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Solvent Extraction of Radionuclides from Aqueous Tank Waste*

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Technology Needs

Disposal of the large volumes of highly radioactive wastes stored in underground tanks at Hanford, Oak Ridge, Savannah River, and Idaho Falls is one of the largest problems facing the U.S. Department of Energy. Acceptable costs of disposal can be achieved only through reduction in the volume of waste that must be committed to a geologic repository and minimization of secondary waste streams. Toward this end, 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 include efficient processes for the separation of Tc, Sr, and Cs from the tank wastes. These programs have sponsored tasks that have in fact led to an array of promising new technologies. The new technologies would presumably be employed in series and would each entail specific process requirements, consumption of materials, effluent streams, stripping (if applicable), and impacts on vitrification. Although implementation would likely produce cost savings compared to baseline processes, in no case does it appear that significant problems and uncertainties have all been eliminated or that further significant economies could not be gained. For example, some proposed technologies require adjustment of the waste stream. Others mix the separated fission products with chemicals or materials that adversely impact vitrification. Further, high concentrations of competing ions in the waste reduce separation efficiency, limiting effective capacity to a fraction of that theoretically obtainable; this increases the quantity of chemicals and materials consumed per unit volume of waste. Finally, it may be possible to achieve large cost savings by reducing the size of the process equipment needed, since the major cost of a new high-level facility derives directly from the mass of concrete used in construction. These facts well justify the development of improved or alternative technologies.

Technology Description

This task aims toward the development of efficient solvent-extraction processes for the removal of the fission products ^{99}Tc , ^{90}Sr , and ^{137}Cs from alkaline tank wastes. Processes already developed or proposed entail direct treatment of the waste solution with the solvent and subsequent stripping of the extracted contaminants from the solvent into a dilute aqueous solution. Working processes to remove Tc(&Sr) separately and Cs separately have been developed; the feasibility of a combined process is under investigation. The SRTALK process [1,2] uses a crown ether in a modified kerosene to remove Tc in the form of pertechnetate from alkaline waste; Sr is co-extracted from certain wastes, such as Oak Ridge Melton Valley Storage Tank (MVST) waste. Figure 1 depicts SRTALK configured as a Tc extraction system, wherein the stripping water is passed through an anion-exchange resin to concentrate the Tc more than 40 times more efficiently than direct treatment of the waste by the anion-exchange resin. If a conventional strong-base resin is employed, the eluant consisting of ethylenediamine and stannous chloride recommended by N. C. Schroeder [3] may be employed. Since the strip solution is slightly acidic, however, a weak-base resin may be employed, potentially allowing elution with a vitrification-compatible solution such as

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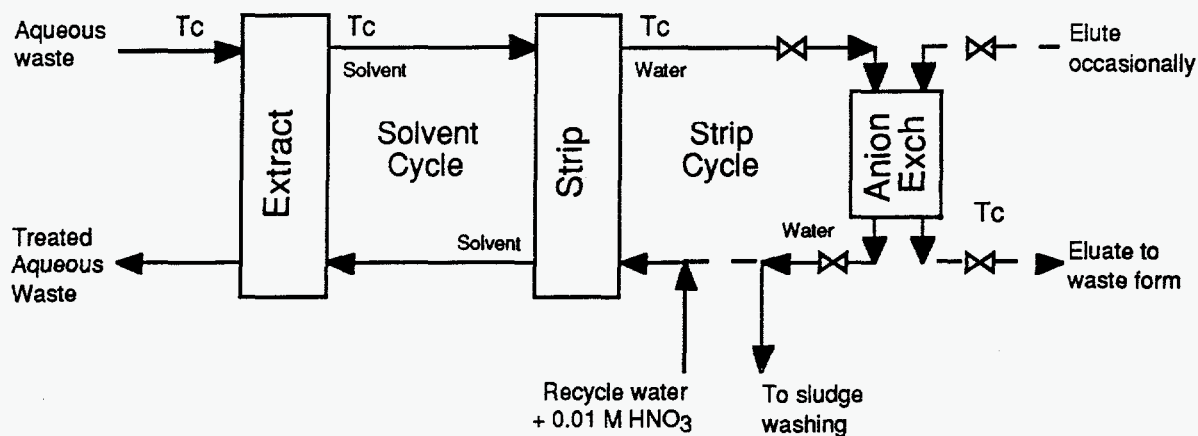


