02 M di-t-BuCH18C6 in 1:1 vol/vol TBP/Isopar® M was contacted in the usual manner with DSSF-7 simulant so that the solvent contained a nominal concentration of technetium (5.3×10^{-5} M). Aliquots of the Tc-laden solvent were then stripped once with equal volumes of either deionized water (control), sodium nitrate solutions of 1.1×10^{-4} to 5.55 M, or potassium nitrate solutions of 1.0×10^{-5} to 1.0 M. The effect on the stripping efficiency is shown in Figure 6, in which the percent Tc stripped from the organic is plotted against the sodium concentration in the stripping phase, or the potassium concentration in the stripping phase. Not surprisingly, the stripping efficiency is less tolerant of the potassium ion concentration than the sodium ion concentration, since potassium is complexed more strongly than sodium by di-t-BuCH18C6. From the plots shown in Figure 6, it appears that for this solvent and aqueous feed solution (DSSF-7), stripping performance does not begin to seriously erode until the [Na] in the stripping solution exceeds 0.1 M, or the [K] in the stripping phase exceeds 0.01 M. It is important to note that the stripping equilibrium is dependent on the <u>total</u> Na and K concentration in the combined organic and aqueous phases during the contact, and that this includes the Na and K dissolved in the solvent, as well as the Na and K in the aqueous stripping phase. An extraction was performed as above using ReO_4^- as a stand-in for TcO_4^- and the solvent phase subjected to three cross-current stripping contacts with deionized water. Analysis of the aqueous strips by Inductively Coupled Plasma Emission Spectroscopy revealed the organic-phase sodium and potassium concentrations prior to stripping to be 8.4 mM and 3.6 mM, respectively, which is a good indication of the <u>organic-phase</u> sodium and potassium concentrations in the analogous Tc-laden solvent prior to stripping. The organic phase Na and K will need to be taken into account for any detailed investigation of stripping performance as a function of Na and K concentrations, and additional experiments to probe the relationship between the stripping ratios and the <u>total</u> [Na] and [K] concentration in the contact (Na and K contained in both the solvent and the stripping solution) are in progress.

CONCLUSIONS
　　　　A series of crown ethers were evaluated for their potential use in a solvent extraction process for removal of technetium from alkaline tank waste media. Di-t-BuCH18C6 was selected as the best performing crown ether that was suitable for a process, and excellent extraction and stripping results from

realistic alkaline waste simulants were obtained, particularly when TBP was employed as the modifier for the aliphatic kerosene Isopar® M. Increasing the volume % of the modifier TBP from 50 to 67% allows the crown ether concentration to be lowered from 0.04 M to 0.02 M, while maintaining essentially the same level of extraction and stripping performance. Stripping efficiency is more sensitive to the total potassium ion than the sodium ion concentration; however adequate stripping can still be achieved provided the concentration build up of these ions is not excessive. Further process related studies, particularly with regard to optimizing performance at the lowest possible cost, are in progress.

ACKNOWLEDGMENTS

REFERENCES

1. Schulz, W.W., "Cyclohexanone solvent extraction of $^{99}TcO_4$ from alkaline nuclear waste solutions," in *Proceedings of the International Solvent Extraction Conference (ISEC '80)*; Liege, Belgium, 1980; paper #108.
2. Tribalat, S.; Beydon, J. Anal. Chim. Acta. **1953**, 8, 22-28.
3. Shanker, R.; Venkateswarlu, K.S.; Shanker, J. J. Less-Common Metals **1968**, 15, 311-316.
4. Chaiko, D.J.; Vojta, Y.; Takeuchi, M., "Extraction of technetium from simulated Hanford wastes," presented at *The Eighth Symposium on Separation Science and Technology for Energy Applications*; Knoxville, TN (United States), October 17-21, 1993.
5. Bonnesen, P.V.; Moyer, B.A.; Armstrong, V.S.; Haverlock, T.J.; Sachleben, R.A.; submitted for publication.
6. Jalhoom, M.G. J. Radioanal. Nucl. Chem. **1986**, 104, 131-139.
7. Korpusov, G.V.; Krylov, Y.S.; Tsalon, S.I. Sov. Radiochem. **1984**, 26, 390-392.
8. A discussion of lot-to-lot variation is given in: Horwitz, E.P.; Dietz, M.L.; Fisher, D.E. Solvent Extr. Ion Exch. **1991**, 9, 1-25.
9. Izatt, R.M.; Bradshaw, J.S.; Nielsen, S.A.; Lamb, J.D.; Christensen, J.J., Sen, D. Chem. Rev. **1985**, 85, 271.
10. Boyd, G.E.; Larson, Q.V. J. Phys. Chem. **1960**, 6, 988.
11. Zaitsev, A.A.; Lebedev, I.A.; Pirozhkov, S.V.; Yakovlev, G.N. Sov. Radiochem. **1964**, 6, 428.
12. Pruett, D.J.; McTaggart, D.R. Radiochim. Acta **1983**, 34, 203.
13. Iqbal, M.; Ejaz, M. J. Radioanal. Chem. **1974**, 23, 51.
14. See for example : Horwitz, E.P.; Kalina, D.G.; Diamond, H.; Vandegrift, G.F.; Schulz, W.W. Solvent Extr. Ion Exch. **1985**, 3, 75.
15. See for example (a) Mohammad, D.; Mahmood, T.; Qureshi, M.A.; Ejaz, M. J. Radioanal. Chem. **1978**, 42, 45, and references cited; (b) Bhatti, M.S.; Zuha, S.; Qureshi, M.A. J. Radioanal. Chem. **1984**, 82, 45, and references cited therein.