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SOLVENT EXTRACTION OF RADIONUCLIDES FROM AQUEOUS TANK WASTE

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Solvent Extraction of Radionuclides from Aqueous Tank Waste

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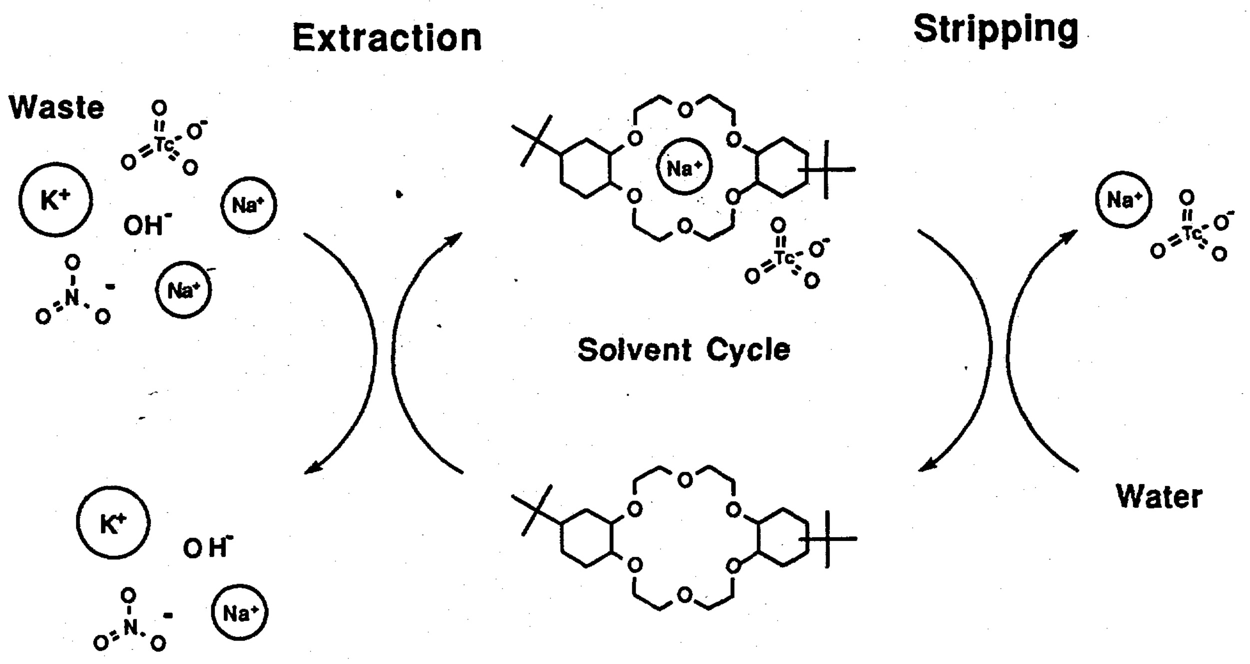
Task Description

The purpose of this task is to develop an efficient solvent-extraction and stripping process for the removal of the fission products Tc-99, Sr-90, and Cs-137 from alkaline tank wastes, such as those stored at Hanford and Oak Ridge. As such, this task expands upon FY 1995's successful development of a solvent-extraction and stripping process for technetium separation from alkaline tank-waste solutions. This process has in fact already been extended to include the capability of removing both Tc and Sr simultaneously. In this form, the process has been given the name SRTALK and will be developed further in this program as a prelude to developing a system capable of removing Tc, Sr, and Cs together. Such a system could potentially simplify and improve fission-product removal from tank waste. In addition, it would possess the advantages already inherent in our Tc solvent-extraction process: no required feed adjustment, economical water stripping, low consumption of materials, and low waste volume.

Technology Needs

Efficient processes for the removal of Tc, Sr, and Cs from highly radioactive waste have been identified as priority needs of the Efficient Separations and Processing (ESP) Crosscutting Program, the Tanks Focus Area (TFA) program, and the Tank Waste Remediation System (TWRS) program. The problem of how to safely dispose of the large volumes of radioactive wastes stored in underground tanks is one of the largest problems facing the U.S. Department of Energy. The general goal being pursued is overall cost savings through both reduction in the volume of waste that must be committed to a geologic repository and minimization of secondary waste streams.