Fig. 1. The SRTALK process for removal of pertechnetate from alkaline tank supernatant waste solutions is shown as a simplified configured system involving concentration of the separated Tc onto an anion-exchange resin. In practice, the solvent extraction would be conducted in continuous counter-current multistage centrifugal contactors, and at least two anion-exchange columns would be employed to permit simultaneous loading and stripping of the resin. The solvent is completely recycled in the process. The strip solution is partly recycled.

sodium hydroxide. The SRTALK system shown in Fig. 1 thus represents a significant value added to anion-exchange technology applied to Tc removal from alkaline waste.

Similarly, an alkaline cesium solvent-extraction process has been developed. Although the process has not yet undergone testing on actual tank waste, it may also be configured in tandem with a follow-on sorption technology in much the same manner shown in Fig. 1 for SRTALK. The low concentration of competing sodium and potassium ions in the strip solution greatly enhances uptake efficiency by certain sorbents. Thus, one may choose, for example, inexpensive zeolite materials that are highly compatible with subsequent vitrification. Again, solvent extraction adds value to sorption technology and to the pretreatment system overall.

Since Tc, Sr, and Cs will be vitrified together in the high-level fraction, however, a process that could separate Tc, Sr, and Cs *simultaneously*, as opposed to sequentially, potentially offers the greatest impact (see below). Figure 2 presents a simplified diagram of a proposed solvent-extraction cycle followed by three possible treatments for the stripping solution. Some degree of recycle of the stripping solution (option a) is expected. Simple evaporation (option c) is possible prior to vitrification; this offers the greatest possible volume reduction with simple operation and no consumption of chemicals, but it is energy intensive. However, if the contaminants are concentrated (option b) by fixed-bed technology, the energy penalty of evaporation can be avoided and vitrification facilitated without any additional secondary waste being produced.

Benefit to DOE/EM

Although the solvent-extraction approach may be viewed as an alternative technology, we prefer to suggest it as enhancing or adding value to solid-phase extraction technology. Since the solvent-extraction process effectively transfers the contaminants to a low-salt solution, the reduced concentration of competing ions means that solid-phase extractants, such as sodium titanate (Sr), zeolites (Sr, Cs), crystalline silicotitanates (Sr, Cs), resorcinol-formaldehyde resin (Cs), resin

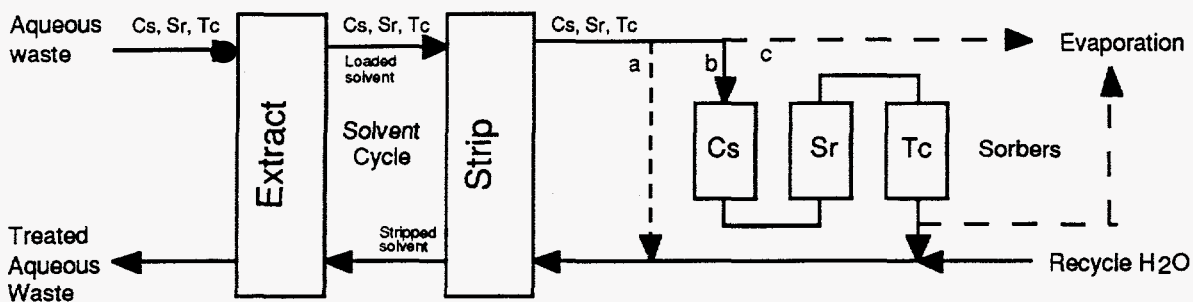


Fig. 2. Proposed combined solvent-extraction process for the separation of Cs, Sr, and Tc from alkaline supernatant tank waste. A new solvent under development is used to remove the fission products simultaneously from the aqueous feed, and the loaded solvent is then stripped with a dilute aqueous solution, allowing the solvent to be recycled. Three options are available for treatment of the stripping solution: a) recycle, b) solid-phase extraction, and c) evaporation.

anion exchange (Tc), or iron filings (Tc), will be able to remove the contaminants with markedly greater efficiency than possible by treating the waste directly with the solid materials. Increased uptake efficiency means that a smaller mass of solid materials will be required, and decontamination factors can be increased. The adverse impact of the sorbent materials upon vitrification could thereby be reduced or even made favorable.

