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SOLVENT EXTRACTION OF TECHNETIUM FROM ALKALINE WASTE MEDIA USING BIS-4,4'(5')[(*tert*-BUTYL)CYCLOHEXANO]-18-CROWN-6*

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ABSTRACT

The crown ether bis-4,4'(5')[(*tert*-butyl)cyclohexano]-18-crown-6 can be utilized in a solvent-extraction process for the removal of technetium (as pertechnetate ion, TcO_4^-) from solutions simulating highly radioactive alkaline defense wastes ("tank wastes") stored at several sites in the United States. The process employs non-halogenated and non-volatile diluents and modifiers and includes an efficient stripping procedure using only water. More than 95% of the pertechnetate present at 6 x 10^{-5} M in Melton Valley (Oak Ridge, TN) and Hanford (Washington) tank-waste simulants was removed following two cross-current extraction contacts using 0.02 M bis-4,4'(5')[(*tert*-butyl)cyclohexano]-18-crown-6 in 2:1 vol/vol TBP/Isopar® M diluent at 25 °C. Similarly, for both simulants, more than 98% of the pertechnetate contained in the solvent was back-extracted following two cross-current stripping contacts using deionized water.

INTRODUCTION

Technetium-99 is a uranium fission product which decays by pure beta emission with a half-life of 2.13 x 10^5 years. It is present in alkaline nuclear-waste media mainly in the +7 oxidation state as the environmentally mobile oxo-anion, pertechnetate (TcO_4^-). Separation of pertechnetate from alkaline nuclear-waste media is currently being considered as part of waste-cleanup and environmental-restoration efforts, particularly with regard to the approximately 6 x 10^7 gallons of neutralized high-level waste (containing an estimated 1.8 metric tons of technetium) stored in 177 waste tanks at the Hanford, Washington, DOE facility. This waste is also highly concentrated in alkali-metal salts of competitor anions such as nitrate, and the nitrate/pertechnetate ratio typically lies in the range of 10^4-10^7 to 1.

Solvent extraction has been employed as a method for the removal of pertechnetate from both acidic and alkaline solutions (Möbius, 1983). Some reagents that have been employed in the extraction of pertechnetate from alkaline media include cyclohexanone (Schulz, 1980), pyridines (Zaitsev et. al., 1964), tetraphenylarsonium chloride (Tribalat and Beydon, 1953), tetraalkylammonium iodides (Shanker et. al., 1968), polyethylene glycols (Chaiko et. al., 1993), and crown ethers (Jalhoom, 1986; Korpusov et. al., 1984). Whereas adequate extraction of pertechnetate from alkaline media was demonstrated by each method, in every case the method described possessed some characteristic which would make it undesirable for a large-scale process. These characteristics included the use of hazardous chemicals as defined by the Resource Conservation and Recovery Act (RCRA) or difficulty in regenerating the extractant solvent.

We describe here the results of our research efforts aimed at developing an efficient solvent-extraction process that utilizes the crown ether bis-4,4'(5')[(*tert*-butyl)cyclohexano]-18-crown-6 for the direct extraction of pertechnetate from high-nitrate-containing alkaline nuclear-waste media and that seeks to avoid many of the problems of the previous methods. The tank wastes at the Hanford site and other locations (e.g., Oak Ridge) 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 crown ethers as potential solvent-extraction reagents for Tc removal (Bonnesen et. al., submitted) because the high-salt condition actually promotes Tc extraction and because an inexpensive water wash effects stripping of the Tc from the solvent. 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. An anion is necessary to conserve charge neutrality, and in this way the pertechnetate anion is also extracted:

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

Here, 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:

$$\overline{(\mathrm{CE})\mathrm{NaTcO_4}} \rightleftharpoons \mathrm{Na^+} + \mathrm{TcO_4^-} + \overline{\mathrm{CE}} \qquad (2)$$

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 equations 1 and 2 represent 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 diluent and modifier with bis-4,4'(5')[(*tert*-butyl)cyclohexano]-18-crown-6 with regard to process economics and development. We specifically desire the best combined extraction and stripping efficiency at the lowest crown ether concentration. Bis-4,4'(5')[(*tert*-butyl)cyclohexano]-18-crown-6 was selected 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 (Horwitz et. al., 1991).

EXPERIMENTAL SECTION

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 prepared by the authors based on an analysis obtained at Oak Ridge on the supernatant solution. A simulant which approximates Hanford tank 101-AW Double-Shell Slurry Feed (DSSF-7) was 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 $NH_4{}^{99}TcO_4$ to give the desired concentration of 6 x 10^{-5} M.

