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**Quarterly Progress Report for the
Chemical Development Section of
the Chemical Technology Division:
October–December 1996**

R. T. Jubin

MANAGED AND OPERATED BY
LOCKHEED MARTIN ENERGY RESEARCH CORPORATION
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

ORNL-27 (3-96)

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Chemical Technology Division

QUARTERLY PROGRESS REPORT FOR THE
CHEMICAL DEVELOPMENT SECTION OF THE
CHEMICAL TECHNOLOGY DIVISION:
OCTOBER-DECEMBER 1996

R. T. Jubin

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Prepared by the
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EXECUTIVE SUMMARY

This report summarizes the major activities conducted in the Chemical Development Section of the Chemical Technology Division at Oak Ridge National Laboratory (ORNL) during the period October–December 1996. The report describes ten tasks conducted in four major areas of research and development within the section. The name of a contact is included with each task in the report, and readers are encouraged to consult these individuals if they need additional information.

The *first major research area—Chemical Processes for Waste Management*—includes the following tasks: Comprehensive Supernate Treatment, Partitioning of Sludge Components by Caustic Leaching, Hot Demonstration of Proposed Commercial Nuclide Removal Technology, Development and Testing of Inorganic Sorbents, and Sludge Treatment Studies.

As part of the Comprehensive Supernate Treatment task, additional batch tests were conducted to determine the effect of organics resulting from degradation of ion exchangers on pertechnetate removal from ORNL Melton Valley Storage Tank (MVST) W-27 supernatant. Additional batch tests were performed to measure the sorption of strontium from the supernatant. Based on the results of these tests, Amberlite IRC-718 was selected for the first column chromatographic run to measure strontium removal from MVST supernatant. Batch tests were also made to determine the conditions for stripping strontium from the Amberlite IRC-718 resin. Based on the results of these tests, nitric acid will be evaluated for stripping the strontium from the column. Preparations were completed for the column test.

Tests using additional Hanford tank sludges and analyses of samples from caustic leaching of sludges from Hanford tanks C-105 and C-107 were continued as part of the Partitioning of Sludge Components by Caustic Leaching task. Chemical and radiochemical analyses of leachates, rinses, and residues from Hanford tanks C-105 and C-107 were completed. Additional leach tests were conducted on sludge samples from tanks S-104 and SX-113, and the resulting solutions and residues are being analyzed.

The Hot Demonstration of Proposed Commercial Nuclide Removal Technology task addressed the continuous removal and concentration of radioactive components from supernatants at the various Department of Energy sites. The primary objective is to evaluate candidate absorbers and ion exchangers under continuous-flow conditions using actual supernatant from the MVSTs. An experimental system contained in a hot-cell facility is being used to test the materials in columns or modules using the same batch of supernatant so that all of them can be compared on the same basis. During the past quarter, UOP's IE-911 crystalline silicotitanate (CST) was retested in support of the Cesium Removal Demonstration (CsRD) Project, with the MVST W-29 feed and the CST used in the CsRD. The column was loaded at 6 column volumes (CV)/h to greater than 90% breakthrough, and the loaded column was submitted for Toxicity Characteristic Leaching Procedure analysis.

Composite microspheres containing sodium titanate embedded in hydrous titanium oxide were prepared for removing strontium from waste tank supernatants as part of the Development and Testing of Inorganic Sorbents task. The microspheres were characterized by thermogravimetric and differential thermal analyses, and their crush strengths were measured. Batch tests were conducted with selected microsphere samples, along with several other sorbents, for measuring the strontium removal from simulated ORNL MVST W-29 supernatant.

Slow-pour density measurements were made on pure hydrous titanium oxide microspheres and air-dried composite microspheres containing sodium titanate. Efforts were also continued to find an immiscible organic medium to use as a replacement for silicone oil for the hexamethylenetetramine internal gelation process. A letter report entitled *Development and Testing of Spheroidal Inorganic Sorbents* was distributed.

Within the Sludge Treatment Studies task, Enhanced Sludge Washing tests were conducted with sludge from Hanford tanks C-105, C-107, C-108, and SX-113, and the filtered process solutions were examined for solids formation. Solids were found in the filtered process solutions from each of these sludges. Acidic treatment of sludge from Hanford underground storage tank B-202 was carried out. There was some indication of solids formation in all of the leachates after filtration.

Within the *second research area—Reactor Fuel Chemistry*—the distribution of iodine in containment during an AP600 design-basis accident was evaluated using models in the "TRENDS" code. The AP600 3BE accident sequence calculations showed that $\text{pH} > 7$ was maintained for at least 30 d and that most of the iodine was in the form of iodide.

Within the *third research area—Thermodynamics*—efforts continued in the Thermodynamics and Kinetics of Energy-Related Materials task. A manuscript entitled "Magnetic Dynamics in Underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$: Direct Observations of a Superconducting Gap" was accepted for publication by *Physical Review Letters*. In addition, work on the two-year collaboration with Dr. Gennady Voronin, of Moscow State University, continued. The objective of this joint effort is to determine the solidification conditions of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Y123), $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y124), $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15+y}$ (Y247), and other related compounds from the melt of yttrium, barium, and copper oxides. These conditions include temperature, pressure, p_{Oxygen} , the chemical composition of the melt, and the phase and chemical compositions of the growing solids. Differential thermal analysis/thermogravimetric analysis and hydrogen reduction have been used to determine the oxygen contents of melts from phase-pure Y123 at partial oxygen pressures ranging from 0.1 to 0.000006 MPa.