Overall, the proposed technologies offer the following major advantages: 1) direct treatability of the waste, 2) safe, economical, and efficient stripping using only water or dilute acid solution, 3) the use of diluents with high flash point, low toxicity, and low water solubility, 4) large volume reduction, 5) back-end concentration options, and 6) excellent compatibility with vitrification. Compared with other extractants, the most important advantage of crown ethers lies in the ease of stripping. Water suffices to strip the solvent, though dilute (0.01 M) nitric acid is preferred for optimum phase-contacting performance, leading to minimal secondary waste production.

Compared to a sequence of three separation technologies, a combined Cs, Sr, and Tc extraction process promises the most compelling benefits. The most important of these is the reduction in space requirements, leading to a proportionate decrease in capital investments to build processing facilities. In addition, the overall operation can be potentially simplified and made safer, and a number of separate waste streams can be eliminated.

Technology Transfer/Collaborations

In the current year, engineering scale-up of the SRTALK process will be carried out at Argonne National Laboratory (ANL) by R. A. Leonard. The ANL effort will entail testing SRTALK solvent on Hanford waste simulant in centrifugal contactors and determining the parameters required to optimize counter-current operation. Centrifugal contactors are preferred, indeed required, to minimize the inventory of expensive solvent by maximizing throughput. In addition, radiation damage to the solvent is minimized, and space requirements are minor by comparison to pulse columns or mixer-settlers. Facilities at ANL include a bank of 2-inch centrifugal contactors.

Testing of Tc solvent extraction (SRTALK) and Cs solvent extraction on actual Hanford supernatant tank waste is being conducted at Pacific Northwest National Laboratories (PNNL) by G. J. Lumetta. These batch tests will validate the simulant tests carried out at Oak Ridge on selected wastes, especially those identified for Phase I of the privatization of the Hanford tank

cleanup. Hot cell facilities are available at PNNL together with quantities of the waste for testing, and analytical protocols have been established.

Collaboration with B. P. Hay at PNNL benefits this task through design of improved extractants. Molecular mechanics and quantum calculations point to specific structures which optimize metal ion binding efficiency and selectivity. Improved performance has already been realized in the SRTALK process, which employs the commercial crown ether bis-(*t*-butylcyclohexano)-18-crown-6. Calculations performed by Hay have identified the most effective isomer of this crown ether, enabling Eichrome Industries to improve the effectiveness of their product. Currently, calculations are being performed to improve the effectiveness of our cesium extractant.

Technology transfer begins with publications and reports together with invention disclosures leading to licensable patents. In this regard, a patent has been granted for the SRTALK process [4]. An invention disclosure for the alkaline cesium extraction process is being drafted. A patent application on pertechnetate separation from nitrate media by supported liquid membranes (SLM) has been filed. Ultimately, the end users whose interest is most important here are the consortia carrying out Phase I of the privatization of the Hanford cleanup. Accordingly, our literature and progress reports are available to these industries for their evaluation. Other technology transfer will involve an industry to manufacture and commercialize our new extractants. Eichrome Industries has expressed interest in new extractants developed under this task. Negotiations with Commodore Membrane Technologies for a license to the SLM technology are in progress.

The TFA and TWRS programs will receive the primary benefit from this ESP program. Support in FY 1998 will be sought for demonstrating the SRTALK process on actual Hanford waste in centrifugal contactors and for engineering development of the alkaline cesium extraction process.