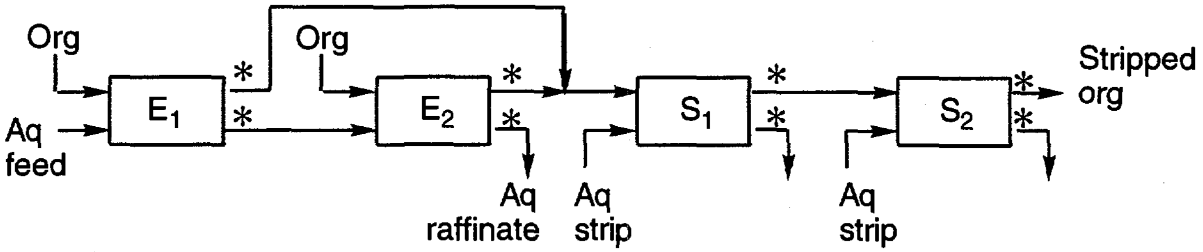
TABLE 1. Waste Simulants Used in This Study.

	Concentration (M)	
Species	MVST W-29	DSSF-7 simulant
Na^+	4.59	7.00
K^+	2.90 x 10^{-1}	9.45 x 10^{-1}
Cs^+	4.3 x 10^{-6}	7.0 x 10^{-5}
Ca^{2+}	8.7 x 10^{-5}	not present
Sr^{2+}	1.1 x 10^{-5}	not present
Al^{3+}	1.65 x 10^{-5}	7.21 x 10^{-1}
OH^- (total)	1.58 x 10^{-1}	4.63
OH^- (free)	1.58 x 10^{-1}	1.75
Cl^-	8.5 x 10^{-2}	1.02 x 10^{-1}
Br^-	6.3 x 10^{-4}	not present
NO_2^-	not present	1.51
NO_3^-	4.52	3.52
CrO_4^{2-}	4.2 x 10^{-5}	not present
SO_4^{2-}	7.0 x 10^{-3}	8.0 x 10^{-3}
CO_3^{2-}	1.00 x 10^{-1}	1.47 x 10^{-1}
PO_4^{3-}	not present	1.4 x 10^{-1}
$^{99}TcO_4^-$	6.0 x 10^{-5}	6.0 x 10^{-5}

[a]MVST W-29 simulant approximates the supernatant liquid in Melton Valley Storage Tank W-29 (Oak Ridge).
[b]DSSF-7 approximates Hanford tank 101-AW Double-Shell Slurry Feed.

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 performance, for this crown can vary from batch to batch (see Horwitz et. al. 1991 for a discussion of this point), and that it is important to use the same batch, or batches of equivalent performance, when making comparisons. Tributylphosphate (TBP) was from Mobil Chemical Co., Edison, New Jersey and was distilled prior to use. Isopar® M (a completely aliphatic isoparaffinic kerosene) was obtained from Exxon Chemical Company, Houston, Texas. Deionized water was used for stripping. All other diluents, modifiers, and reagents were used as received without further purification. All diluent blends were prepared on a volume basis. Beta liquid scintillation counting of ^{99}Tc was performed using a Packard Tricarb® Model 4530 counter and Packard Ultima Gold™ XR scintillation cocktail.

Synthetic waste solutions were contacted with equal volumes of solvent for 1 hour at 25 ± 1°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, the aqueous and organic phases were subsampled and the ^{99}Tc activity in each phase determined. 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 the scheme below:



Scheme 1. Contacting procedure 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).

All tests were run in duplicate, and the technetium extraction ratios ($[\mathrm{Tc}]_{\mathrm{org}}/[\mathrm{Tc}]_{\mathrm{aq}}$) 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

As was shown in Table 1, both waste simulants are extremely concentrated in sodium nitrate, with nitrate/pertechnetate concentration ratios of 75,300 to 1 for the MVST W-29 simulant and 58,700 to 1 for the DSSF-7 simulant. The Tc concentration of 6.0×10^{-5} M was selected as a representative concentration for Tc in most Hanford tanks, though Melton Valley waste probably contains much lower concentrations. 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. Requirements that an ideal diluent (or modified diluent) should meet include low volatility with 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) are 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 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 TBP (Boyd and Larson, 1960) and pyridines (Zaitsev et al., 1964) as extractants for pertechnetate, and this formed a starting point for the selection of candidate modifiers to the base aliphatic kerosene diluent. In addition, TBP is a modifier in the TRUEX process (Horwitz et. al., 1985) and is generally a well-known modifier in the field of solvent extraction.