The *fourth major research area—Processes for Waste Management*—includes work on these tasks: Ion-Exchange Process for Heavy Metals Removal, Search for Technetium in Natural Metallurgical Residues, and Waste Form Development and Testing of a Glass- and Cement-Based Dedicated Hot-Cell Facility.

The first of these tasks—Ion-Exchange Process for Heavy Metals Removal—is the demonstration of a pilot-scale ion-exchange system to remove heavy metals from multiple (originally just from an acid mine site) sites using the most effective commercially available sorbent based on laboratory screening experiments. This system would run concurrently with three novel treatment systems and serve as baseline technology. This project is administered by the National Institute of Environmental Renewal. The ion-exchange system consists of a filter system to remove suspended solids followed by two 4-in.-diam by 5-ft-long ion-exchange columns in series to remove the metal-ion contaminants. The exiting water is periodically sampled and analyzed for breakthrough. The system is designed to flow up to 2.2 L/min of contaminated water and is also set up for regeneration and precipitation of the regenerant. The entire system is controlled by a programmable logic controller that is operated by a modem and is located in a trailer.

The demonstration of the ion-exchange process at Tobyhanna Army Depot was completed during the past quarter. The operation of the ion-exchange system was intermittent due to three

operational problems; however, the system was still able to process 17,000 L, or 1130 CV, of wastewater without breakthrough. The columns were regenerated, and the sludge was disposed of. Samples of the sludge and supernatant from the regeneration were taken for later analyses. The system is packed and ready for transportation back to ORNL.

In the Search for Technetium in Natural Metallurgical Residues task, work is in progress to search for naturally occurring technetium isotopes at a depth of 2000 m below the earth in tin minerals, where they are theorized to be forming from solar radiation at the proper energy. If successful, this work may resolve a modern-day physics question regarding a long debate over baryon instability.

As part of the final task within this area—Waste Form Development and Testing of a Glass- and Cement-Based Dedicated Hot-Cell Facility—a dedicated hot-cell facility at ORNL has been modified and equipped to form glass- and cement-based waste forms for comparative, waste form performance testing. The test work will employ actual transuranic waste and surrogate waste representing typical sludge from the Oak Ridge MVSTs.

1. CHEMICAL PROCESSES FOR WASTE MANAGEMENT

B. Z. Egan

1.1 COMPREHENSIVE SUPERNATANT TREATMENT (D. J. Davidson, J. L. Collins, K. K. Anderson, and B. Z. Egan)

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Summary: Additional batch tests were conducted to determine the effect of organics resulting from degradation of ion exchangers on pertechnetate removal from Oak Ridge National Laboratory (ORNL) Melton Valley Storage Tank (MVST) W-27 supernatant. Additional batch tests were performed to measure the sorption of strontium from the supernatant. Based on the results of these tests, Amberlite IRC-718 was selected for the first column chromatographic run to measure strontium removal from MVST supernatant. Batch tests were also made to determine the conditions for stripping strontium from the Amberlite IRC-718 resin. Based on the results of these tests, nitric acid will be evaluated for stripping the strontium from the column. Preparations were completed for the column test.

1.1.1 Purpose and Scope

This task involves testing sorbent materials for removing cesium, strontium, and technetium from the saline solutions in U.S. Department of Energy (DOE) storage tank supernatant at Oak Ridge and other sites. Batch tests are used to evaluate and select the most promising materials for supernatant treatment to reduce the amount of waste for final disposal. Small-column tests are made on selected sorbents to verify the batch data and to obtain additional data for process design. Methods will be evaluated for recovering the radionuclides from the sorbents.

Supernatants used in the tests have been retrieved from MVST W-25, W-27, and W-29. These supernatants have many similarities to those in tanks at other DOE sites. Efforts will be made to obtain samples of tank supernatants from Hanford for comparison. Many sorbents have been proposed for waste treatment, but most have not been tested on actual waste solutions.

1.1.2 Progress

A column chromatographic test using Eichrom ABEC-5000 to remove pertechnetate from a treated MVST W-27 supernatant yielded a lower removal than expected. The cause of the low removal was suspected to be the presence of organics introduced during ion-exchange treatment for cesium removal. Additional batch tests were conducted using column effluents from two different ion-exchange columns used to remove cesium. The pertechnetate distribution from these treated supernatants was tested using both Reillex HPQ and Eichrom ABEC-5000 sorbents. The liquid-to-

sorbent ratio was 100 with a mixing time of 24 h. The resulting samples were analyzed for technetium by inductively coupled plasma-mass spectroscopy. All of the tests gave lower technetium distribution ratios. It is suspected that the lower values resulted from reduction and/or complexation of the technetium by organics from the ion-exchange columns used to remove the cesium.

The characteristics of selected sorbents to be evaluated for strontium removal were determined. The moisture contents of Amberlite IRC-718, Chelex 100, and Duolite C-467 were measured, and the stabilities of these sorbents in 0.1, 1, and 2 *M* nitric acid were verified.

