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TASK SUMMARY

COMPREHENSIVE SUPERNATE TREATMENT*

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DISCLAIMER

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TECHNOLOGY NEED

Millions of gallons of radioactive waste are stored in tanks at sites managed by the Department of Energy (DOE). Sites containing this waste include Hanford, West Valley, Idaho Falls, Oak Ridge National Laboratory (ORNL), and the Savannah River Site. These wastes consist of sludges and supernates composed predominantly of nonradioactive chemicals. Concentration of the radioactive components by separation from the nonradioactive chemicals would allow the bulk of the material to be handled as low-level waste and result in volume reduction of the waste required for final disposal. Several technologies are available to treat the supernate or dissolved sludge from the tanks. However, due to the chemical complexity associated with the tank contents, determining which technology will be best requires research using actual samples from the tanks.

The tanks contain cesium, strontium, and technetium radionuclides which are the major contributors to the radioactivity in the supernates. Ion exchange has been effectively used for some radionuclide separations. However, these supernates contain high concentrations of sodium, potassium, chloride, and nitrates that interfere with some separation methods.

Identification of the best sorbents for separation of these radionuclides can best be accomplished by conducting tests using supernate samples from storage tanks. For these studies, supernate samples were collected from the Melton Valley Storage Tank (MVST) farm at ORNL. These samples were used to evaluate the selected sorbents for removing cesium, strontium, and technetium.

TECHNOLOGY DESCRIPTION

This task involves the recovery of the liquid (supernatant or supernate) portions of ORNL MVST waste in a hot cell and treatment of the supernate to separate and remove the radionuclides. The supernate is utilized in testing various sorbent materials for removing cesium, strontium, and technetium from the highly alkaline, saline solutions. Batch tests are used to evaluate and select the most promising materials for supernate treatment to reduce the amount of waste for final disposal. Once the sorbents have been selected based on the results from the batch tests, small column tests are made to verify the batch data. Additional data from these tests can be used for process design.

The sorption tests emphasize evaluation of newly developed sorbents and engineered forms of sorbents. Methods are also evaluated for recovering the radionuclides from the sorbents, including evaluating conditions for eluting ion exchange resins.

A final report will summarize the results and compare the results with those of other investigators, along with recommendations for separating and concentrating radionuclides from DOE storage tank supernates at Oak Ridge and other sites. Documentation of the data and the significance of the findings will be compared, and recommendations will be provided to likely users of the data in EM-30. This program will also provide input to the supernate treatment process demonstration projects at ORNL.

BENEFIT TO DOE/EM

Information developed in this program is expected to apply to tank waste supernates found at most DOE sites, especially highly alkaline supernates with high concentrations of salts. The proposed methods would result in smaller volumes associated with the radioactive component of the waste and thus minimize storage needs. The bulk of the remaining materials could then be treated to remove other components like nitrates and other toxic or hazardous components in the stream with minimal shielding requirements. A final report will be issued summarizing these results, comparing them to other results for the same sorbents, and providing recommendations for unit operations for use in the separation and concentration of the radionuclides from DOE storage tank supernates at ORNL and other DOE sites.

TECHNOLOGY TRANSFER/COLLABORATIONS

Results from this program directly influence and provide input to demonstration projects currently under way at ORNL. These demonstrations involve removing cesium and other radionuclides from supernates from the MVST.

Information developed by this task will be submitted to the DOE Program Manager for dissemination. Results will be presented to Waste Management personnel at other DOE sites, and researchers at other sites will be kept informed of progress. Results will be presented at DOE workshops, program reviews, and technical meetings.

SCIENTIFIC BACKGROUND

Previous studies at ORNL have focused on cesium and strontium separations. These studies tested several sorbents to remove cesium from the MVST W-25 supernate. Sorbents selected for testing included resorcinol/formaldehyde (R-F) resin, Duolite CS-100, crystalline silicotitanate (CST), potassium cobalt hexacyanoferrate, and composite microspheres of hydrous titanium oxide/potassium cobalt hexacyanoferrate and hydrous titanium oxide/sodium cobalt hexacyanoferrate. Potassium cobalt hexacyanoferrate gave the highest cesium distribution ratio; however, of the commercially available sorbents, the R-F and CST worked best.