A number of promising technologies as separate unit operations have been under development in USDOE programs for the removal of Tc, Sr, and Cs from alkaline tank supernate. These technologies would presumably be employed in series and would each entail separate process requirements, consumption of materials, effluent streams, stripping (if applicable), and impacts on vitrification. Although the emerging technologies individually remove their target contaminants effectively, it was our thought that a single extractant that could remove Tc, Sr, and Cs together and transfer them to water, which can then be simply evaporated to produce a tiny effluent volume, would offer compelling advantages. The overall process would immediately become simpler in that only one technology is involved, and the space requirements could significantly shrink. Consumption of chemicals and production of new waste would be minimal, limited essentially to replacement of extractant. Stripping is accomplished with water, allowing the high-level effluent to be reduced to a trivial volume in a simple manner and leading to little chemical impact on vitrification processing.

Scientific Background

As depicted in the above figure, our technetium extraction process occurs by extraction of an ion pair, where the crown ether binds the cation to form a large, hydrophobic cation. As in anion-exchange processes, the preferred counter-anion generally corresponds to the one having the lowest hydration energy. Pertechnetate anion possesses the lowest hydration energy among the major anions, such as nitrate, in the tank supernate and is thus selected. Typical TcO_4^-/NO_3^- selectivities obtained exceed 10^3. Of the commercial crown ethers, 4,4',(5')-di-t-butyldicyclohexane-18-crown-6 performs most effectively in extraction from alkaline sodium *nitrate solutions. Concentrations in the range 0.01 - 0.05 M in the solvent generally suffice to* yield Tc distribution coefficients in the useful range 1 - 10. Under these conditions, essentially complete stripping occurs in two or three water washes. We have found that TBP in kerosene (Isopar® M preferred) at ratios of 1:1 to 2:1 perform effectively.

It should be pointed out that our process depends on the extraction of Tc in the heptavalent state. Ordinarily, the standard reduction potentials favor this state in alkaline solutions exposed to air. Recent results at LANL (Norm Schroeder) have shown that the Hanford complexant concentrate (CC) contains a significant fraction of Tc in a form not extractable as pertechnetate. Although this result is likely applicable only to the special case of CC waste, where chelating agents can stabilize lower oxidation states, some investigation of the state of Tc in other Hanford tanks is needed.

The chemical literature provides many examples of solvent extraction of alkali and alkaline-earth metal ions by crown ethers. In particular, systems selective for Cs and Sr have been reported, though their applicability for decontamination of alkaline waste has not been demonstrated. The SREX process developed by the Horwitz group at Argonne represents an excellent example of application of crown ethers for Sr (and Tc) decontamination of acidic waste solutions using solvent extraction. The crown ether employed in SREX, 4,4',(5')-di-t-butyldicyclohexane-18-crown-6, is the same crown ether that we have found to be the most effective for Tc on the alkaline side. The commercial product consists of a mixture of isomers whose abilities to bind and extract Sr^{2+} ions vary considerably. Aided by molecular-mechanics calculations performed by Benjamin P. Hay at PNL, the Horwitz group has been identifying the most effective isomer, leading to continued improvements in the commercial product marketed by Eichrome.

Technical Approach

Tank wastes at the Hanford site and other locations (e.g., MVST at Oak Ridge) are typically strongly alkaline and contain Tc, Sr, Cs, and other radioactive contaminants. In proposed treatment processes, these contaminants may be found in the aqueous supernates, or they may be solubilized from the sludge during sludge washing or leaching. Since these aqueous streams will contain complicated and variable mixtures of salts, highly efficient separation methods are needed. Whereas it has commonly been thought that applicable separation methods must also be extremely selective, this work addresses the question of whether a *group* selection for Tc, Sr, and Cs can be made practical. Such a disparate trio of elements would ordinarily seem to have little chance of simultaneous extraction, but our tests (see below) together with available literature (see above) reveal that crown ethers may well offer this ability.

Owing to its high selectivity and good mass-transfer properties, solvent extraction offers a potentially attractive vehicle for the combined Tc, Sr, and Cs 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. Use of centrifugal contactors should provide for efficient recycle of the solvent, minimizing inventory requirements, solvent entrainment losses, and solvent radiation degradation. Solvent extraction has proven to be effective in many nuclear separations, establishing a good foundation for application to tank waste.