Several batch tests were completed to select sorbents for use in chromatographic columns for strontium removal from MVST W-27 supernatant. Strontium, spiked with ^{85}Sr , was added to the MVST W-27 supernatant to give a strontium concentration of 1 ppm. The solution was then filtered and analyzed for strontium prior to use. Duplicate 50-mg samples of sorbents—including Amberlite IRC-718, Duolite C-467, Chelex 100, Ionsiv IE-911 (UOP), sodium titanate (Allied Signal), and sodium titanate/polyacrylonitrile microspheres—were prepared. Five-milliliter volumes of supernatant were added to the 50-mg samples of sorbents in preweighed centrifuge tubes. The samples were mixed on a shaker for 24 h. The sorbent and supernatant were separated by centrifugation. The supernatant was then filtered through 0.2- μm filters, and aliquots were analyzed for strontium using an LKB Wallac Compugamma counter. The inorganic sorbents gave the highest strontium distribution ratios, approximately 3000 mL/g. Of the organic sorbents, the Amberlite IRC-718 gave the highest strontium distribution ratio, 1200 mL/g. Based on these batch tests, Amberlite IRC-718 was chosen as the sorbent for the first chromatographic run.

The ability to remove the strontium from the resin is equally important. Therefore, tests were conducted using the previously loaded sorbents and contacting them with either 0.1 or 1 *M* nitric acid to measure the strontium removal. After a 30-min mixing time, the solution was separated from the sorbent and filtered through a 0.2- μm filter; a 1-mL sample was then taken for analysis. The procedure was repeated four times, and on the fourth time the mixing time was extended to 65 h. Up to 63% of the strontium was removed from the resin. It was decided to use nitric acid to test the stripping of strontium from the loaded Amberlite IRC-718 in the planned column test.

A program summary was prepared for inclusion in the document from the Technical Exchange Meeting to be held in January 1997 in Gaithersburg, Maryland.

A draft letter report describing the results obtained during FY 1996 was completed and distributed. The report summarizes the results from batch tests using various sorbents to remove

cesium, strontium, and technetium, as well as results from small chromatographic column tests to remove technetium from ORNL MVST supernatant.

1.2 PARTITIONING OF SLUDGE COMPONENTS BY CAUSTIC LEACHING (B. Z. Egan, B. B. Spencer, J. L. Collins, D. D. Ensor,* and C. W. Chase)

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Summary: Tests using additional Hanford tank sludges and analyses of samples from caustic leaching of sludges from Hanford tanks C-105 and C-107 were continued. Chemical and radiochemical analyses of leachates, rinses, and residues from Hanford tanks C-105 and C-107 were completed. Additional leach tests were conducted on sludge samples from tanks S-104 and SX-113, and the resulting solutions and residues are being analyzed.

1.2.1 Purpose and Scope

Many underground storage tanks contain high concentrations of nonradioactive materials—such as aluminum, chromium, and phosphates—that can significantly increase the volume of the final high-level-waste (HLW) waste form for disposal. There is increasing emphasis on removing these materials through “Enhanced Sludge Washing,” such as taking advantage of the solubilities of these materials under very caustic conditions to partition the radioactive and nonradioactive components. The behavior of some of the components, such as chromium and phosphate, is also important to vitrification processes. An objective of this project is to measure the caustic dissolution behavior of sludge components from ORNL MVST sludge, surrogate Hanford sludges, and selected Hanford sludge samples. If the nonradioactive components can be preferentially solubilized, then the volume of the remaining radioactive waste to be treated and/or stored would be significantly reduced.

1.2.2 Progress

This task addresses the potential for removing aluminum and other nonradioactive components from Hanford waste tank sludges by extraction with caustic solutions, thereby reducing the amount of sludge that must undergo acid digestion or vitrification for disposal. Dissolution of aluminum, chromium, and other metals with sodium hydroxide from actual sludge samples is being evaluated using different temperatures, sodium hydroxide concentrations, leaching times, etc.

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Several tests to measure the caustic dissolution behavior of sludges from Hanford tanks S-104 and SX-113 have been completed. Material balances for some species, such as silicon and phosphorus, are poor and indicate either difficulty in their analysis or reprecipitation prior to sampling for analysis. For other materials, such as aluminum and chromium, the material balances are much better, so the effects of different leaching parameters can be described with greater confidence.

Analyses of leachates, rinses, and residues from leaching tests on samples of sludges from Hanford tanks C-105 and C-107 were completed. Leaching with 6.33 *M* NaOH for 21.7 h at 70°C resulted in the dissolution of 97% of the aluminum, 71% of the chromium, and 94% of the phosphorus from the C-105 sludge, and 85% of the aluminum, 70% of the chromium, and 94% of the phosphorus from the C-107 sludge, based on analyses of the residues. Additional radiochemical analyses of the residues showed that these leaching conditions also resulted in the dissolution of about 12% of the plutonium and 75% of the cesium from the C-105 sludge, as well as about 53% of the cesium from C-107 sludge. These results will be compared with results obtained on the caustic leaching behavior of C-107 sludge under different conditions by Lumetta, of Pacific Northwest National Laboratory (PNNL); Temer, of Los Alamos National Laboratory; and Brooks, of PNNL.

