INVESTIGATING THE SOLVENT EXTRACTION OF TECHNETIUM(VII) FROM ALKALINE SODIUM NITRATE SOLUTION BY CROWN ETHERS

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ABSTRACT

Schemes under development for treatment and long-term disposal of radioactive defense wastes in the United States include steps for the removal of key fission products before vitrification of the waste. A need to remove the long-lived radionuclide technetium has been identified, but prior technology has been less than satisfactory. An analysis of anion-exchange principles in combination with the chemistry of crown ethers has led us to propose a new process for separating technetium from tank waste. The basis of selectivity in this system is similar to that of classical anion exchange, but the process can be readily reversed with a water strip. Candidate extraction solvents have been identified, and a process cycle has been tested.

INTRODUCTION

If options for transmutation of radionuclides are to be comprehensively evaluated in the United States, long-term risk factors demand consideration of the vast quantities of accumulated waste from past weapons production. At the Hanford site alone, approximately 2.4 x 10^5 m^3 of highly radioactive wastes stored in 177 underground tanks await treatment [1]. Current agreements dictate disposal by vitrification and long-term storage. Treatment of the waste prior to vitrification likely will involve separation of certain fission products including ^{90}Sr, ^{137}Cs, and ^{99}Tc, and thus methods for achieving these separations are being investigated actively. Among the radionuclides of interest, ^{99}Tc poses a long-term risk because of its environmental mobility and long half life of 2.1 x 10^5 y. In addition, its volatility as Tc_2O_7 poses problems in off-gas treatment during vitrification. Because of these long- and short-term issues, we have been investigating the separation chemistry applicable to the removal of technetium from alkaline media. At the outset of this work, it was necessary to consider the fundamental nature of technetium chemistry together with the principles that give rise to high selectivity for technetium in a background of concentrated salts. These principles may be applied through the chemistry of crown ethers, and a process has now been proposed for technetium solvent extraction employing crown ethers. The approach employed in carrying out this work relies on a "synergism" between basic and applied research. Accordingly, the applied research identifies certain problems to solve and exploits known chemistry, while the basic research establishes applicable underlying principles of behavior. In this paper, we outline the problem regarding separation of technetium from highly alkaline media, propose a basic chemical strategy based on the use of crown ethers, and present selected supporting experimental data.

THE PROBLEM

Waste solutions of concern initially include the supernatant liquid in the tanks. Later, solutions resulting from washing tank solids, comprising salt cake and hydrolytic precipitates, with water will be considered. Thus, any method for treating the supernatant solutions should ideally be able to handle streams from these washes also. The bulk of the waste is simply sodium nitrate and water. Hydroxide, converted partially to carbonate, gives the high alkalinity of the solutions. Other constituents in high concentration include aluminate, nitrite, phosphate, and sulfate. Some of the tanks contain chelating agents and their degradation products up to a few weight percent. At this writing, characterization data remain far from complete, but it is already clear that a wide variation in composition will be encountered in processing. In particular, data concerning the technetium content of the wastes has been lacking, partly because of the difficulty in measuring trace levels of a pure beta emitter. The total tank inventory of technetium at Hanford has been estimated at 1.8 metric tons and is thought to exist primarily in the supernatant solutions rather than in the sludge [1]. The levels of technetium in these solutions will then be of the order of 10^{-4} M on average.

Owing to its high selectivity and good mass-transfer properties, solvent extraction offers a potentially attractive vehicle for technetium removal from tank waste. The high ionic strength of the feed promotes good phase separation and minimizes (by "salting out") the solubility of organic solvent components in the aqueous phase. In addition, traces of solvent which may escape into the raffinate pose little difficulty for the high-temperature processes to follow.

A number of solvent-extraction systems have been demonstrated to remove technetium from aqueous solutions. Specifically applicable to alkaline solutions are pure solvents such as cyclohexanone and anion-exchange reagents such as quaternary amines. Pure solvents were shown to weakly extract sodium pertechnetate from alkaline solutions [2]. These included simple monofunctional ketones, alcohols, trialkylphosphates, nitriles, nitro compounds, and nitrogen bases. The extractions were promoted by high dielectric constant and high molar concentration of the polar group. Within a given family of solvents, the extraction ability decreases as the number of carbon atoms in the solvent molecule increases. Thus, to obtain usable distribution coefficients, the low molecular-weight compounds in a series must be employed. But as the number of carbon atoms in the solvent molecule decreases, the solubility in water increases, the volatility increases, and the ability to extract other electrolytes increases. Despite these disadvantages, it has been proposed to remove technetium from alkaline, high-salt solutions by methyl ethyl ketone [3] or by cyclohexanone [4]. The latter was in fact considered a strong candidate for removal of technetium from Hanford waste, but formation of emulsions on stripping was considered a disadvantage [4]. Both of these ketones possess low flash points, which would present safety concerns and regulatory burdens associated with production of "mixed wastes," defined in the United States as containing a hazardous substance (in this case, the two solvents possess the ignitability characteristic under U.S. regulations) and radionuclides.

