

**TASK SUMMARY: HOT DEMONSTRATION OF PROPOSED
COMMERCIAL NUCLIDE REMOVAL TECHNOLOGY**

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Task Description

This task covers the development and operation of an experimental test unit which is located in a Building 4501 hot cell. This equipment is designed to test radionuclide removal technologies under continuous operation on actual Oak Ridge National Laboratory (ORNL) Melton Valley Storage Tank (MVST) supernatant, Savannah River Site (SRS) high-level waste supernatant, and Hanford supernatant. The latter two may be simulated by adding the appropriate chemicals and/or nuclides to the MVST supernatant. The technologies tested will be housed in modules which can be attached to the experimental system inside the hot cell and continuously fed the test supernatant until the nuclide of interest exhausts the capacity of the module. This task works closely with the Efficient Separations and Processing (ESP) and the Tank Focus Area (TFA) in order to ultimately transfer the technologies being developed to the end user. This task complements the Comprehensive Sludge/Supernatant tasks by using larger-scale, continuous equipment to verify and expand the batch studies done by that task.

The experimental unit will be tested by conducting cesium removal operations utilizing the ion-exchange materials that have been proposed for the ORNL Cesium Removal Demonstration Project (CRDP) and tested in batch tests by the Comprehensive Sludge/Supernatant task at a scale that passes up to 20 L of MVST supernatant continuously through the test module until the cesium "breaks through." This may require anywhere from 5–10 resin or test volumes up to more than 1000 test volumes of supernatant to pass through the module. This work will support the design of the CRDP at ORNL.

For the testing of the ESP modules, the experimental unit will be operated at a scale of 1–2 L per test. A large sample (≥ 20 L) of MVST supernatant will be acquired for the module testing so that all modules can be evaluated using the same feed. Testing will consist of using the modules or systems supplied by the ESP for cesium removal until the unit has reached its capacity. Feed supernatant (MVST supernatant, SRS high-level waste supernatant, Hanford supernatant, and MVST supernatant modified to simulate Hanford or Savannah River supernatant) will pass through the module at a prescribed flow rate, and the effluent from the module will pass through a gamma detector for on-line analysis. The effluent will also be collected in fractions for later analysis as required. The volume of supernatant will pass through the test module until 50% breakthrough (or other appropriate end point) and exhaustion of capacity are determined. The capability for testing actual supernatant treatment technologies can be used for other tests based upon requests by the TFA and the ESP.

Once testing on the cesium removal has been completed on the desired modules, experiments will be initiated on the removal of other nuclides of interest that may include strontium-90, technetium-99, ruthenium, and/or others. These isotopes require different resins for removal than does cesium. After the initial testing of these materials in the Comprehensive Supernatant task, they will be tested in the continuous-flow system. The materials supplied to remove technetium-99 may be produced and tested in other ESP programs.

Technology Needs

Radionuclides represent only a small fraction of the components in millions of gallons of storage tank supernatant at various sites, including Oak Ridge, Hanford, Savannah River, and Idaho. Most of the radioactivity is contributed by cesium, strontium, and technetium along with high concentrations of sodium and potassium salts. The purpose of this task is to test and select sorbents and commercial removal technologies supplied by ESP for removing and concentrating the radionuclides, thereby reducing the volume of waste to be stored or disposed.

Technical Approach

A 60-L supernatant sample was retrieved from MVSTs and characterized. This supernatant has many similarities to supernatants in tanks at other DOE sites. These supernatants will be utilized in testing various sorbents, including resorcinol-formaldehyde resin (RF resin), potassium cobalt hexacyanoferrate, crystalline silicotitanates, SuperLig® (IBC Advanced Technologies, Inc., American Fork, Utah), and other cesium removal materials supplied by the ESP Program from commercial manufacturers. Many of these sorbents have been proposed for waste treatment, but most have not been tested on actual waste supernatant solutions in a simulation of actual operating conditions. Several additional sorbents for other radionuclides will be tested as they become available in a form that can be used in the cell.

Initial candidate sorbents for cesium removal are the RF resin and the granular potassium cobalt hexacyanoferrates. Sodium and potassium are competitors for cesium removal. In the continuous column tests of the above materials, 5–50 mL of sorbents is placed in a column and the supernatant to be treated passes continuously through the bed until the resin is at least 50% exhausted. The results of these tests will be compared with the batch results and small-column tests results obtained in the Comprehensive Supernatant Treatment task (B. Z. Egan). The results will supply the CRDP (T. E. Kent) with the information to determine the design parameters for that project. The rate of removal, resin required, and regeneration requirements are important design parameters, and the loading capacity of each sorbent will help to determine the size of the column required and define the final volume of solid waste to be disposed.

