

Solvent Extraction of Radionuclides from Aqueous Tank Waste

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EM Focus Area: high-level waste tank remediation

Task Description

The purpose of this task is to develop an efficient solvent-extraction and stripping process to remove the fission products ⁹⁹Tc, ⁹⁰Sr, and ¹³⁷Cs from alkaline tank wastes, such as those stored at Hanford and Oak Ridge. As such, this task expands on FY 1995's successful development of a solvent-extraction and stripping process for technetium separation from alkaline tank-waste solutions. This process now includes the capability of removing both technetium and strontium simultaneously. In this form, the process has been named SRTALK and will be developed further in this program as a prelude to developing a system capable of removing technetium, strontium, and cesium.

Such a system could potentially simplify and improve fission-product removal from tank waste. In addition, it would possess advantages already inherent in our technetium 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 technetium, strontium, and cesium from highly radioactive waste are priority needs of the ESP, the Tank Focus Area (TFA) program, and the Tank Waste Remediation System (TWRS) program. How to safely dispose of the large volumes of radioactive wastes stored in underground tanks is one of the largest problems

facing DOE. The general goal being pursued is overall cost savings through both reducing the volume of waste that must be committed to a geologic repository and minimizing secondary waste streams.

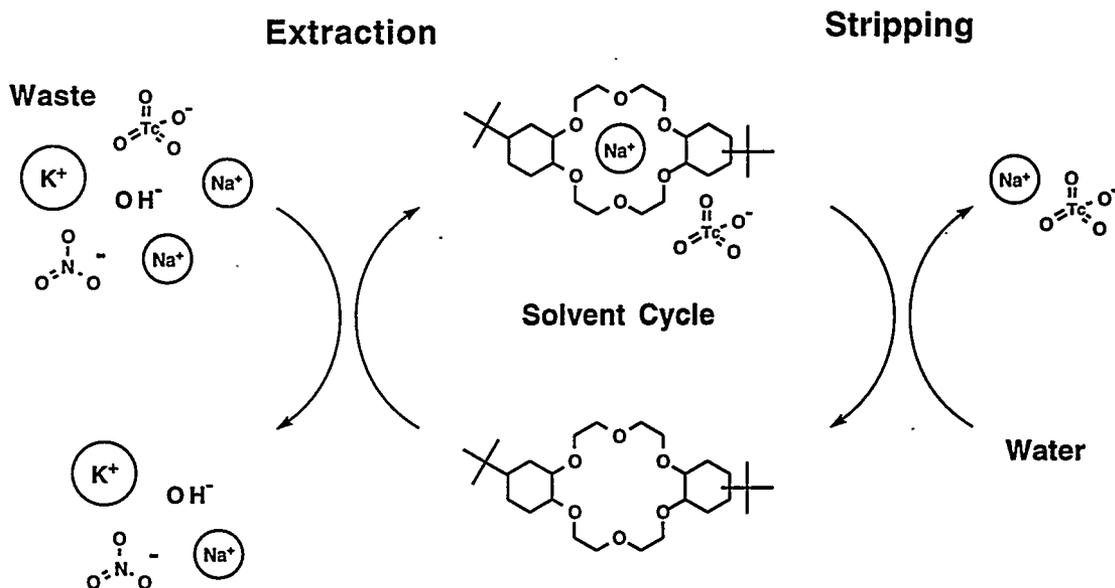
Several promising technologies as separate unit operations have been under development in DOE programs to remove technetium, strontium, and cesium from alkaline tank supernate. These technologies would presumably be employed in series and would each entail separate process requirements, consumption of materials, effluent streams, stripping (if applicable), and impacts on vitrification.

Although the emerging technologies individually remove their target contaminants effectively, there may be compelling advantages to a single extractant that could remove technetium, strontium, and cesium together and transfer them to water, which can then be simply evaporated to produce a miniscule effluent volume. The overall process would be simpler in that a single technology is involved, and the space requirements could significantly shrink. Chemical consumption and new waste production would be minimal, limited essentially to replacement of extractant. Stripping would be accomplished with water, allowing the high-level effluent to be reduced to a minimal volume in a simple manner and leading to little chemical impact on vitrification processing.

Scientific Background

As depicted in the 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,

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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 $\text{TcO}_4^-/\text{NO}_3^-$ selectivities exceed 10^3 .

Of the commercial crown ethers, 4,4',(5')-di-t-butyl-18-crown-6 performs most effectively in extraction from alkaline sodium nitrate solutions. Concentrations ranging from 0.01 to 0.05 M in the solvent yield technetium distribution coefficients in the useful range of 1 to 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.

