Advanced Integrated Solvent Extraction and Ion Exchange Systems

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EM Focus Area: high-level waste tank remediation

Task Description

Advanced integrated solvent extraction (SX) and ion exchange (IX) systems are a series of novel SX and IX processes that extract and recover uranium and transuranics (TRUs) (neptunium, plutonium, americium) and fission products ^{90}Sr, ^{99}Tc, and ^{137}Cs from acidic high-level liquid waste and that sorb and recover ^{90}Sr, ^{99}Tc, and ^{137}Cs from alkaline supernatant high-level liquid waste. Each system is based on the use of new selective liquid extractants or chromatographic materials. The purpose of the integrated SX and IX processes is to minimize the quantity of waste that must be vitrified and buried in a deep geologic repository by producing raffinates (from SX) and effluent streams (from IX) that will meet the specifications of Class A low-level waste.

The first objective of the program involves development and testing of a new technetium selective resin (ABEC-5000) and a new cesium-strontium selective resin (Diphonix-CS) that should have applicability for removing technetium, cesium, and strontium from the highly alkaline supernatant liquid in the single- and double-shell storage tanks at Hanford. Studies will involve the measurement of the influence of major constituents and radiolysis on the uptake and recovery of technetium by the ABEC-5000 resin and on the uptake and recovery of cesium and strontium by the Diphonix-CS resin. After completion of these initial characterization studies, the two resins will be tested in a column mode using simulated alkaline waste. Figure 1 depicts the Advanced Integrated IX Systems in individual columns or in a mixed-bed mode.

The second major task is to develop an advanced acid-side SX process that will remove in one step ^{90}Sr, ^{99}Tc, ^{137}Cs, and TRUs from acidic high-level waste (HLW). Lanthanides would also be extracted together with TRUs. The process is called TOREX (for total radionuclide extraction) and is based on the use of a mixture of strontium-, cesium-, and TRU-(technetium) selective extractants in a novel combined phase modifier-diluent reagent (Figure 2).

The TOREX process is designed to remove the desired radioisotopes at high nitric acid concentration and achieve recoveries at low acid concentrations. Selective stripping of strontium and cesium from TRUs and technetium is possible. The major advantage in performing a TOREX-type process is the significant reduction in the size of the processing facility to pretreat HLW. Studies in FY 1996 will focus on developing and batch testing the TOREX process solvent.

The second part of the advanced integrated SX program is continuation of the development of a front-end combined CSEX-SREX process. Proof-of-principle studies were carried out in FY 1995. FY 1996 studies will involve the hot testing of the process in a continuous countercurrent solvent extraction mode using Argonne National Laboratory (ANL) centrifugal contactors.

Technology Needs

The advanced integrated solvent extraction and ion exchange systems could be applied to the chemical pretreatment of waste retrieved from storage tanks at DOE defense sites (e.g., at Idaho National Engineering Laboratory, Hanford, Savannah River). The objective of these processes is to minimize the amount of waste that must be vitrified by reducing the level of alpha activity and reducing the concentrations of ^{90}Sr, ^{99}Tc, and ^{137}Cs in the dissolved high-level sludge waste and ^{90}Sr, ^{99}Tc, and ^{137}Cs in the alkaline supernatant HLW.