In FY 1996 and FY 1997, the tests will be continued using modules that are supplied by ESP to remove cesium, strontium, technetium and other nuclides as requested by ESP. These may include tests demonstrating the removal of technetium from MVST supernatant using materials and methods such as solvent extraction and special ion-exchange materials developed by other ESP programs. In addition, MVST supernatant may be supplied to these developers after it has been treated for cesium and/or strontium removal in the earlier tests. This will be followed by cleanup and decontamination of the experimental facilities and documentation of the results. The final product will be a data base and a final report which summarizes 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.

Accomplishments

Installation of experimental equipment for the cesium removal project in the hot cell C, the procedures used during the experiment, as well as several ion-exchange material tests were completed in FY 1995. The equipment consists of tanks, pumps, tubing and fittings, filters, instrumentation, and connections

for testing cesium removal materials in a continuous-flow system. Capabilities of the system include the ability to operate remotely, on-line monitoring of the column effluent to detect cesium breakthroughs from the material in the module, and the ability to treat ion-exchange resin in the module with any desired eluent or wash solution and monitor the effluent for removal of cesium from the module. The column feed tank receives supernatant from the storage tank through 0.45- μm filters, and the module effluent is passed through 0.45- μm filters before passing through the detector. The column can be treated in place to allow repeated cycling of the resin between cesium loading and removal; gamma counts can be made before and after elution; and loaded columns can be drained, capped and stored in the cell for future testing or disposal.

The feed supernatant for the tests was obtained from MVST W-27 in April 1995. Approximately 56 L of the supernatant, enough for the planned tests, is in storage in Building 4501. Tank W-27 contains supernatant at pH 7.2 and has the lowest potassium and ^{137}Cs levels of the available tanks. This allows the supernatant to be more easily handled than that from other tanks. For some absorber tests, this supernatant will be adjusted back to the pH standard in other tanks, about 12.5–13.0. Analysis of the present sample after pH adjustment to 12.8 and filtration showed about 9.3×10^{-6} Ci/mL of ^{137}Cs .

The first experiment used RF obtained from Jane Bibler at SRS. The feed rate during operation was about 1.4 mL/min and resulted in a feed rate of about 7 column volumes (CV) per hour. The original 12.5 cm³ of resin shrank to 11.5 cm³ when feed started to flow through the bed and remained at that volume throughout the run. The fractions were weighed, and samples were taken for counting the ^{137}Cs . The number of column volumes to 50% breakthrough was about 45. During the run about 0.5 L of feed containing 4.42 mCi of ^{137}Cs was fed to the column.

A second experiment was done with RF resin in which the feed rate through the bed was reduced to about 2.8–3.0 CV/h. During the first 4 CV of feed through the bed, the bed volume decreased from the original 12.5 to about 10.6 cm³, which changed the rate of CV per hour to about 2.9–3.0. After about 25 CV, the bed volume was 10.2 cm³. The final bed volume after the run was 9.9 cm³. The 50% breakthrough occurred at about 40 CV, and the shape of the curve was very similar to that in the first RF run.

Another experiment used CS-100 obtained from Lane Bray, lot #2-850001, from Rohm & Haas. The feed rate through the column was set at about 0.7 cm³/min, which is about 2.9 bed volumes per hour, and was constant throughout the run. Flow was continued until the in-cell detector showed that over 60% breakthrough had been achieved. The run was continued to over 80% breakthrough. The number of column volumes to 50% breakthrough was about 12.5. During operation, the column bed height remained constant and no change in color or appearance was seen.

In addition to the above runs, experiments using SuperLig® 644C resin and additional RF resin with a series of five loading/elution/regeneration cycles, crystalline silicotitanates, and 3M Web with SuperLig were made. Final results for these runs have not yet been released.

Benefits

Technologies evaluated in this task are expected to apply to the remediation of tank waste supernatants at most DOE sites, particularly highly alkaline supernatants that contain high concentrations of salts. Separation and concentration of the soluble radionuclides, particularly cesium, 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.

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.

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