Our process depends on the extraction of technetium in the heptavalent state. Ordinarily, the standard reduction potentials favor this state in alkaline solutions exposed to air. Recent results by Norm Schroeder at Los Alamos National Laboratory (LANL) have shown that the Hanford complexant concentrate (CC) contains a significant fraction of technetium 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, the state of technetium in other Hanford tanks should be investigated.

The chemical literature provides many examples of solvent extraction of alkali and alkaline-earth metal ions by crown ethers. In particular, systems selective for cesium and strontium have been reported, though their applicability for decontamination of alkaline waste has not been demonstrated.

The SREX process developed by Phil Horwitz's group at Argonne National Laboratory (ANL) is an excellent example of application of crown ethers for strontium (and technetium) decontamination of acidic waste solutions using solvent extraction. The crown ether employed in SREX, 4,4',(5')-di-t-butyl-18-crown-6, is the same crown ether we have found to be the most effective for technetium on the alkaline side. The commercial product is a mixture of isomers whose abilities to bind and extract Sr^{2+} ions vary considerably. Aided by molecular-mechanics calculations performed by Ben Hay at Pacific Northwest National Laboratory (PNNL), Horwitz's group has been

identifying the most effective isomer, leading to continued improvements in the commercial product marketed by Eichrom Industries.

Technical Approach

Tank wastes at the Hanford Site and elsewhere (e.g., Melton Valley Storage Tanks at Oak Ridge) are typically strongly alkaline and contain technetium, strontium, cesium, and other radioactive contaminants. In proposed treatment processes, these contaminants may be found in the aqueous supernates, or may be solubilized from the sludge during sludge washing or leaching. Because these aqueous streams will contain complicated and variable mixtures of salts, highly efficient separation methods are needed:

Whereas it has been commonly thought that applicable separation methods must also be extremely selective, this work addresses the question of making a practical *group* selection for technetium, strontium, and cesium. 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.

Because of its high selectivity and good mass-transfer properties, solvent extraction is a potentially attractive vehicle for combined technetium, strontium, and cesium 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. Centrifugal contactors should provide 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 technetium from alkaline supernatant and water stripping as needed by potential users. For example, PNNL has proposed to test the

process on simulated and actual Hanford supernatant in 2-cm centrifugal contactors. We plan to continue investigating appropriate extractants, diluents, and modifiers for the combined extraction of technetium, strontium, and cesium. Key issues are achieving high extraction and stripping ratios for *all* of these, as some factors that enhance cesium extraction might suppress technetium stripping. This may additionally involve some combined effort with optimizing cesium and strontium extractants.

First, we will define a workable solvent, then we will begin process cycle development and seek ways to optimize the process. Intermediate stages will include demonstration of processes capable of combined technetium and strontium (SRTALK) extraction and combined cesium and technetium extraction from alkaline tank supernate (see figure).

Accomplishments

Technetium Alone. A solvent-extraction and stripping process has been defined for removing technetium from alkaline tank waste. A patent covering this process was issued, and we have refined the process to include an anion-exchange method for removing and concentrating technetium 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 ORNL'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. The SRTALK process is under development to simultaneously extract technetium and strontium from alkaline tank-waste supernate. Results using a MVST simulant have shown that combined extraction and stripping efficiencies of

96% and 99% for technetium, respectively, and 62% and >99% for strontium, are attainable with two-stage extraction and two-stage stripping at unit phase ratio. Work toward increasing the extraction efficiency for strontium has produced excellent results from simple alkaline sodium nitrate solutions.

Cesium and Technetium/Cesium. Results to date reveal cesium 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 technetium and cesium extraction and stripping results from MVST W-29 simulant have shown that combined extraction and stripping efficiencies of respectively 96% and 83% for technetium, and 37% and 93% for cesium, are attainable with two-stage extraction and two-stage stripping at unit phase ratio.

Benefits

The TFA and TWRS will receive the primary benefit from this program. By removing and concentrating fission products directly from tank waste, increased safety and effectiveness in processing tank wastes, and large cost savings will be obtained because of reducing the high-level waste volume that must be committed to a geologic repository.

Compared with a sequence of three fixed-bed technologies, a combined technetium, strontium, and cesium extraction process could simplify processing and reduce space requirements. An effluent of these contaminants in only water allows manyfold 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

Industrial partners 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 strontium and technetium. Further development of large-scale manufacturing procedures is still needed to reduce the cost of 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 PNNL and ANL have expressed interest in testing the technetium solvent-extraction process for the TFA. Interaction with Ben Hay at PNNL 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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