Extraction of technetium by anion-exchange solvent extraction may be accomplished from both acid and alkaline solutions [2]. A number of organic salts having bulky cations have been employed for this purpose, but the most common reagents are the long-chain quaternary ammonium salts. Such anion exchangers have been shown to be capable of removing pertechnetate from alkaline solutions containing high concentrations of sodium nitrate [5]. To strip the resulting solvent, one must either replace the pertechnetate with an anion more strongly held by the solvent or to change the form of the technetium. Both options require the addition of chemicals to the system and potentially add to the overall waste volume. The former option can be accomplished by contact with strong nitric or perchloric acid solutions [6]. The latter may possibly be accomplished by reduction [5].

In view of these points, a new process for removal of technetium from highly alkaline media is desirable. The process would ideally involve chemicals which have low aqueous solubility, low volatility, low toxicity, minimal regulatory burdens, and good stability. Further, the process should require the addition of no new chemicals to the waste stream. Rapid throughput dictates that the process also have good kinetics and fast phase disengagement; this must be regarded as essential for efficient use, and minimum inventory, of expensive extractants. High selectivity will be needed to improve the performance of post-processing steps for the isolation of a concentrated technetium stream, especially if transmutation is considered an end-option.

CHEMICAL PRINCIPLES

From available reduction potentials [7], the pertechnetate ion, TcO_4^-, is the most stable form of technetium in aerobic, noncomplexing environments from pH 0 to 14. In the absence of complexants, Tc(IV) is the only other important oxidation state in solution, but it readily oxidizes to TcO_4^- ion in the presence of air and radiolytic conditions [7]. Organic complexants are not known to interact with the TcO_4^- ion in aqueous solution, but lower oxidation states of technetium form a variety of complexes [8,9]. However, formation of these complexes still generally requires reducing conditions. Thus, the applicable state of technetium in the tank wastes is reasonably expected to be the TcO_4^- ion. As a cautionary note, in view of the lack of direct analytical data concerning the exact form of technetium in the Hanford tank wastes, the possibility of other forms of technetium cannot be ruled out, especially since some of the wastes contain high concentrations of complexants. Keeping this possibility in mind for consideration as data becomes available, we nevertheless presume at this stage that the major separation problem

Table 1. Ion Size and Hydration Data for Representative Anions

Anion	Ionic Radius (nm)[a]	Thermochemical Radius (nm)[b]	$-\Delta G_h(M^+)$[c] kJ mol^{-1}	$d_{M\text{-}O}$[d] (nm)
F^-	0.130	0.126	472	
OH^-	0.137	0.133	439	
Cl^-	0.181	0.172	347	
NO_2^-		0.192	339	0.125
Br^-	0.196	0.188	321	
NO_3^-		0.179	306	0.125
I^-	0.220	0.210	283	
MnO_4^-		0.229	245	0.159
ClO_4^-		0.240	214	0.144
TcO_4^-		(0.241 est)		0.171
ReO_4^-		(0.244 est)		0.174
IO_4^-		0.249		0.179
CO_3^{2-}		0.178	1479	
SO_4^{2-}		0.258	1090	
PO_4^{3-}		0.238	2754	

[a]Effective ionic radii from crystallographic data [11]. [b]Determined from lattice energies; these values are applicable to thermodynamic calculations for nonspherical anions [12,13]. Values for TcO_4^- and ReO_4^- anions were estimated by adding 0.70 (difference between the thermochemical radius and $d_{M\text{-}O}$ for MnO_4^-) to $d_{M\text{-}O}$. [c]Free energies of hydration taken from the tabulation in ref. [14]. [d]Mean bond distances between central atom M and the oxygen atoms in selected oxyanions [15,16].

of interest involves removing trace levels of TcO_4^- anion from high concentrations of other anions, including OH^-, NO_3^-, NO_2^-, CO_3^{2-}, SO_4^{2-}, $Al(OH)_4^-$, and PO_4^{3-}. A method that achieves this end without adjusting the waste in some manner must obviously possess extreme selectivity for the TcO_4^- anion.