Additional leach tests were conducted using sludge samples from Hanford tanks S-104 and SX-133. The leaching conditions were changed in an attempt to increase the caustic dissolution of the sludges. The temperature was increased to 80°C, and the leach time was increased to 126 h. The NaOH concentration was 6.3 *M*. Due to a gear malfunction in the mixer, it was estimated that effective mixing was maintained for only about 72 h of the total (126 h) leaching time. Following the leaches, the residues were rinsed three times with "inhibited" water containing 0.01 *M* NaOH and 0.01 *M* sodium nitrite. These leach conditions resulted in the dissolution of about 60% of the S-104 sludge, and about 45% of the SX-113 sludge, based on the masses of the original sludges and the remaining residues. The leachates, rinses, and residues have been submitted for chemical and radiochemical analyses.

Two sludge samples from Hanford tank C-104 were received. Preparations are under way to conduct caustic leach tests on these samples.

A poster entitled "Caustic Leaching Treatment of Radioactive Sludges" was presented at the AIChE Meeting in Chicago in November 1996. A letter report entitled *Partitioning of Sludge Components by Caustic Leaching* was prepared and distributed.

1.3 HOT DEMONSTRATION OF PROPOSED COMMERCIAL NUCLIDE REMOVAL TECHNOLOGY (D. D. Lee and J. R. Travis)

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Summary: This task covers work in the continuous removal and concentration of radioactive components of supernatant at the various DOE sites. The primary objective is to evaluate candidate absorbers and ion exchangers under continuous-flow conditions using actual supernatant from the MVSTs. An experimental system contained in a hot-cell facility is being used to test the materials in columns or modules using the same batch of supernatant so all of them can be compared on the same basis. During the past quarter, UOP's IE-911 crystalline silicotitanate (CST) was retested in support of the Cesium Removal Demonstration (CsRD) Project, with the MVST W-29 feed and the CST used in the CsRD. The column was loaded at 6 column volumes (CV)/h to greater than 90% breakthrough, and the loaded column was submitted for Toxicity Characteristic Leaching Procedure (TCLP) analysis.

1.3.1 Purpose and Scope

This task covers the operation of an experimental test unit that is located in a Building 4501 hot cell. This equipment is designed to test radionuclide removal technologies under continuous operation on actual ORNL MVST supernatant, Savannah River HLW 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 are housed in modules or placed in columns that 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. Initial candidate sorbents for cesium removal are the resorcinol/formaldehyde resin, CSTs, Superlig® 644 resin, and granular potassium cobalt hexacyanoferrate. Sodium and potassium are competitors for cesium removal. The results of these tests will be compared with batch results and small-column test results obtained in the Comprehensive Supernate Treatment task (B. Z. Egan). The results will be used to supply the CsRD Project (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 help define the final volume of solid waste to be disposed of.

This task works in close cooperation with the Efficient Separations and Processing Crosscutting Program (ESP) and the Tank Focus Area (TFA) in order to ultimately transfer the technologies being developed to the end user. As part of this work, TFA requested through ESP that we test the electrodialysis-ion-exchange (ED/IX) system from AEA Technology in the United

Kingdom because ORNL was the only site with sufficient available supernatant for testing this multiple-cycle system.

1.3.2 Progress

1.3.2.1 Bench-Scale Qualification of the CST and W-29 Supernatant for the CsRD

The CsRD experiment was designed to test on a small scale the CST commercial sorbent with the MVST supernatant to be used in the CsRD demonstration, which would treat up to 25,000 gal of supernatant from MVST W-29. The CST to be used in the CsRD was purchased from UOP as IONSIV IE-911 Lot no. 99909681003 and was prepared according to the manufacturer's directions by personnel in Building 2528 in the CsRD mockup system. The objectives were as follows:

1. qualify the batch of CST sorbent to be used in the CsRD,
2. test the MVST supernatant that will be processed by the CsRD,
3. determine if the CST sorbent removes other radionuclides or Resource Conservation and Recovery Act (RCRA) metals,
4. provide performance data from a small-scale column that can be compared directly with the larger CsRD columns for the determination of scaleup parameters,
5. determine if the supernatant contains particulates that will be removed by the filter on the CsRD, and
6. determine if the spent sorbent is a hazardous waste under RCRA regulations (40 CFR 261 Subpart C).

The planned operating conditions were as follows: the flow rate was 6 CV/h of supernatant through the bed using a CST volume of approximately 10 mL in the 1.45-cm-ID glass column; samples were to be taken at intervals of approximately 50 to 60 CV for analytical determinations; the column loading would be continued until at least 90% breakthrough of the cesium occurred; and the loaded column would be submitted for TCLP analysis.

1.3.2.2 Experimental Results

Preparation of the MVST supernatant. The supernatant was sampled on August 8, 1996, by ORNL Waste Operations and CsRD personnel, in three 2-gal polypropylene containers. For this experiment, the feed bottle labeled W29080896-3 was transferred to the feed port of Cell C, where the lid was removed and the feed transfer lid was placed in position for transfer to the test system

feed tank. This bottle was used for the first 750 CV of the run. When the bottle was empty, it was removed and bottle W29080896-1 was used for the second half of the experiment.