The effect of cesium concentration on sorbent effectiveness was examined. Increasing the cesium concentration in the supernate did not affect the cesium distribution ratios of potassium cobalt hexacyanoferrate or CST. However, with R-F resin the cesium distribution ratios decreased as the cesium concentration increased. Increasing the potassium concentration resulted in major decreases in cesium sorption on R-F resin. On the other hand, cesium distribution ratios for CST and potassium cobalt hexacyanoferrate did not appear to be affected by an increase in potassium concentration.

Some of the same sorbents may be used to remove strontium simultaneously with the cesium. Batch tests were conducted using several sorbents to determine how effectively they could remove strontium from MVST W-29 supernate. The sorbents included R-F, CST, sodium titanate, hydrous titanium oxide/polyacrylonitrile, sodium titanate/polyacrylonitrile, titanium monohydrogen phosphate microspheres, Amberlite IRC-718, Duolite C-467, and Chelex 100. The powder forms of the inorganic sorbents were the most effective for removing strontium. Of the engineered forms tested, the titanium monohydrogen phosphate microspheres were slightly better than the polyacrylonitrile composites. The most effective organic resin tested was the Duolite C-467.

Speciation may determine the extent of technetium removal. The technetium can be present as the pertechnetate anion, or as complexes of technetium in lower oxidation states. Radiolytic effects, organic solvents, and complexants may result in reduction, complexation, and precipitation of technetium.

Batch studies on technetium removal were conducted at Los Alamos National Laboratory by Schroeder et al. and by Marsh, Svitra, and Bowen. Some 17 sorbents were tested. Several sorbents gave technetium distribution ratios between 100 and 1000 mL/g. In batch tests at ORNL, Reillex HPQ, Reillex 402, Amberlite IRA 904, and Amberlite IRA 400 were all effective in removing pertechnetate from MVST W-29 supernate.

In this program, additional batch tests and some small column tests have been completed to further evaluate the removal of cesium, strontium, and technetium from tank supernates. Recent tests have focused on technetium and strontium removal using small columns.

TECHNICAL APPROACH

Samples of tank supernates have been retrieved from various tanks at the MVST farm including W-25, W-27, and W-29. Characterization of these materials has revealed the wide range of similarities to supernates found in tanks at other DOE sites. Removal of cesium, strontium, and technetium from these highly alkaline, saline supernates is tested using various sorbents, including R-F resin, CST, sodium cobalt hexacyanoferrate, potassium cobalt hexacyanoferrate, sodium titanate, and ion exchange resins such as Duolite CS-100, Amberlite IRC-718, Reillex HPQ and 402, and SuperLig 644C. Many of these sorbents have been proposed for waste treatment, but most have not been tested on actual waste solutions.

Initially, batch tests are used to evaluate and select the most promising materials for supernate treatment. Candidate sorbents for cesium removal include the R-F resin, CST, and hexacyanoferrates. Primary candidates for strontium removal are sodium titanate, silicotitanate, and Amberlite IRC-718; Reillex HPQ anion exchange resin has been proposed for pertechnetate ion removal. New engineered forms of some of the inorganic sorbents such as the CSTs, immobilized crown ethers, and microspheres composed of sodium titanate and sodium titanate blends will be tested as they become available. Sodium and potassium are competitors for cesium removal, and nitrate can be a competitor for pertechnetate exchange. The rate of removal is also an important parameter, as well as the loading capacity of each sorbent.

In the batch tests, 5 to 10 mL of supernate are mixed with 1 to 100 mg of sorbent, and the amount of radionuclide removal is measured. Based on the batch tests results, small column tests are made on selected sorbents to verify the batch data and to obtain additional data for process design.

Most of the sorption studies have focused on radionuclide removal. Some efforts are directed toward elution or stripping of the sorbed radionuclides.