Extraction and stripping results for both DSSF-7 and MVST W-29 waste simulants are shown in Table 2. Excellent coalescence on both extraction and stripping was observed for all systems, but particularly for the TBP/Isopar® M systems, which at crown ether concentrations of 0.02 M and above also gave the best combined extraction and stripping performance. Excellent extraction efficiency is attainable at 0.01 M [CE] using the pyridines 4-(1-butylpentyl)pyridine as a pure diluent, or 4-(3-phenylpropyl)pyridine diluted with diisopropylbenzene; however, the stripping efficiency is not quite as good as that obtained using the TBP/Isopar® M blends. 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 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. Due to the high cost of the crown ether, the latter system is more favorable economically.

TABLE 2

Extraction of Pertechnetate from DSSF-7 and MVST W-29 Waste Simulants by di-t-BuCH18C6 in Selected Diluents. Stripping by Back-Extraction with Water.[a]

[CE], M	**Simulant**	**Diluent[b]**	E_{Tc}	**% Extr[c]**	**% Strip[c]**
0.02	DSSF-7	2:1 TBP / Isopar® M	8.67 ± 0.27	98.93	99.08
0.02	MVST W-29	2:1 TBP / Isopar® M	3.90 ± 0.06	95.84	98.60
0.04	DSSF-7	1:1 TBP / Isopar® M	8.46 ± 0.21	98.88	99.60
0.02	DSSF-7	1:1 TBP / Isopar® M	4.77 ± 0.01	97.00	99.79
0.01	DSSF-7	1:1 TBP / Isopar® M	2.55 ± 0.01	92.06	99.26
0.02	DSSF-7	4-(1-butylpentyl)pyridine	11.61 ± 0.79	99.37	90.99
0.01	DSSF-7	4-(1-butylpentyl)pyridine	6.56 ± 0.20	98.25	91.73
0.01	DSSF-7	4-(3-phenylpropyl)pyridine / diisopropylbenzene	4.77 ± 0.03	96.95	95.75

[a] 25 °C, 1:1 phase ratio, 1 h contacts.
[b] Ratios are by volume. [c] After two extraction steps and two stripping steps.

The extraction of sodium and potassium from DSSF-7 waste simulant using 1:1 TBP / Isopar® both with and without di-t-BuCH18C6 was also measured. The results, summarized in Table 3, show that the extraction ratio for K increases dramatically both overall, and relative to, Na upon addition of the crown ether. Further, technetium is extracted with a high degree of selectivity over Na and K (as is shown in the E_{Tc}/E_{Na} and E_{Tc}/E_K ratios). The overall selectivity for Tc over both alkali metals increases from 660 for the diluent alone to 940 upon addition of the crown ether. These numbers provide an estimation of the selectivity for Tc over the other most prevalent extractable anions in the DSSF-7 waste simulant: nitrate, hydroxide, and nitrite. After correcting for the Na and K extracted by the diluent alone, the crown ether is 17.5% loaded with potassium and 7.7% loaded with sodium, indicating that although the waste simulant is 7.4 times more concentrated in sodium to begin with, it is likely the potassium concentration that is more important in determining the overall concentration of the active extractant: the cationic crown ether-alkali metal complex. This is not surprising, as di-t-BuCH18C6 is known to bind potassium more strongly than sodium (Izatt et. al., 1985). Thus, extraction would be strongest from tanks which are highly concentrated in potassium as well as sodium. Variation of extraction and stripping performance due to tank-to-tank variability in sodium and potassium concentrations may be compensated by adjusting the volumes (or flow rates) of the solvent relative to the aqueous feed in a contactor.

TABLE 3

Extraction of Sodium and Potassium from DSSF-7 Waste Simulant by 1:1 TBP / Isopar® M Diluent with and without di-t-BuCH18C6.[a] Comparison to Technetium Extraction.

[CE], M	Simulant	E_{Tc}	$E_{\mathrm{Na}}{}^{b}$	$E_{\mathrm{K}}{}^{b}$	$E_{\mathrm{Tc}}/E_{\mathrm{Na}}$	$E_{\mathrm{Tc}}/E_{\mathrm{K}}$
none	DSSF-7	7.09×10^{-1}	9.55×10^{-4}	1.25×10^{-4}	740	5670
0.02	DSSF-7	4.77	1.18×10^{-3}	3.86×10^{-3}	4040	1240

[a] 25 °C, 1:1 phase ratio, 1 h contacts.

[b] Extraction ratios for sodium and potassium were determined by ICP emission spectroscopy.

CONCLUSIONS

An efficient solvent extraction and stripping cycle for pertechnetate from realistic alkaline waste simulants can be obtained using di-t-BuCH18C6 dissolved in TBP modified Isopar® M aliphatic kerosene, allowing for more than 95% of the Tc contained in the waste simulants to be removed upon two cross-current contacts, and more than 98% of the Tc to be stripped from the solvent upon two cross-current stripping contacts using only water. This is achievable at relatively low (0.02 M) crown ether concentration.

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