The radioactive cesium in feed samples was determined using an Aptec intrinsic germanium detector and a Nuclear Data multichannel analyzer system in Room 126A. Samples from the first feed bottle (W29080896-3) showed about 13.0 $\mu\text{Ci/mL}$ of ^{137}Cs and 0.24 $\mu\text{Ci/mL}$ of ^{134}Cs , for a $^{137}\text{Cs}/^{134}\text{Cs}$ ratio of 54. Samples from the second feed bottle (W29080896-1) showed about 11.9 $\mu\text{Ci/mL}$ of ^{137}Cs and 0.18 $\mu\text{Ci/mL}$ of ^{134}Cs , for a $^{137}\text{Cs}/^{134}\text{Cs}$ ratio of 67. The value of 13.0 $\mu\text{Ci/mL}$ was used for the feed concentration for the column loading calculations through about 800 CV. The breakthrough for the remainder of the run was calculated based on a gradual change between the two feeds. The Aptec detector is calibrated at 30-cm distance from the detector head with National Institute of Standards and Technology Standard Reference Material 4275C-88. The samples were counted at that distance.

Column preparation. The ion-exchange column was prepared on the day the run started. The CST had previously been backwashed, adjusted to pH 12.5 with caustic, and then air dried. A total of 6.1 cm of CST was added to the column and tapped to at least a volume of 10.2 mL. The sorbent weighed 13.202 g. The packed bed was then fluidized to remove fines using a simulant containing 4.5 M NaNO_3 and 0.1 N NaOH . A total of 40 mL of simulant was pumped through the column, and the bed was tapped to the most settled position of 6.1 cm. The level of simulant was then lowered to about 1 cm above the bed, and the column was secured after adding the top tubing connections and clamping the inlet and outlet tubes.

Conduct of CST loading. When all preparations had been completed, the feed pump and valves were configured to pump supernatant to the column, from the column through the filter and the detector, and to the fraction collector. After about 3 CV, the rate was fairly stable; after 6 CV, there was very little variation from flow check to flow check throughout the rest of the loading operation.

The cell detector data collection and the fraction collector were started after it had been determined that liquid had passed through the filter. Flow continued with the periodic sampling for more than 210 h for greater than 1200 CV of the W-29 feed treated. At about 750 CV, the first bottle of feed was empty, and the second (W29080896-1) was put in position and the feed tank filled from it. (Subsequent analysis of this bottle revealed that it contained about 10% less ^{137}Cs than bottles 2 and 3 that were previously used, and this change was accounted for in the data analysis.)

When the loading was complete, the experimental system was shut down by stopping feed to the column, emptying the lines back to the feed tank, and adding 50 mL of simulant (4.5 *N* NaNO₃ and 0.1 *N* NaOH) to the eluant tank to rinse the supernatant from the column and system. During the rinse, the detector counts continued to increase as had been seen in the previous rinse. The ¹³⁷Cs level increased slightly during the 1-h rinse. Following the simulant rinse, the system was rinsed with deionized water, and the detector counts decreased (as expected) from about 95% breakthrough level to less than 5% breakthrough in about 2 h. After the rinse showed that supernatant had been removed from the system, the column was drained for counting and transport purposes. The column was isolated from the system. The inlet and outlet tubes were then clamped, and the column was prepared for removal from the cell.

Results of loading. The eluant samples from the column were collected and sampled. Samples of the eluant from about every 60 CV, starting at 20 CV, were analyzed for ¹³⁷Cs. The loading curve is almost identical to the first CsRD support test at the same operating conditions.

The column containing the loaded sorbent was packaged for transport and sent for analysis by TCLP. Samples of the feeds and effluent from the column were also analyzed to determine the pH and the cesium concentrations. Those results have not yet been received.

1.4 DEVELOPMENT AND TESTING OF INORGANIC SORBENTS (J. L. Collins and K. K. Anderson)

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Summary: Composite microspheres containing sodium titanate embedded in hydrous titanium oxide were prepared for removing strontium from waste tank supernatants. The microspheres were characterized by thermogravimetric analysis (TGA) and differential thermal analysis (DTA), and their crush strengths were measured. Batch tests have been conducted with selected microsphere samples, along with several other sorbents, for measuring the strontium removal from simulated ORNL MVST W-29 supernatant.

Slow-pour density measurements were made on pure hydrous titanium oxide microspheres and air-dried composite microspheres containing sodium titanate. Efforts were also continued to find an immiscible organic medium to use as a replacement for silicone oil for the hexamethylene-tetramine (HMTA) internal gelation process.

A letter report entitled *Development and Testing of Spheroidal Inorganic Sorbents* was distributed.

1.4.1 Purpose and Scope

The general objectives of this task are to develop, prepare, and test new and unique inorganic ion exchangers made as microspheres by the internal gelation process to remove fission products, actinides, and other metals (such as the RCRA metals) from waste streams occurring at various DOE sites. Initial emphasis will be on materials for removing radionuclides from supernatants from waste storage tanks.