Scientific Background

The SRTALK Tc extraction process operates by extraction of an alkali metal pertechnetate ion pair, where the crown ether binds a sodium or potassium cation to form a large, hydrophobic cation [1,2,5]. The preferred counter-anion generally corresponds to the one having the lowest hydration energy. Among the abundant anions in the waste, the pertechnetate anion possesses the lowest hydration energy and thus is selected. Typical $\text{TcO}_4^-/\text{NO}_3^-$ selectivities obtained are on the order of 500 to 1000. Of the commercial crown ethers, bis-(*t*-butylcyclohexano)-18-crown-6 performs most effectively. Concentrations in the range 0.01 to 0.05 M in the solvent generally suffice to yield Tc distribution coefficients in the useful range 1 to 10. Under these conditions, essentially complete stripping occurs in two to three contacts with water or, for best phase disengagement, 5-10 mM nitric acid. The types of diluent and modifier employed strongly control the efficiency of extraction and stripping. An aliphatic kerosene, Isopar[®] L, modified with tributylphosphate (TBP) at ratios of 1:1 to 1:2 performs effectively.

It should be pointed out that the process described depends on the extraction of Tc in the heptavalent state (i.e., pertechnetate). Ordinarily, the standard reduction potentials favor this state in alkaline solutions exposed to air. However, certain conditions can change this expectation; for example, recent results of N. C. Schroeder (LANL) [6] and D. L. Blanchard (PNNL) [7] have shown that the Hanford complexant concentrate (CC) waste contains a significant fraction of Tc in a form not extractable as pertechnetate anion. Even a double-shell slurry feed tank waste (AW-101) involves a low, but real, fraction of nonextractable Tc. Further investigation of the state of Tc in other Hanford tanks is needed. In FY 1997, the ability of the SRTALK process to remove non-pertechnetate Tc will be examined in batch tests.

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 [8], though their applicability for decontamination of alkaline tank waste has not yet been demonstrated. Our efforts toward a combined solvent-extraction system will in part be based on such reported extractants and on more effective compounds designed and synthesized under this program.

Technical Approach

Whereas it has been commonly thought that separation methods applicable to complex matrices must be made 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 reveal that crown ethers may well offer this ability.

Owing to its high selectivity, good mass-transfer properties, and versatility, 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, entrainment losses, and radiation degradation. Solvent extraction has proven to be effective in many nuclear separations, establishing a good foundation for further application.

In FY 1997, efforts will be dedicated to finding appropriate extractants, diluents, and modifiers for the combined extraction of Tc, Sr, and Cs. Key issues involve achieving sufficiently high extraction and stripping ratios for all of these contaminants, as some factors which enhance Cs extraction might prove deleterious for Tc or Sr. As mentioned above, the SRTALK process will undergo engineering scale-up to centrifugal contactors at ANL. An alkaline cesium extraction process will be further developed and tested on actual waste. Specific extractants for strontium will be identified, and the possibility of non-pertechnetate Tc extraction will be investigated.

Accomplishments

SRTALK Process Demonstrated in Mixer-Settler Test of Pertechnetate Extraction.

A mixer-settler test of the SRTALK crown-ether process was completed, successfully demonstrating continuous extraction and stripping cycles in the solvent extraction of pertechnetate from tank-waste simulant. The test specifically demonstrated practically complete extraction from a simulant of Hanford double-shell slurry feed (DSSF-7) containing 97.0 $\mu\text{Ci/L}$ $^{99}\text{TcO}_4^-$ and subsequent transfer of 95% of the pertechnetate to a dilute solution of nitric acid. Previous tests have shown that this separation could be performed batchwise on the scale of a few milliliters in laboratory vials. Good batch results had been obtained for various simulated and actual supernatant tank wastes; actual waste samples tested included Hanford double-shell slurry feed from tank AW-101 (test done by G. J. Lumetta and co-workers at PNNL) and Oak Ridge MVST tank W-29. However, the present mixer-settler results demonstrate the viability of the process in continuous counter-current equipment and thereby mark the passage of SRTALK process development into the engineering domain.