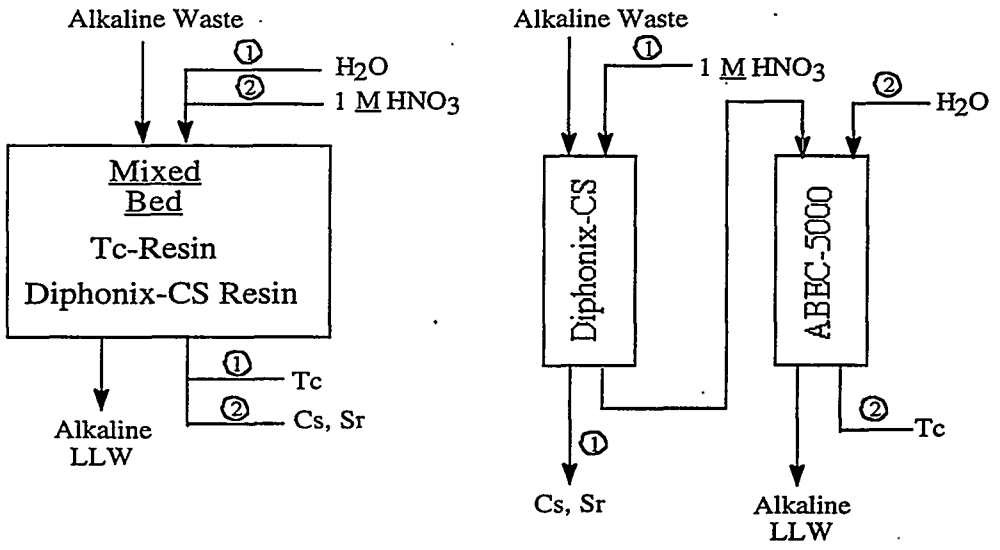

Figure 1. Advanced Integrated IX Systems

Scientific Background

During the last 2 years, members of the Chemical Separations Group, Chemistry Division, ANL, in collaboration with Professor Robin Rogers, Northern Illinois University (NIU), DeKalb, Illinois, and Professor Spiro Alexandratos, University of Tennessee, Knoxville, have made significant progress in developing new resins that may apply to alkaline waste treatment. The NIU/ANL team has developed a new resin that shows high efficiency for the uptake of pertechnetate ions ($D_{Tc} = 10^2$ to 10^3) from high concentrations of salt solutions including sodium hydroxide. Elution of the pertechnetate salt can be achieved using water or dilute nitric acid. Additional studies are needed to adapt and test this new resin for removing ^{99}Tc from the alkaline supernatant solution in the Hanford single- and double-shell storage tanks.

The UT/ANL team has under development a new ion exchange resin belonging to the Diphonix family that has the capability of removing both cesium and strontium from moderate to concentrated sodium hydroxide solutions. The new resin, called Diphonix-CS, can removing both cesium and strontium simultaneously.

Concurrent with the development of new resins for alkaline-side waste treatment, we have made significant advances in the development of an acid-side SX system for cesium and strontium extraction and recovery. The combination of a large ionic radius and low charge makes the selective extraction of cesium and strontium from highly acidic nitrate media difficult. Nevertheless, by exploiting the principles of molecular recognition and solvation effects, we have developed cesium and strontium extractants that can be combined in a plutonium-uranium extraction (PUREX) -like system that can selectively extract cesium and strontium from highly acidic nitrate media. Both cesium and strontium are readily recovered using dilute nitric acid. This combined CSEX-SREX system has been tested in a batch countercurrent mode in FY 1995. Acidic waste simultant from Lockheed Idaho Technology Company (LITCO) was used for the test and results were very favorable. Advantages of a combined CSEX-SREX extraction process at the beginning of a pretreatment sequence include removal of all the major gamma emitters and the need for considerably less shielding in all subsequent processing.

An even larger savings in cost could be achieved if all the major radioisotopes that create problems in waste management, namely, ^{90}Sr, ^{99}Tc, ^{137}Cs, and TRUs, could be isolated in a single process. The TOREX process would involve the use of individual cesium, strontium, and TRU extractants. (The TRU

extractant also extracts technetium.) Each extractant would have to be present in a relatively low concentration; for example, <0.20 *M*, to allow sufficient room for the phase modifier and diluent. The former is needed to reduce third-phase formation and the latter to reduce viscosity. We have found that lauryl nitrile can serve as both a phase modifier and a diluent. This observation increases the likelihood that a TOREX process is feasible.