Inorganic sorbents are being developed for removing strontium from aqueous waste and process streams. Attempts are being made to prepare pure sodium titanate microspheres, as well as composite microspheres consisting of hydrous titanium oxide or titanium monohydrogen phosphate embedded with fine powders of sodium titanate or silicotitanate. Two methods are being evaluated for conversion of hydrous titanium oxide microspheres to sodium titanate microspheres. One method involves heating the hydrous titanium oxide microspheres, prepared by the internal gelation process, with sodium hydroxide at elevated temperatures in a sealed reactor vessel. The other method involves an alkoxide conversion of the hydrous titanium oxide microspheres.

1.4.2 Progress

The initial microspheres produced by the internal gelation process will be made of materials that have already been shown to be highly effective as cesium and strontium sorbents. The initial effort is to make a more column-usable inorganic ion exchanger for removing strontium from waste tank supernatants. Composite microspheres containing varying amounts of sodium titanate homogeneously embedded in microspheres of hydrous titanium oxide have been prepared by utilizing the internal gelation process.

The average crush strength for each composite microsphere composition was determined dynamometrically. (This is the force in grams needed to crush or squash the microspheres.) For these measurements, ten microspheres were randomly chosen from each composition. The crush strength of the gel spheres of each composition was 58 ± 3 g. For comparison, samples of NaTiO-PAN and TiP-PAN sorbents obtained from F. Sebesta, of the Czech Technical University of the Czech Republic, could support $\sim 60 \pm 4$ g before being crushed. In general, the crush strength of air-dried microspheres was much higher, with an average of 2500 g for sodium titanate/hydrous titanium oxide microspheres and 275 g for the sodium titanate/hydrous titanium phosphate microspheres. The average crush strength for the commercially available granular sodium titanate was 425 g; for the IONSIV®IE911, it was 105 g. Dynamometric measurements were also made on samples of air-dried

composite microspheres that had been soaked in water for about 72 h. After soaking in water, the sodium titanate/hydrous titanium oxide microspheres could support up to 2000 g; the sodium titanate/hydrous titanium phosphate supported about 100 g.

A sample of air-dried microspheres containing 16.8% sodium titanate in hydrous titanium oxide was analyzed by TGA and DTA. The sample was slowly heated to $\sim 1000^{\circ}\text{C}$ in a flowing dry-air atmosphere. About 74% of the sample mass was vaporized by the time the temperature reached $\sim 450^{\circ}\text{C}$. Thereafter, the mass remained fairly constant. Both the TGA and DTA heating profiles indicated that there was exothermal conversion of the hydroxide to oxide between 350 and 450°C . The range of microsphere size before heating was 200 to $600\text{ }\mu\text{m}$ and after heating was 40 to $60\text{ }\mu\text{m}$. The crush strength was $150 \pm 25\text{ g}$.

Slow-pour density measurements were made on pure hydrous titanium oxide microspheres and air-dried composite microspheres. Values for commercial granular sodium titanate and IONSIV IE-911 were also determined for comparison. Our experience has shown that the slow-pour method is more reliable than the tap-density method. The slow-pour method involves pouring sorbent particles slowly into a tared, graduated cylinder and measuring the mass and volume. The procedure is repeated with several samples to get an average value. These relative density measurements are useful guides in correlating the crystallinity of sorbents. Previous studies have shown that, in general, materials of small crystallite size are less porous than materials of large crystallite size. The slow-pour density of the hydrous titanium oxide/sodium titanate composite microspheres (30 to 70 mesh) ranged from 1.00 to 1.05 g/mL. The composite containing the highest amount of sodium titanate also had the highest slow-pour density. The slow-pour density of pure hydrous titanium oxide was 0.98 g/mL. Average values of 1.09 and 1.10 g/mL were obtained for the commercial granular sodium titanate and IONSIV IE-911, respectively.

Batch sorption tests were conducted with several strontium-selective sorbents for comparison with the sorption data obtained with composite microspheres. As was the case in previous batch tests, the sorbents were soaked in deionized water for about 72 h prior to testing. A simulated supernatant containing 3.9 M sodium nitrate, 1.0 M NaOH, 0.14 M sodium carbonate, 0.1 M NaCl, 0.25 M potassium nitrate, 0.0001 M calcium carbonate, and 1 ppm strontium was used. The strontium was added as strontium nitrate, which was traced with ^{85}Sr for easier analysis. Each batch test involved mixing about 5 mL of the simulated supernatant solution with 0.050 g (air-dried weight) of sorbent for 1 and 24 h. Samples of IONSIV®IE-911 (Lot no. 999096810003), a granular form of CST obtained from UOP, and hydrous titanium oxide powder (HTIO-FR), obtained from the

Recherche Appliquee Du Nord Company of France, were tested. The distribution ratios and percentages of strontium removed were as follows: 2900 mL/g and 93.4% for 1-h IONSIV®IE-911 tests, 2400 mL/g and 92.2% for the 24-h IONSIV®IE-911 tests, 2600 mL/g and 92.6% for 1-h HTIO-FR powder tests, and 4300 mL/g and 95.4% for the 24-h HTIO-FR powder tests.