In Table 1 are listed the ionic radii of various anions together with selected M-O bond distances $d_{M\text{-}O}$ and free energies of hydration $\Delta G_h(M^+)$. Since the concept of anion size loses some definition in comparing oxyanions of different geometries, thermochemical radii derived from lattice energies are also included in the table. One may see that the strength of anion hydration decreases (i.e., the free energy of hydration becomes less negative) as anion size increases. Unfortunately, thermochemical radii and $\Delta G_h(M^+)$ values are not available for TcO_4^-, but from M-O bond distances, it may be estimated that this anion (and its closely related analog ReO_4^-) is effectively larger and less strongly hydrated than the abundant anions OH^-, CO_3^{2-}, NO_2^-, NO_3^-, SO_4^{2-}, and PO_4^{3-}.

Anion-exchange principles as applied to solvent extraction or resin ion exchange have long been known to predict selectivity for large, poorly hydrated anions [10]. Consider the anion-exchange reaction below:

$$R^+X^-\,(org) + Y^-\,(aq) \rightleftharpoons R^+Y^-\,(org) + X^-\,(aq) \qquad (1)$$

Here R^+ is a lipophilic cation which is paired with exchangeable anion X^- in the organic phase. In the most general terms, the hydration of the anion usually predominates in controlling the free energy of anion exchange. Hydration free energy varies inversely with ionic radius through the Born equation, and thus, it may be expected that anion exchange in eq. 1 will be favored when Y^- is larger than X^-. One study of relevance to the present problem showed that anion exchange involving tetraheptylammonium salts in benzene follows the order $ReO_4^- > ClO_4^- > Br^- > NO_3^- > Cl^-$ [17]. From the results of that study, it may be concluded that one must employ bulky cations and solvents of relatively low dielectric constant. Thus, it should be possible to separate TcO_4^- from smaller anions by anion exchange (eq. 1). The question arises as to the severity of the competition from nitrate, which is more concentrated in the waste by a factor of at least 10^4. As pointed out above, data show that the requisite selectivity is attainable, giving acceptable distribution coefficients from concentrated nitrate media [5,6].

In view of the desirable selectivity characteristic of anion exchange, an improved process would result by replacing the quaternary ammonium cation by another bulky cation that can be reversibly decomposed. Crown ethers offer an ideal vehicle for the reversible formation of lipophilic salts having a bulky cation. By analogy to eq. 1, one may write an anion-exchange reaction in which the cation R^+ is replaced by the complex $[MB]^+$ resulting from inclusion of a metal cation M^+ by the neutral crown ether B:

$$[MB]^+X^-\,(org) + Y^-\,(aq) \rightleftharpoons [MB]^+Y^-\,(org) + X^-\,(aq) \qquad (2)$$

It follows that such a reaction favors large, poorly hydrated anions such as TcO_4^-.

Formation of the organic-phase salts $[MB]^+X^-$ and $[MB]^+Y^-$ starting with only crown ether in the organic phase may be written as ion-pair extractions:

$$M^+\,(aq) + X^-\,(aq) + B\,(org) \rightleftharpoons [MB]^+X^-\,(org) \qquad (3)$$

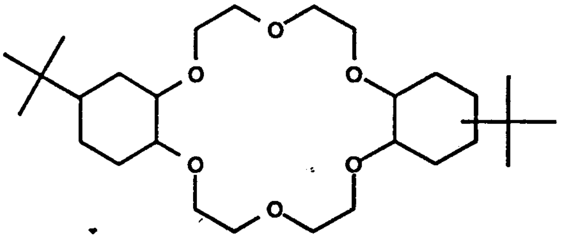
$$M^+\,(aq) + Y^-\,(aq) + B\,(org) \rightleftharpoons [MB]^+Y^-\,(org) \qquad (4)$$

It may be noted that eq. 2 is simply the resultant reaction upon subtracting eq. 3 from eq. 4. If eqs. 3 and 4 lie far to the right, then the resultant chemistry may best be given by eq. 2. In considering the tank-waste problem, let X^-, Y^-, and M^+ respectively be the ion of interest TcO_4^-, the major competitor anion NO_3^-, and an abundant cation Na^+ (or K^+).

Although ion-pair extraction differs in its equilibrium properties from anion exchange, the selectivity for large, poorly hydrated anions is retained provided the cationic complex $[MB]^+$ is sufficiently bulky. This may be shown by examining the equilibrium constants $K_{X,Y}$, $K_{ex,MBX}$, and $K_{ex,MBY}$ corresponding to eqs. 2, 3, and 4. Since $K_{X,Y} > 1$ for Y^- larger than X^- and $K_{X,Y} = K_{ex,MBY}/K_{ex,MBX}$, then $K_{ex,MBY} > K_{ex,MBX}$ for Y^- larger than X^-. That is, the efficiency of ion-pair extraction increases with increasing anion size.