The solvent used in the mixer-settler experiment consisted of 0.02 M bis-(*t*-butylcyclohexano)-18-crown-6) in a kerosene process diluent (Isopar[®] L) containing TBP modifier at 1:1 vol/vol concentration. Completed in August, 1996, the first half of the test demonstrated a continuous three-stage extraction cycle. Excellent phase disengagement was observed over the course of the 4-hour run, which consumed approximately 4 liters of each phase at equal flow rates of

Table 1. Batch-equilibrium sorption results for pertechnetate from aqueous stripping solution from SRTALK mixer-settler experiment for selected synthetic and commercial anion exchange resins. Uncertainties in K'_d values are $\pm 5\%$. Results for sorption of pertechnetate directly from DSSF-7 simulant are provided for comparison.^a

Resin	1 hr K'_d Strip sol'n (mL/g)	4 hr K'_d Strip sol'n (mL/g)	2 hr K'_d DSSF-7 (mL/g) ^a	6 hr K'_d DSSF-7 (mL/g) ^a
Reillex™-HPQ	12000	13300	293	332
Purolite® A-520E	20400	31800	392	527
Sybron Ionac® SR-6	17900	40000	105	188
VP02-152 (laboratory)	27100	42400	Not determined	Not determined
VP02-217 (laboratory)	33800	62200	Not determined	Not determined

^a Data for sorption of Tc from DSSF-7 reported by N. C. Schroeder [3].

approximately 15 mL/min. Stage-to-stage efficiency was good, with an average steady-state decontamination factor of 6.7 ± 1.2 per stage, resulting in an overall removal of more than 99.6% of the technetium from the waste simulant. The resulting solvent containing the extracted technetium was stripped in a subsequent three-stage continuous mixer-settler test conducted in September. The solvent was stripped with 10 mM nitric acid using the same laboratory mixer-settler equipment used in the extraction cycle, under the same flow conditions. Phase coalescence was again excellent, and 95% of the Tc contained in the solvent was removed following the three-stage contact with the strip solution. Measurements of the other components in the strip solution revealed that the process has a high selectivity for pertechnetate, increasing the ratio of pertechnetate to nitrate (the chief competing anion) more than five hundred-fold in the strip solution relative to the aqueous feed. It must be recognized that the process does not concentrate the Tc, however, but rather separates it from the high concentration of electrolytes in the waste. Concentration is then effected in the follow-on anion exchange step.

The pertechnetate contained in the mixer-settler strip solution was concentrated with very high efficiency on an anion-exchange resin. Table 1 illustrates the comparative performance for anion exchange from our strip solution from the mixer-settler experiment and from a DSSF-7 simulant [3]. The resins used include a variety of commercially available resins, as well as resins prepared by S. D. Alexandratos (University of Tennessee, Knoxville) under another ESP-supported task [9]. It can be seen that using solvent extraction to remove pertechnetate from the waste, followed by stripping and anion-exchange, allows pertechnetate to be concentrated from a large volume of waste into a small volume of resin. The efficiency by which the resin is utilized in this manner obviously far surpasses the efficiency of the resin when contacted directly with the waste.

Extraction and Stripping of Cesium from Alkaline and Acidic Waste Simulants.

We have developed a new solvent for the extraction of cesium from alkaline and acidic tank waste. The best solvent composition so far tested can deliver Cs distribution ratios of 1.8 from a Hanford tank AW-101 waste simulant and 5.4 from a tank AP-106 waste simulant with only 0.02 M extractant. Stripping performance is good; following extraction from the AW-101 simulant, 97% of the Cs contained in the organic solution can be removed following two aqueous stripping contacts (1:1 phase ratio). Cesium can also be extracted from an acidic waste simulant (1 M

sodium nitrate, 1 M nitric acid, 1 mM cesium nitrate) using this solvent at only 0.01 M extractant; a Cs distribution ratio of 1.6 was obtained, and >99% of the extracted Cs was stripped in two contacts. An invention disclosure on the Cs extraction and stripping process is being drafted.

Extraction and Stripping of Strontium from Alkaline Waste Simulants. We are in the process of screening extractants and modifiers to be used in a solvent for the extraction of strontium from alkaline waste. To date, we can obtain strontium distribution ratios of near unity from both mildly alkaline waste simulants such as that approximating tank AP-106 (free hydroxide concentration = 0.08 M), and simulants where the free hydroxide concentration is 1.0 M. Work is in progress to further investigate strontium extraction and to obtain higher distribution ratios prior to formulating a solvent for the combined extraction of cesium, strontium, and pertechnetate.

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