Batch sorption tests were also conducted using composite microspheres that had been heated for 24 h at 110°C. As in previous batch tests, the microspheres were soaked in deionized water for about 72 h prior to testing with the same simulated supernatant and procedure previously described. The strontium distribution ratios ranged from 12,200 to 17,300 mL/g, corresponding to 98.3 to 98.8% strontium removal, values that are comparable to the 98.3% removal by the granular sodium titanate.

Samples of sodium titanate microspheres that were made by J. Motl, a former guest scientist and professor from Czech Technical University of the Czech Republic, were also tested. As a proof-of-principle experiment, Dr. Motl employed an alkoxide conversion method described in a paper by O. J. Heinonen et al. ("Sorption of Strontium (II) and Radio Strontium Ions on Sodium Titanate," *Radiochim. Acta* 28, 93-96, 1981) to convert hydrous titanium oxide microspherical gel spheres made by the HMTA internal gelation process to sodium titanate microspheres. Analyses of the converted microspheres showed that the composition was ~70% tetrasodium nonatitanate. This work provided the initial indication that this type of conversion process can be optimized to produce a very effective sodium titanate microspherical sorbent of good strength with a low tendency for surface erosion. The results from earlier unreported batch test sorption data in which these microspheres were tested for removal of strontium from MVST W-29 supernatant containing 1.5 ppm strontium looked promising, with strontium distribution ratios up to 10,400 mL/g (98.0% removal). Using the MVST W-29 simulant (1 ppm strontium) that is being used to test the composite microspheres, the strontium distribution ratios for 1- and 24-h tests were 2400 and 5600 mL/g (92.3 and 96.4% removal).

Efforts were continued to try to find an immiscible organic medium to use as a replacement for silicone oil for the HMTA internal gelation process that is employed in this program to prepare microspheres. The focus of the search is binary mixtures. The silicone oil that is currently used works well, but its use requires additional washing of the microspheres with a more volatile organic solvent such as trichloroethylene to remove the oil prior to washing them with ammonium hydroxide solutions. A mixture of perchloroethylene and isoamyl alcohol appears to be a good substitute, but additional tests are needed. Some of the factors that are important include density of the solvent;

effect on maximum gelation temperature, settling rate, heat transfer rate, drop diameter, etc.; flammability; and ease of removal by draining or volatilizing.

A task summary, "Development and Testing of Spheroidal Inorganic Sorbents," was prepared for the ESP Technical Exchange Meeting proceedings document. A letter report with the same title was distributed.

1.5 SLUDGE TREATMENT STUDIES (E. C. Beahm, S. A. Bush, C. F. Weber, T. A. Dillow, and R. D. Hunt)

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Summary: Enhanced Sludge Washing tests were conducted with sludge from Hanford tanks C-105, C-107, C-108, and SX-113, and the filtered process solutions were examined for solids formation. Solids were found in the filtered process solutions from each of these sludges. Acidic treatment of sludge from Hanford underground storage tank B-202 was carried out. There was some indication of solids formation in all of the leachates after filtration.

1.5.1 Purpose and Scope

A particular objective of sludge treatment studies is to obtain a low-volume high-activity waste stream and a high-volume low-activity waste stream. Two aspects of sludge treatment should be well delineated and predictable: (1) the distribution of chemical species between aqueous solutions and solids and (2) potential problems due to chemical interactions that could result in process difficulties or safety concerns.

1.5.2 Progress

1.5.2.1 Enhanced Sludge Washing

The formation of solids in Enhanced Sludge Washing can occur when the temperature of a leachate or wash solution is decreased or when a caustic solution is diluted by washing with inhibited water. The formation of solids in filtered process solutions can lead to difficulties in pumping and separations, and it may result in depositions on equipment surfaces.

Sludge samples from Hanford underground storage tanks C-104 and B-202 were separately treated with 3.4 M sodium hydroxide and then washed three times with inhibited water. The ratio of the volume of sodium hydroxide to mass of sludge was 10 mL/g based on the initial sludge mass. The tests were conducted at approximately 75°C throughout all operations, including mixing and

filtration. After the tests were completed, the leachates and wash solutions were allowed to cool to ambient temperature.

Less than one day after the sludge samples from tanks C-104 and B-202 were treated, the formation of solids in filtered leachates and wash solutions was observed. In most solutions, fine particulate solids formed within a few hours after cooling to ambient temperature. In one case, with the first wash after leaching of C-104 sludge, a material resembling egg whites suspended in water was seen. The solids will be analyzed after turbidity measurements, and observation indicates that additional solids are no longer forming.

Enhanced Sludge Washing of sludge from Hanford tanks C-108 and SX-113 resulted in the formation of solids in the leachates. These sludges were leached with 3 *M* sodium hydroxide and washed three times with inhibited water. The leachate from the C-108 test developed a gel-like mass. Analysis of this material using scanning electron microscopy and energy-dispersive X rays (SEM-EDX) showed that the mass contained sodium and phosphorus. This is similar to the material previously identified in leachates from T-104 sludge tests.

The filtered leachates from the SX-113 test produced a significant amount of particulate material. Analysis by SEM-EDX showed that this material contained sodium and silicon. This could be any of a group of sodium silicates that exist in the sodium hydroxide-silica-water system. It was clear from the analysis that most of the particulates in the SX-113 leachate contained sodium and silicon. However, there were a small number of particles that contained uranium.