The effect of anion size on ion-pair extraction has been reported by a few workers and qualitatively agrees with the above expectations. The efficiency of extraction of the alkali metals Li^+ - Cs^+ by the crown ether dicyclohexano-18-crown-6 (presumably mixed isomers) in dichloroethane was found to follow the order $ClO_4^- > I^- > NO_3^- > Br^- > OH^- > Cl^- > F^-$ [18]. This order may at once be recognized as resembling the order of anion selectivity by use of lipophilic tertiary alkyl ammonium salts $ClO_4^- > NO_3^- > Cl^- > F^-$ [19]. By comparison with Table 1, it may also be seen that the extraction of alkali metal salts by the crown ether indeed increases with both increasing anion size and decreasing strength of hydration.

Not surprisingly, the extraction of TcO_4^- anion from aqueous electrolyte solutions has been reported for several crown ethers. Dicyclohexano-18-crown-6 (DCH18C6) was shown to extract TcO_4^- from nitric acid into trichlorobenzene [20]; the postulated organic species was $[K(DCH18C6)]TcO_4$. The related crown ether dibenzo-18-crown-6 extracts TcO_4^- from sulfuric acid into 1,2-dichloroethane [21]. In the SREX process for the extraction of Sr^{2+} from nitric acid [22], the crown ether 4,4'(5')-di(*tert*-butylcyclohexano)-18-crown-6 (Fig. 1) in 1-octanol also extracts TcO_4^-. Crown ethers have been employed in the analysis of Tc in radioactive effluents by solvent extraction [23]. On the alkaline side, several crown ethers were found to extract TcO_4^- from sodium hydroxide into benzene, nitrobenzene, and several halogenated diluents [24]; the organic-phase species was thought to be $[Na(DCH18C6)]TcO_4$.



4,4',(5')-di(*t*-butyldicyclohexano)-18-crown-6
DtBuCH18C6

Figure 1. Preferred crown ether for technetium extraction. Commercial material consists of a mixture of isomers.

Many crystal structures of alkali metal complexes of the form $[MB]^+X^-$ have been reported, and the encirclement of metal cations by crown ethers of sufficient size has been demonstrated repeatedly. A complex related to the present work has the formula $[Na(benzo\text{-}15\text{-}crown\text{-}5)]ReO_4$ [25]. In the crystal structure, the sodium cation occupies a nearly planar cavity formed by the five oxygen atoms of the

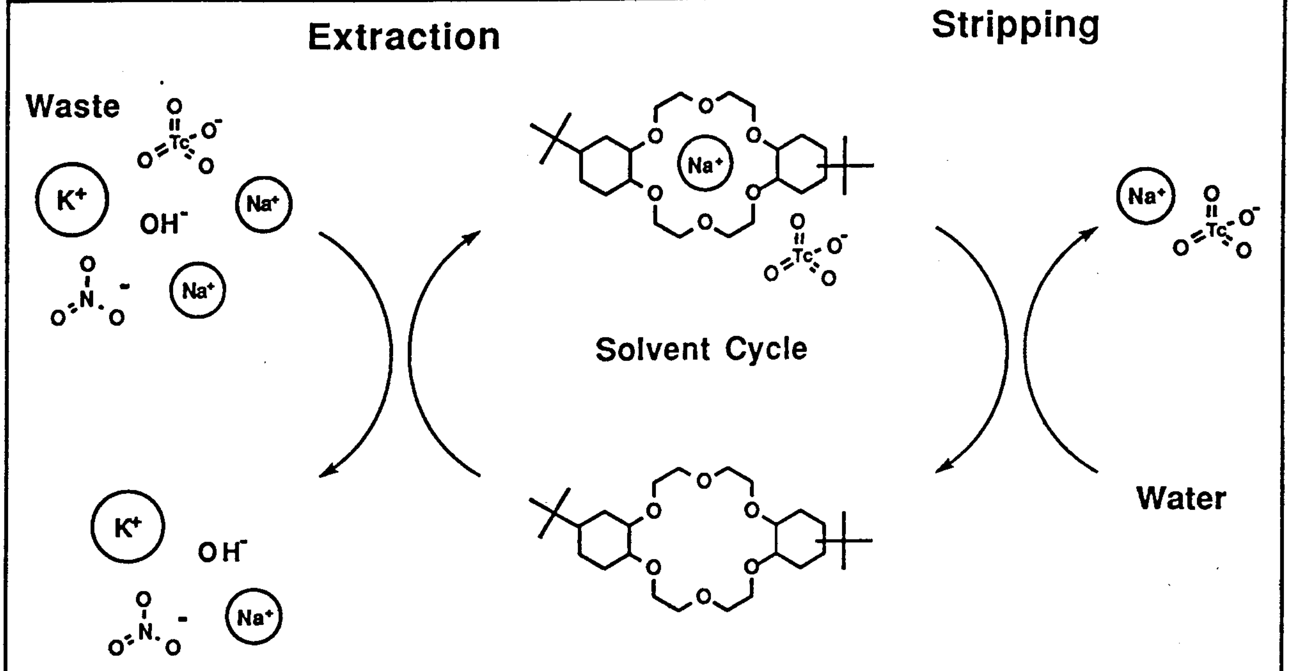


Figure 2. Simplified conception of a process for the extraction of pertechnetate anion from an alkaline nitrate waste solution using a crown ether. In the extraction section, the crown ether forms an ion-pair complex in which the sodium is bound by the crown ether and pertechnetate is the preferred counter anion. This complex decomposes when the solvent is contacted with water in the stripping section.

