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TASK SUMMARY

COMPREHENSIVE SUPERNATE TREATMENT*

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COMPREHENSIVE SUPERNATE TREATMENT

Task Description

This task involves the recovery of the liquid (supernatant or supernate) portions of ORNL Melton Valley Storage Tank (MVST) waste in a hot cell and treatment of the supernate to separate and remove the radionuclides. The supernate will be utilized in testing various sorbent materials for removing cesium, strontium, and technetium from the highly alkaline, saline solutions. These batch tests will be used to evaluate and select the most promising materials for supernate treatment to reduce the amount of waste for final disposal. Small column tests will be made on selected sorbents to verify the batch data and to obtain additional data for process design. Efforts will be made to obtain samples of tank supernate from Hanford for comparison.

The sorption tests will emphasize evaluation of newly developed sorbents and engineered forms of sorbents such as crystalline silicotitanates and Superlig materials. Methods will be evaluated for recovering the radionuclides from the sorbents. This will include evaluating conditions for eluting ion exchange resins, as well as evaluating the stability and storage properties of some of the inorganic sorbents which bind the radionuclides irreversibly.

A final report will summarize the results, along with recommendations for unit operations that could be used to separate and concentrate radionuclides from DOE storage tank supernates at Oak Ridge and other sites. This program will also provide input to the supernate treatment process demonstration projects at ORNL.

Technology Needs

DOE is faced with remediating millions of gallons of high-level and low-level radioactive waste in underground storage tanks at various sites, including Oak Ridge, Hanford, Savannah River, and Idaho. A large portion of the waste is in the form of liquid solution (supernate) which contains the soluble radionuclides along with high concentrations of sodium and potassium salts. The radioactivity is derived primarily from cesium, strontium, and technetium. In many cases the radionuclides constitute only a small portion, less than 1%, of the waste. If these radioactive components could be removed and concentrated, the volume of waste to be disposed of or stored as HLW could be reduced by a factor of 20 to 100.

Technical Approach

Supernate samples have been retrieved from Melton Valley Storage Tanks W-25 and W-29 and characterized. These supernates have many similarities to supernates in tanks at other DOE sites. These supernates are utilized in testing various sorbents, including resorcinol-formaldehyde resin ("R-F Resin"), crystalline sodium silicotitanate (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 644, for removing cesium, strontium, and technetium from the highly alkaline, saline solutions. Many of these sorbents have been proposed for waste treatment, but most have not been tested on actual waste supernate solutions.

Initially, batch tests are used to evaluate and select the most promising materials for supernate treatment. Candidate sorbents for cesium removal include the resorcinol-formaldehyde resin, crystalline sodium silicotitanate, 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 crystalline silicotitanates and immobilized crown ethers 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, 5–10 mL of supernate are mixed with 1–100 mg of sorbent, and the amount of radionuclide removal is measured. Based upon the batch test results, small column tests will be made on selected sorbents to verify the batch data and to obtain additional data for process design. Efforts will be made to obtain samples of tank supernate from Hanford for comparison.

Most of the sorption studies have focused on radionuclide removal. Additional efforts will be directed toward elution or stripping and on the storage or disposition of loaded sorbents that cannot be eluted.

Accomplishments

Approximately 1 L of supernate from MVST W-25 was prepared for batch tests by filtering it through 0.45 micrometer nylon filters to remove the particulates. The specific gravity and the total solids content of the supernate were 1.232 g/mL and 0.338 g/mL, respectively. The pH was 12.6. About 94% of the activity in the supernate is contributed by Cs-137. Other radionuclides in the supernate include Cs-134, Co-60, and Sr-90. The major cations in the supernate are sodium (3.87 *M*) and potassium (0.36 *M*) and the major anions are nitrate (3.8 *M*) and chloride (0.1 *M*). Smaller amounts of aluminum, chromium, zinc, and calcium are present.

The distribution coefficients and percentage removal of cesium from MVST W-25 supernate using several ion-exchange materials have been measured. The ion exchangers tested include resorcinol/formaldehyde resin (R-F resin from Boulder Scientific), crystalline sodium silicotitanate (from Sandia National Laboratories), Duolite CS-100 (Rohm and Haas), granular and powdered potassium cobalt hexacyanoferrate, and composite microspheres containing sodium and potassium cobalt hexacyanoferrates in hydrous titanium oxide and phosphate (prepared at ORNL). In typical experiments, 10 mL of supernate was mixed with 50 mg of sorbent for periods ranging from 15 minutes to 144 hours. The cesium distribution coefficients were 34–44 mL/g for CS-100, 138–764 mL/g for the R-F, 451–958 mL/g for the CST, and 26,000–46,000 mL/g for granular potassium cobalt hexacyanoferrate.

Nine different ion exchangers have been tested to determine the removal of strontium from MVST supernate. The exchangers tested were Amberlite IRC-718, sodium titanate (ST), crystalline silicotitanate (CST), resorcinol/formaldehyde resin (R-F), hydrous titanium oxide/polyacrylonitrile (TiO-Pan), sodium titanate/polyacrylonitrile (NaTiO-PAN), titanium monohydrogen phosphate microspheres, Duolite C-467, and Chelex 100. The inorganic ion exchangers outperformed the organic resins in removing the strontium, with the fine powders of NaTiO and CST giving the best results. For the organic resins tested, Duolite C-467 gave the most favorable results overall.

Several sorbents, including Reillex HPQ, Reillex 402, Amberlite IRA-904, and Amberlite IRA-400 were tested in batch tests for removing pertechnetate from MVST supernate. All of the anion exchangers removed the pertechnetate anion reasonably well. The hydroxide forms of the exchangers appeared to be superior to the nitrate forms. Overall, the hydroxide form of Reillex 402 gave the most promising results.

Benefits

A final report will summarize the results, along with recommendations for unit operations that could be used to separate and concentrate radionuclides from DOE storage tank supernatants at Oak Ridge and other DOE sites. Technologies evaluated in this task are expected to apply to the remediation of tank waste supernates at most DOE sites, particularly highly alkaline supernates that contain high concentrations of salts.

Separation and concentration of the soluble radionuclides would result in a much smaller amount of radioactive waste for disposal or long term storage. Removal of the radioactive components would also reduce shielding requirements and make downstream handling much easier for removing nitrates and any other toxic or hazardous components in the salt solution.

Results from this program will 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 Melton Valley Storage Tanks.

Technology Transfer

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.

References

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Keywords

Supernate, tank waste, cesium, strontium, technetium, ion exchange.

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