In FY 1996 we plan to develop the process flowsheet for the solvent extraction of Tc from alkaline supernate and water stripping as needed by potential users. For example, PNL proposes to test the process on simulated and actual Hanford supernate in 2-cm centrifugal contactors. We plan to pursue our investigation of appropriate extractants, diluents, and modifiers for the combined extraction of Tc, Sr, and Cs. Key issues will entail achieving high extraction and stripping ratios for ALL of these, as some factors which enhance Cs extraction might suppress Tc stripping, etc. This may additionally involve some synthetic effort with regard to optimizing the extractants for Cs and Sr. Our first task will be to define a workable solvent; we will then begin process cycle development and seek ways to optimize the process. Intermediate stages of our work will entail demonstration of processes capable of combined Tc and Sr (SRTALK) extraction and combined Cs and Tc extraction from alkaline tank supernate (see below).

Accomplishments

Technetium alone. A solvent-extraction and stripping process has been defined for removing technetium from alkaline tank waste. A patent covering this process has been issued, and we have refined the process to include an anion-exchange method for removing and concentrating Tc from the stripping water, so that the stripping water can be recycled back into the process. A highly effective solvent for the process contains 4,4',(5')-di-t-butyldicyclohexane-18-crown-6 dissolved in TBP-modified isoparaffinic kerosene. The solvent has been tested on actual tank waste from Oak Ridge's Melton Valley (MVST); performance was equivalent to that obtained with waste simulants. Extraction and stripping efficiencies of 98% or better are attainable with two-stage extraction and two-stage stripping at unit phase ratio using waste simulants.

Technetium/Strontium. A process named SRTALK is under development to simultaneously extract Tc and Sr from alkaline tank-waste supernate. Results to date using a MVST simulant have shown that combined extraction and stripping efficiencies of respectively 96% and 99% for Tc, and 62% and >99% for Sr, are attainable with two-stage extraction and two-stage stripping at unit phase ratio. Work in progress toward increasing the extraction efficiency for Sr has produced excellent results from simple alkaline sodium nitrate solutions.

Cesium and Technetium/Cesium. Our results to date reveal Cs extraction and stripping efficiencies from actual MVST W-29 waste of 89% and >99%, respectively, following four equal-volume cross-current extraction contacts, and four equal-volume cross-current stripping contacts using only water. Combined Tc and Cs extraction and stripping results from MVST W-29 simulant have shown that combined extraction and stripping efficiencies of respectively 96% and 83% for Tc, and 37% and 93% for Cs, are attainable with two-stage extraction and two-stage stripping at unit phase ratio.

Benefits

The Tanks Waste Focus Area and TWRS will receive the primary benefit from this program. By the removal and concentration of fission products directly from tank waste, it will be possible to increase safety and effectiveness in processing tank wastes and to obtain large cost savings associated with reduction in the high-level waste volume that must be committed to a geologic repository. Compared with a sequence of three fixed-bed technologies, a combined Cs, Sr, and Tc extraction process could simplify processing and reduce space requirements. An effluent of these contaminants in only water allows many-fold concentration by simple evaporation or sorption onto known solid materials. The proposed technology offers the following major advantages: 1) direct treatability of the waste, 2) safe, economical, and efficient stripping using only water, 3) no additions of chemicals to the extraction or stripping cycle, and 4) use of diluents with high flash point, low toxicity, and low water solubility.

Technology Transfer/Collaborators

Industry will be needed to supply crown ethers and other extractants in large quantities at reasonable cost. Eichrom Industries has a proven record in the production and sale of a key crown ether for solvent extraction of Sr and Tc. Further development of large-scale preparative procedures is still needed to effect savings on these expensive materials. In addition, the assistance of industry will prove valuable in designing and fabricating the appropriate contacting equipment for pilot- and plant-scale use. Both PNL and Argonne have expressed interest in testing the Tc solvent-extraction process for the Tanks Focus Area. Interaction with Benjamin P. Hay (PNL) has provided insight into conformational effects and design of crown ethers.

Keywords

crown ether, technetium, cesium, strontium, fission products, tank waste, alkaline, process, solvent extraction

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