crown ether. Each sodium cation is coordinated to two perrhenate anions at the apical positions, forming a pentagonal bipyramid of oxygen atoms. The perrhenate anions each bridge two sodium cations so as to form linear chains. The crown ether presents hydrocarbon groups to the environment and thereby renders the entire complex lipophilic.

Mass-action properties of the equilibrium given by eq. 3 make crown ethers especially adaptable to economical extraction of TcO_4^-. It may be seen that the driving force of ion-pair extractions, such as eqs. 3 and 4, increases with increasing concentration of cations M^+ in the aqueous solution. Thus, concentrated salt solutions, as found in tank waste, are optimum for such a process. To reverse the extraction, the solvent containing the extracted $NaTcO_4$ needs only to be contacted with water, releasing the $NaTcO_4$. Figure 2 depicts in simplified terms the extraction and stripping process envisioned.

EXTRACTION RESULTS

To test the concepts presented above, a series of experiments have been carried out to determine the most effective crown ether and solvent system for removal of technetium from tank waste [26]. Initial systematic studies of extraction behavior were carried out with the diluent 1-octanol, though evaluation of the diluent effect (see below) has subsequently indicated better diluents for practical use. Among the available crown ethers, DCH18C6 gave the strongest extraction of $NaTcO_4$ from alkaline nitrate media. Solutions of DCH18C6 in 1-octanol extracted Tc rapidly, reaching equilibrium in a few minutes of dispersing the two phases. However, DCH18C6 probably does not have the needed lipophilicity to minimize its own distribution to the aqueous phase; because of the expense of the crown ether, such losses dominate process economics. Thus, DtBuCH18C6 (Fig. 1) currently offers the best properties for development of a process. The *t*-butyl groups provide the requisite lipophilicity but involve some trade-offs: increased cost of the crown ether, increased isomeric complexity owing to the random substitution at the 4' or 5' positions of the cyclohexane ring, and a slightly lower Tc distribution coefficient.

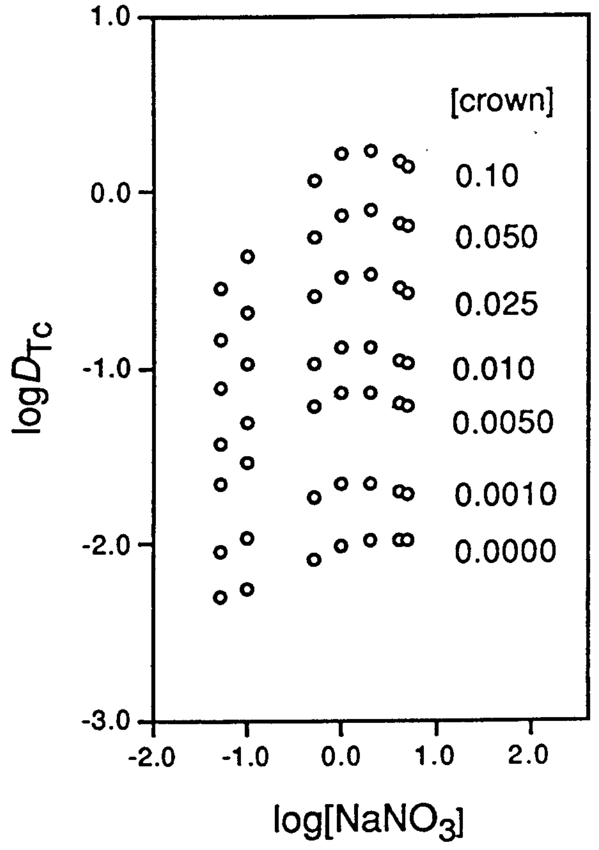


Figure 3. Extraction of pertechnetate by *cis-syn-cis*-dicyclohexano-18-crown-6 in 1-octanol at 25 °C as a function of the initial aqueous-phase concentration of $NaNO_3$. The pure isomer of DCH18C6 was used so as to obtain best reproducibility. The initial Tc concentration was 3.47×10^{-5} M, and the phase ratio was 1:1.