ACCOMPLISHMENTS

The MVST supernates were used in batch and column studies to evaluate sorbents for removal of cesium, strontium, and technetium (as pertechnetate). For the strontium and technetium batch tests, the cesium was first removed from some of the supernates by ion exchange. However, for column tests of technetium removal, the cesium was always removed from the supernates by treatment with ion exchangers. The parameters for the batch tests included the use of various sorbents, mixing times, supernate to sorbent ratios, and sorbent pretreatment. Some of the results from the batch tests are summarized in Table 1. The distribution ratio is defined as follows: $D = [C_o - C_f)/C_f][V/m]$, where C_o is the initial concentration of

radionuclide in the supernate; C_t is the concentration at time, t; V is the volume of supernate; and m is the mass of sorbent.

The sorbents were selected for cesium removal based on a survey of the literature and included SuperLig 644C, IONSIV IE-911, R-F, potassium cobalt hexacyanoferrate, and CST. Supernates were obtained from tanks W-27 and W-29. Pretreatment of SuperLig 644C and IONSIV IE-911 with 0.1 *M* NaOH did not affect the cesium distribution ratios, viz., 1250 mL/g using "as-received" resin and 1220 mL/g for the sorbent pretreated 0.01 M NaOH. However, these values were still less than the distribution ratio obtained for the potassium cobalt hexacyanoferrate. The cesium distribution ratios for this sorbent were 2350 mL/g after mixing for 0.25 h.

Because of the presence of organic liquids in some of the underground storage tanks, tests were conducted to determine the possible effects of the organic liquids on ion exchangers for cesium removal. In one set of tests, treatment of the R-F resin, SuperLig 644C, and CST sorbents by soaking in tributyl phosphate reduced the cesium distribution ratio from 525 to 75 mL/g for the R-F resin, from 480 to 330 mL/g for the SuperLig 644C resin, and from 1000 to 570 mL/g for the CST.

For strontium removal, the sorbents selected for testing included sodium titanate, MERSORB-S, and CST. The granular sodium titanate gave strontium distribution ratios ranging from 380 to 1400 mL/g. Results from the MERSORB-S gave strontium distribution ratios ranging from 317 to 520 mL/g. These values were less than the 24,000 mL/g obtained when using CST powder.

Batch contact studies to test sorbent effectiveness for technetium (pertechnetate) removal included use of NUSORB LP70-S impregnated with one of three amines – Aliquat, TEDA, or piccoline; Eichrom ABEC-5000; an experimental anion resin developed by the University of Tennessee; Purolite A-520-E; Amberlite IRA-904; Reillex HP and HPQ; and Amberlite IRA-400. The MVST W-29 supernate depleted in cesium and strontium and spiked with pertechnetate was used for these tests. The technetium (pertechnetate) distribution ratio obtained for the amine-impregnated NUSORB LP70-S sorbents did not vary greatly, ranging from 380 to 450 mL/g after a 24 h mixing time. Eichrom ABEC-5000 reached a similar value after only 2 h. Subsequent loading tests with ABEC-5000 along with Purolite A-520-E, Amberlite IRA-904, Reillex-HP and -HPQ, and Amberlite IRA-400 resulted in maximum loading of about 2000 mg of technetium per kilogram of sorbent.

Based on the results obtained from the batch studies, column runs were conducted using Reillex-HPQ and Eichrom ABEC-5000-XL. The supernate used was column effluent from which the cesium had been previously removed by column chromatography. Using a column bed of 10.4 cm^3 of Reillex-HPQ and a flow rate of 6 bed volumes (BV)/h, a 50% technetium breakthrough was observed at approximately 45 BV (Fig. 1). Using a solution consisting of 0.017 *M* stannous chloride, 0.1 *M* ethylenediamine, and 0.075 *M* sodium hydroxide, a total of 1.2 mg of technetium was eluted in 7 BV.

The column behavior of Eichrom ABEC-5000-XL is still under study. Additional batch and column tests are planned to evaluate sorbents for strontium removal.

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KEYWORDS

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