Accomplishments

The Combined CSEX/SREX Process for the simultaneous extraction of cesium and strontium from acidic nitrate media has been successfully batch tested in a countercurrent mode using a dissolved calcine waste simulant from LITCO. The process uses a solvent formulation comprised of 0.05 *M* di-t-butylcyclohexano-18-crown-6, 0.1 *M* Crown 100' (a proprietary cesium selective macrocyclic polyether), 1.2 *M* tri-n-butylphosphate, and 5% (n/n) lauryl nitrile in an isoparaffinic hydrocarbon diluent. The countercurrent test run indicates that >98% of the cesium and strontium initially present in the feed solution can be removed in only four extraction stages. Both cesium and strontium are readily recovered by stripping the process solvent with 0.1 *M* HNO_3.

Considerable progress has been made to date on the synthesis and characterization of both ABEC-5000 and Diphonix-CS resins. The ABEC-5000 resin has been evaluated for technetium uptake as a function of sodium hydroxide concentration and as a function of sodium nitrate, nitrite, carbonate, aluminate, and citrate concentration in 2 and 4 *M* NaOH. The distribution ratios of technetium are in the range of 10^2 to 10^3 and are very insensitive to the above list of anions over a wide range of concentrations. Technetium uptake measurements with simulated 101-SY, neutralized current acid waste, and single-shell tank waste solutions have also been made. The dry weight D_{Tc} is in the 1×10^2 to 2×10^2 range with all three waste solutions. Elution of technetium from packed bed with H_2O has also been demonstrated.

Benefits

The anticipated benefit of the advanced integrated solvent extraction and ion exchange systems is the minimization of high-level waste that must be vitrified and buried in a deep geologic repository and the recovery of valuable TRUs (e.g., ^{237}Np), uranium, ^{90}Sr, ^{99}Tc, and ^{137}Cs that could have beneficial uses. The advanced integrated solvent extraction and ion

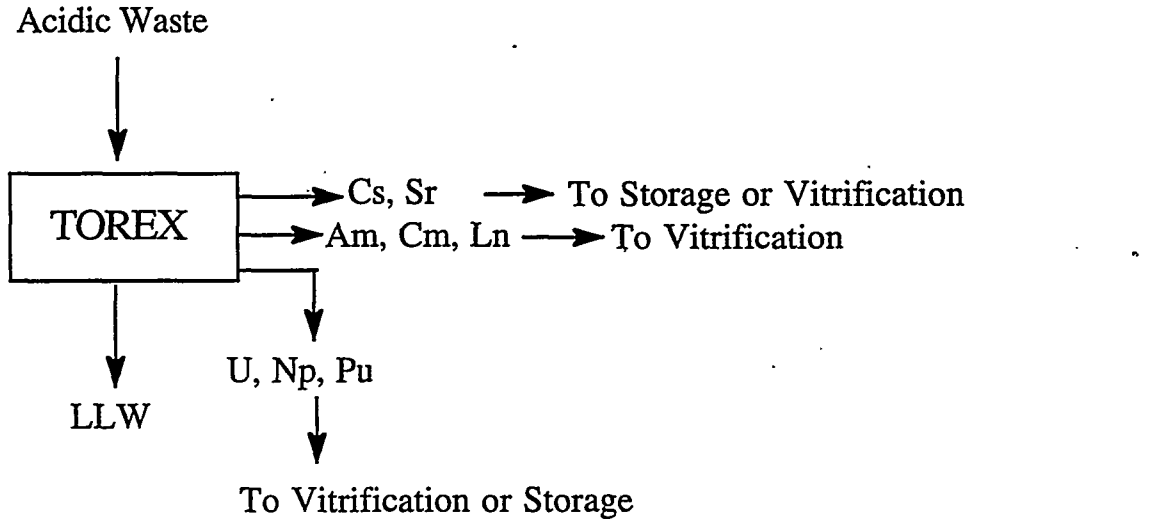

Figure 2. Total Radionuclide Extraction (TOREX) Process Systems

exchange systems should also reduce the cost of chemical pretreatment of waste by reducing the amount of equipment and size of the processing facility.

Keywords

Solvent extraction, ion exchange, high-level waste, TRUs, ^{90}Sr, ^{99}Tc, ^{137}Cs

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