Figure 3 shows the extraction of trace pertechnetate from sodium nitrate solutions by 1-octanol solutions of the *cis-syn-cis* isomer of DCH18C6. It may be seen that the Tc distribution coefficient D_{Tc} ($[Tc]_{org}/[Tc]_{aq}$) increases as the sodium nitrate concentration increases up to approximately 1 M. This trend qualitatively follows expectations based

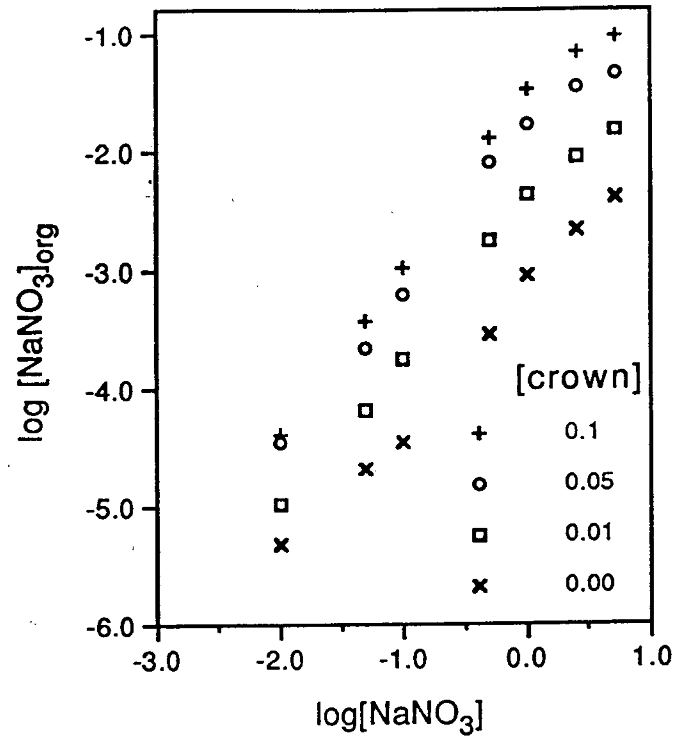


Figure 4. Extraction of sodium nitrate by *cis-syn-cis*-dicyclohexano-18-crown-6 in 1-octanol at 25 °C as a function of the initial aqueous-phase concentration of $NaNO_3$. The phase ratio was 1:1.

on eq. 3. However, the curves exhibit maxima as the controlling equilibria apparently shift to a situation in which further addition of sodium nitrate impairs the extraction of pertechnetate. Such could be the case if the crown ether becomes significantly loaded with competing sodium nitrate (eq. 4), whereupon the extractant effectively becomes $[Na(DtBuCH18C6)]TcO_4$ and the equilibrium effectively becomes anion exchange (eq. 2).

Indeed, the crown ether extracts significant levels of sodium nitrate, as shown in Fig. 4. The sodium distribution coefficient D_{Na} also increases with increasing sodium nitrate concentration, reaching a maximum at approximately 1 M $NaNO_3$. At that point, the concentration of sodium in the solvent approaches the crown ether concentration. Although the data in Figs. 3 and 4 provide qualitative confirmation of the expectations put forth in the preceding section, the actual description of the equilibria in the system is complicated and remains under investigation. Among the complications being elucidated is the non-negligible extraction of sodium nitrate, hydroxide, and pertechnetate by 1-octanol alone, as can be seen in Figs. 3 and 4. In addition, the diluent has sufficient polarity ($\varepsilon > 10$) to partially dissociate the ion pairs in the organic phase. It also contains significant concentrations of water.

The strength of pertechnetate extraction from alkaline sodium nitrate by crown ethers depends markedly on the type of diluent employed (25). Polar diluents perform particularly well, but many of them have unwanted properties such as high loss to the aqueous phase, toxicity, environmental restrictions, and volatility.

Table 2. Pertechnetate Extraction and Stripping Employing the Crown Ether 4,4'(5')-di(*t*-butylcyclohexano)-18-crown-6[a].

Simulant	% Tc Extracted[d]	% Tc Stripped[d]
Simple[b]	89.46 ± 0.07	97.67 ± 0.03
DSSF-7[c]	97.20 ± 0.08	95.90 ±1.10

[a] The solvent consisted of the crown ether at 0.01 M concentration in a 1:1 v:v mixture of 4-(1-butylpentyl)pyridine in Isopar® M.

[b] Simple simulant is 0.1 M NaOH, 5.0 M $NaNO_3$.

[c] DSSF-7 approximates Hanford tank 101-AW Double-Shell Slurry Feed.

[d] After two contacts at a 1:1 phase ratio at 25 °C; deionized water was used for stripping.

