

TRANSFERRING IONS FROM ONE LIQUID PHASE TO ANOTHER:
*FUNDAMENTAL PRINCIPLES AND THEIR APPLICATION TO NUCLEAR-WASTE
SEPARATIONS WITH CROWN ETHERS*

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The field of liquid-liquid extraction, commonly called solvent extraction, has grown extensively in the past half century to become an economically significant family of techniques in industry, analytical chemistry, and research. Precisely because of its usefulness, liquid-liquid extraction has continued to evolve in terms of physical configuration (e.g., solvent extraction, liquid membranes, and extraction chromatography) and chemistry. Some of the major developments have in fact been driven by the needs of pollution prevention and include the use of sophisticated and highly selective extractants.

Historically, industrial-scale solvent extraction has its roots in the nuclear industry, as related to the recovery of uranium and thorium from ores and the reprocessing of irradiated nuclear fuels. Even in its early development, solvent extraction was recognized to offer substantial advantages in waste minimization. For example, the replacement of precipitation processes with solvent-extraction processes such as PUREX reduced waste production in nuclear separations by well over an order of magnitude.¹ Now, the legacy of nuclear-weapons production lies before us in the form of stored radioactive wastes and contaminated sites. In the USA, highly radioactive wastes stored in underground storage tanks at Hanford, Idaho Falls, Savannah River, and Oak Ridge await treatment and ultimate safe disposition. As the USDOE turns from Cold War priorities to dealing with such "tank wastes" and other legacy matters, considerable investments are being made in developing new technologies and deciding among treatment options. Whether consciously or not, technologists and decision makers have often been applying green principles in this regard, preferring options that consume less raw materials and produce lower waste volumes, sometimes even when the needed technologies have not yet been proven viable. Tank wastes in particular represent an excellent case in point. At the former plutonium-production site at Hanford, Washington, 55 million gallons of highly alkaline wastes are stored in underground tanks.² Although the entire bulk of this waste could be mixed with glass frit and vitrified, the cost of such a massive operation together with subsequent geologic storage of the resulting increased waste volume would be prohibitively expensive. Instead, a more rational approach recognizes that less than 0.1% of the mass of the waste is in the form of harmful radionuclides and that separation of this small, high-level fraction from the waste can greatly reduce the overall cost while concentrating the hazard into a more manageable volume.³ How to achieve this worthwhile end has been the subject of intensive research for the past 5-10 years at several USDOE facilities.

In our own laboratories, we are testing the feasibility of using solvent extraction to remove the key radionuclides ⁹⁹Tc, ⁹⁰Sr, and ¹³⁷Cs from the Hanford waste solutions.⁴ This had effectively been proposed in a scheme exploiting largely known processes for removing radionuclides from acid solution.⁵ It was our thought, however, that it would be advantageous to develop new solvent-extraction methods capable of removing the contaminants directly from the alkaline waste, thereby obviating the addition of a huge quantity of acid. As discussed widely in the literature, crown ethers hold some promise as selective extractants for the removal of the Cs and Sr from nuclear waste.⁶ Figure 1

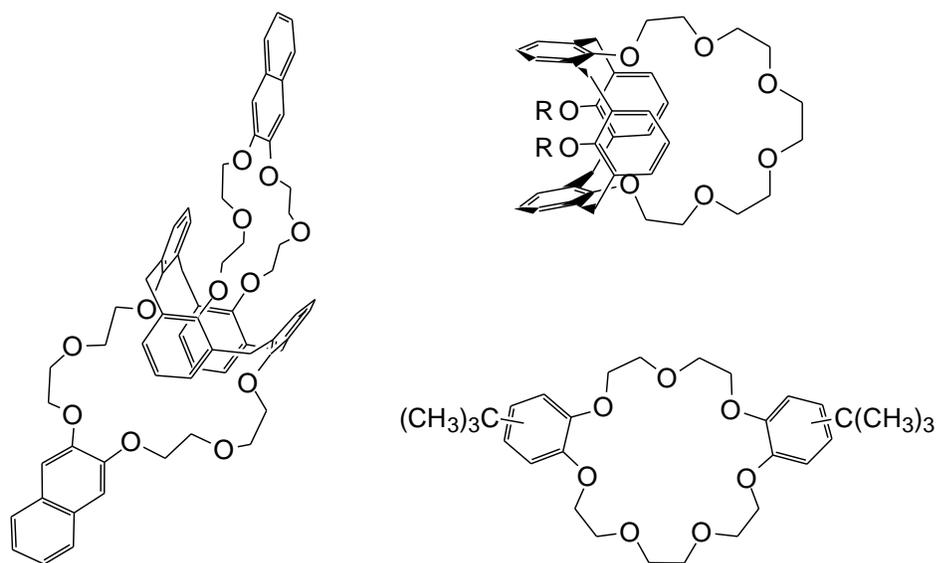


Figure 1. Representative crown compounds potentially useful for the selective separation of Cs^+ ion from nuclear waste: *alt*-calix[4]arene-bis-(2,3-naphtho-crown-6) (left), 1,3-dialkoxycalix[4]arene-crown-6 (upper right), and bis-(*t*-butylbenzo)-21-crown-7 (lower right).

depicts three representative types of crown compounds proposed for extraction of Cs^+ ion from nuclear wastes. Various substituted calix[4]arene-crown-6 and calix[4]arene-bis-crown-6 compounds have been reported to possess Cs/Na selectivities in excess of 10^4 .⁷ X-ray structures have shown that these compounds are highly preorganized and enforce a cation-arene pi interaction in a well-defined cavity.⁸ Lipophilic crown ethers derived from dibenzo-21-crown-7 are also selective for cesium, but since Cs/Na selectivities are "only" 10^2 , these compounds cannot match the performance of the calix-crown-6 compounds under the severe test posed by the Hanford tank waste.⁹ Increased selectivity effectively translates to a reduced high-level waste volume, because the degree to which competing ions such as Na^+ are co-extracted is greatly reduced.