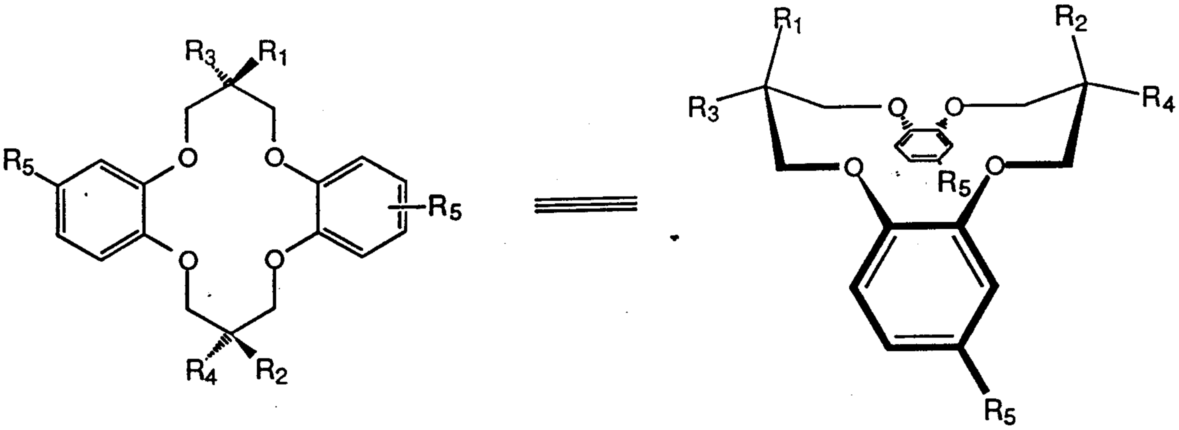
Table 3. Waste Simulants Used in This Study.

Species	Concentration (M)	
	Simple Simulant[a]	DSSF-7 simulant[b]
Na^+	5.10	6.999
K^+	not present	0.945
Cs^+	not present	7.0×10^{-5}
Al^{3+}	not present	0.721
OH^- (total)	0.1	4.634
OH^- (free)	0.1	1.750
NO_2^-	not present	1.512
NO_3^-	5.00	3.521
Cl^-	not present	0.102
SO_4^{2-}	not present	0.008
CO_3^{2-}	not present	0.147
PO_4^{3-}	not present	0.014
$^{99}TcO_4^-$	6.0×10^{-5}	6.0×10^{-5}

[a]Simple simulant is 0.1 M NaOH, 5.0 M $NaNO_3$.
[b]DSSF-7 approximates Hanford tank 101-AW Double-Shell Slurry Feed.

Moreover, distribution coefficients tend to be so strong that stripping with water can no longer be carried out. In fact, the maximum in the dependence of D_{Tc} on the aqueous sodium nitrate concentration appears to shift to the left with the strongest diluents such as nitrobenzene. Good properties were, however, found with modified alkane diluents. Effective modifiers include 4-substituted pyridines, ketones, and tributyl phosphate (TBP). Data for a pyridine modifier are given in Table 2. Table 3 defines the aqueous phases employed, including a simple simulant together with a more complex tank-waste simulant. As shown in Table 2, pertechnetate can be readily removed from such media and then stripped from the solvent with water.

Based on the commercially available crown ether DtBuCH18C6, solvent systems such as the one shown in Table 2 appear to be suitable for process development. However, improvements could yet have significant impact on process economics. It may be noted that only a small fraction of the total capacity of the crown ether is used, and thus owing to the expense of the crown ether, strong incentive exists to reduce the crown-ether concentration. A possible avenue toward this end lies in more effective binding and encapsulation of the sodium cation. To explore this possibility, the series of crown ethers shown in Figure 5 is being synthesized and studied. The series is built upon the rigid framework of dibenzo-14-crown-4, which provides the base from which 3-dimensional coordination of the cation can be supplied by the upright sidearms. The best performance found at this writing has



R_5 = H					R_5 = *t*-Octyl				
	R_1	R_2	R_3	R_4		R_1	R_2	R_3	R_4
1	H	H	H	H	11	H	H	H	H
2	OH	H	H	H	12	OH	H	H	H
3	OAc	H	H	H	13	OAc	H	H	H
4	OCH_3	H	H	H	14	OCH_3	H	H	H
5	OCH_2COCH_3	H	H	H	15	OCH_2COCH_3	H	H	H
6	OH	OH	H	H	16	OH	OH	H	H
7	OAc	OAc	H	H	17	OAc	OAc	H	H
8	OCH_3	OCH_3	H	H	18	OCH_3	OCH_3	H	H
9	OCH_2COCH_3	OCH_2COCH_3	H	H	19	OCH_2COCH_3	OCH_2COCH_3	H	H
10	OH	OH	CH_3	CH_3	20	OH	OH	CH_3	CH_3

Figure 5. New crown ethers for extraction of alkali metal salts. The compounds are built upon dibenzo-14-crown-4. Alkyl substituents on the benzo rings supply lipophilicity.

been obtained with the *cis*-bis(oxyacetone) compound, which gives approximately the same Tc distribution coefficient as DtBuCH18C6.