It is important to recognize that, in addition to high selectivity for Cs, a major advantage of crown ethers lies in the reversibility of the extraction. Equilibrium analysis of the extraction process shows that the driving force on extraction derives from the high nitrate concentration in the waste.¹⁰ A key reaction is simply formation of the 1:1 complex:



If the resulting solvent loaded with cesium nitrate is then contacted with water, the equilibrium reverses in accord with mass action.⁹ The water can then be evaporated or passed through ion-exchange columns to concentrate the contaminants without the addition of chemicals. Overall, the process potentially offers good separation of the contaminant from the waste, high concentration factor, and low secondary waste, all essential "green" properties when dealing with nuclear waste. This process may be contrasted with other methodologies employing ion-exchange principles, whereby stripping may be effected only by treating the solvent or ion-exchange material with high concentrations of chemical

stripping reagents. One is then left with another separation problem and large secondary waste production associated with further processing of the stripping solution.

Removal of the radionuclide ^{99}Tc from the waste poses a different chemical problem, in that much of the Tc in the waste is in the form of the tetraoxo anion pertechnetate (TcO_4^-). Crown ethers do not complex pertechnetate directly, but it is easy to see from Eq. 1 that, like nitrate, pertechnetate could function as the extracted co-anion to preserve charge neutrality in the overall ion-pair extraction. In a recent review article,¹¹ we evaluated a number of relevant factors such as electrostatics, solvent cohesion, and hydrogen bonding. These principles dictate that the transfer of ions from water to an organic solvent environment generally favors ions having small charge-to-radius ratio, and this selectivity rule indeed persists in anion-transfer and exchange processes. Since pertechnetate has a smaller charge-to-radius ratio and correspondingly lower hydration energy than the inorganic ions such as hydroxide, nitrate, nitrite, chloride, sulfate, and carbonate abundant in the waste, separations based on this simple principle can effect the needed separation of pertechnetate from the waste. Indeed, it has been possible to develop a process based upon a crown ether to remove Tc as pertechnetate from alkaline nuclear waste. Called SRTALK, the process features the favorable water stripping discussed above and thus has the "green" benefit of minimal secondary waste production.¹²⁻¹⁴ As shown in the scheme in Fig. 2, SRTALK employs the crown ether bis-(*t*-butylcyclohexano)-18-crown-6 as the preferred extractant (among many tested)¹³ for sodium (and also potassium), which is abundant in the waste. Although nitrate represents a competing ion, practical selectivities on the order of 10^3 for pertechnetate vs. nitrate have been attainable in solvents composed of an aliphatic kerosene (Isopar[®] L) containing polar modifiers such as tributylphosphate (TBP).

Further improvements can be obtained by tailoring the solvent-extraction system to separate more than one radionuclide at a time. We showed that under certain conditions SRTALK simultaneously separates Sr^{2+} and TcO_4^- ions from alkaline nitrate media.¹³ Likewise,

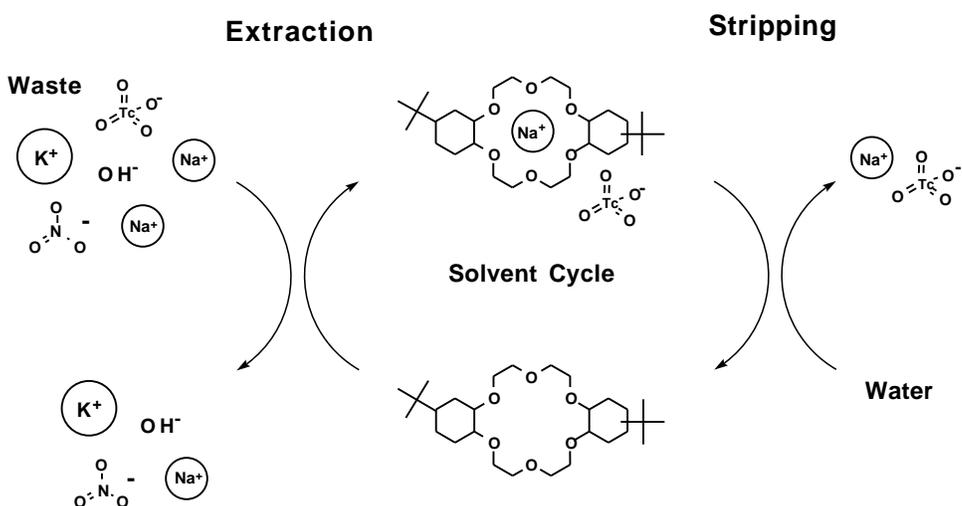


Figure 2. Depiction of the SRTALK process for separation of Tc as pertechnetate anion TcO_4^- from alkaline nitrate waste. The crown ether forms a large lipophilic cation upon binding sodium (or potassium) ion, and pertechnetate transfers to the solvent phase as the preferred co-anion. Stripping is easily effected with water or a dilute electrolyte solution such as 10 mM nitric acid.

we have noted the co-extraction of Cs⁺ and TcO₄⁻ ions from alkaline nitrate solutions. In both examples, the crown compound binds the target cationic contaminant, accompanied by the anionic co-contaminant TcO₄⁻. It has even been possible to show that Cs, Sr, and Tc can be simultaneously extracted in a single step. A "suite" of radionuclide separation processes applicable to alkaline nuclear waste has now reached the development stage.⁴

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