X-ray crystal structures show that the dibenzo-14-crown-4 compounds complex sodium ion. As shown in the example in Fig. 6, the *cis*-bis(diol) derivative binds Na^+ ion with its six available donor atoms. As expected, the dibenzo-14-crown-4 ether provides the base of four ether oxygens, and the hydroxy sidearms coordinate the cation on opposite sides. The perrhenate anion coordinates to the sodium cation in monodentate fashion. Only one of two unique crown ether molecules is shown. The other holds a sodium cation in a similar manner, and this cation receives coordination from a second oxygen atom of the perrhenate anion shown. Thus, the anion bridges two crown-ether-sodium complexes. A second perrhenate anion (not shown) is not coordinated to any sodium cation but rather interacts with one of the hydroxy ligands by hydrogen bonding. Details of the structure will be published in full elsewhere. As for the structure of the complex in solution, the crystal structure provides no definite information, but rather only possibilities. Experiments are in progress to gain information on solution stoichiometry and structure by extraction, NMR, and other methods.

CONCLUSIONS

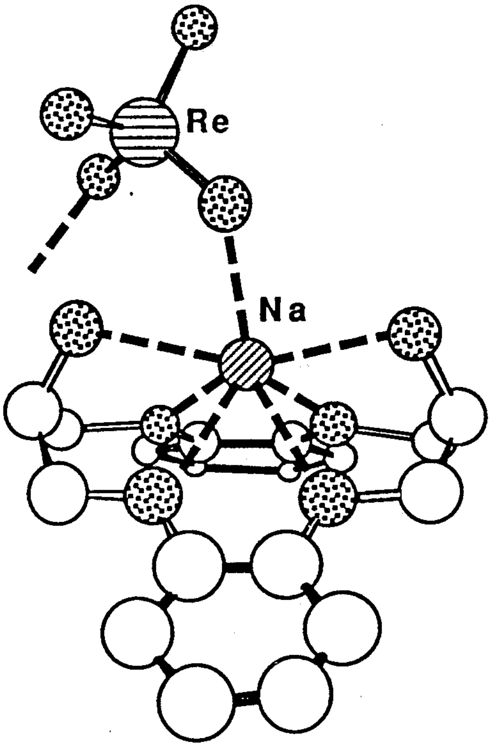


Figure 6. Portion of the crystal structure of [Na(*cis-sym*-dibenzo-14-crown-4-diol)]ReO_4. Hydrogen atoms have been omitted for clarity.

Anion-exchange principles as applied to solvent extraction or resin ion exchange have long been known to predict selectivity for large, poorly hydrated anions. Although typical anion-exchange extractants function effectively in the separation of pertechnetate anion from highly alkaline media, stripping presents difficulties because a means to reverse the anion-exchange process is inherently lacking. By contrast, crown ethers offer an ideal vehicle for the reversible formation of lipophilic salts having a bulky cation. In this case, the bulky cation forms via the inclusion of a metal cation by the crown ether, resulting in the co-extraction of the metal cation and an aqueous anion for charge neutrality. One may view the extracted anions as exchangeable with other aqueous anions, a process again expected to favor large, poorly hydrated anions such as pertechnetate. Thus, the resulting selectivity in the overall extraction of a metal salt by a crown ether is determined largely by the effective binding of the metal cation by the crown ether and the hydrophobicity of the anion. Such an extraction is driven by high concentrations of alkali metal cations and is reversed by contacting the loaded solvent with water or solutions containing low concentrations of extractable metal salts.

Experiments have shown that solvents containing crown ethers indeed reversibly extract pertechnetate anion from aqueous solutions containing alkali metal salts, including a simulant of Hanford tank waste. Dependencies of the technetium distribution ratios on the concentrations of system components have been determined for *cis-syn-cis*-dicyclohexano-18-crown-6 in 1-octanol. Qualitatively, the dependencies agree with the expected ion-pair extraction. A number of commercially available crown ethers have been examined and compared with several novel crown ethers based on the dibenzo-14-crown-4 framework. Structural properties of a sodium perrhenate complex with *cis-sym*-dibenzo-14-crown-4-diol have been characterized by X-ray crystallography, showing the encapsulation of the sodium cation by the six oxygen atoms of the crown ether.

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