1.5.2.2 Acid Treatment

Acidic treatment of Hanford underground storage tank B-202 sludge with nitric acid resulted in the formation of solids in filtered leachates and wash solutions. Analyses of these solids revealed that a gel material contained silica along with some potassium, calcium, iron, and manganese. It is known that metals such as calcium can enhance the formation of silica gel; therefore, this result is not surprising. Two phases were embedded in the gel. One was barium sulfate. The other could not be identified; however, the only metal that it contained was bismuth. In addition, particles of a reddish precipitate separate from the gel were found to contain bismuth and chromium as the only metals.

2. REACTOR FUEL CHEMISTRY

E. C. Beahm

TECHNICAL ASSISTANCE IN REVIEW OF ADVANCED REACTORS (E. C. Beahm and C. F. Weber)

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Summary: The distribution of iodine in containment during an AP600 design-basis accident was evaluated using models in the "TRENDS" code. The AP600 3BE accident sequence calculations showed that $\text{pH} > 7$ was maintained for at least 30 d and that most of the iodine was in the form of iodide.

2.1 PURPOSE AND SCOPE

The objective of this project is to provide assistance to the U.S. Nuclear Regulatory Commission staff in reviewing the four advanced reactor designs submitted under 10 CFR Part 52. This work specifically addresses the following issues: (1) the distribution of iodine species in containment following a loss-of-coolant accident, (2) the generation of HCl and HNO_3 by irradiation and heating in containment, (3) the formation of elemental iodine in containment water that has both chloride and iodide ions, and (4) the evaluation of pH levels in containment water.

2.2 PROGRESS

The distribution of iodine in containment during an AP600 design-basis accident was evaluated using models in the "TRENDS" code. The AP600 3BE accident sequence calculations showed that $\text{pH} > 7$ was maintained for at least 30 d. Because the pH was maintained above 7, most of the iodine was in the form of iodide. Only $3 \times 10^{-3} \%$ was aqueous iodine, and only $1 \times 10^{-6} \%$ was iodine in the vapor phase.

3. THERMODYNAMICS

E. C. Beahm

THERMODYNAMICS AND KINETICS OF ENERGY-RELATED MATERIALS (E. C. Beahm and R. D. Hunt)

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Summary: A manuscript entitled "Magnetic Dynamics in Underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$: Direct Observations of a Superconducting Gap" was accepted for publication by *Physical Review Letters*. In addition, work on the two-year collaboration with Dr. Gennady Voronin, of Moscow State University, continued. The goal of this joint effort is to determine the solidification conditions of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Y123), $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y124), $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15+y}$ (Y247), and other related compounds from the melt of yttrium, barium, and copper oxides. These conditions include temperature, pressure, p_{Oxygen} , the chemical composition of the melt, and the phase and chemical compositions of the growing solids. DTA/TGA and hydrogen reduction have been used to determine the oxygen contents of melts from phase-pure Y123 at partial oxygen pressures ranging from 0.1 to 0.000006 MPa.

3.1 PURPOSE AND SCOPE

The objectives of this program are the measurement and interpretation of chemical thermodynamics in applied-technology ceramic systems. Presently, this project is concerned with phase equilibria and thermodynamics of the R-Ba-Ca-Cu-O system, where R represents Y, La, Pr, and Nd. Emphasis is being placed on the phase fields that include the superconducting compounds.

3.2 PROGRESS

A manuscript, "Magnetic Dynamics in Underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$: Direct Observation of a Superconducting Gap," by P. Dai, M. Yethiraj, H. A. Mook, T. B. Lindemer, and F. Dogan, was accepted for publication by *Physical Review Letters*.

Experimental work on the two-year collaboration with Dr. Gennady Voronin, of Moscow State University, continued. The goal of this joint effort is to determine the solidification conditions of the Y123, $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y124), $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15+y}$ (Y247), and other related compounds from the melt of yttrium, barium, and copper oxides. These conditions include temperature, pressure, p_{Oxygen} , chemical composition of the melt, and phase and chemical composition of the growing solids. The liquidus and solidus surfaces in the four-component yttrium-barium-copper-oxygen (YBCO) system will be determined in terms of temperature, composition, and oxygen chemical potential. In addition,

all co-nodes in the heterogeneous areas of the phase diagram and the metastable states of the system will be evaluated.

Our approach is different from that used in the early studies on the solidification of the YBCO liquid solution since our work focuses on the thermodynamic properties of the YBCO system. The crystallization conditions of the phases from the melt are calculated based on the experimental results, and thermodynamic properties of the liquid and solid phases can then be determined. Therefore, the task includes three consecutive steps.

1. Thermodynamic properties of the YBCO melts will be experimentally determined with the selected compositions at temperatures from 1200 to 1500 K and partial oxygen pressures from 0.1 to 0.000006 MPa.
2. A thermodynamic model of the YBCO liquid solution will be developed. The description of its thermodynamic properties by analytical function will permit both interpolation and extrapolation of thermodynamic properties.
3. Thermodynamic calculations of the crystallization conditions of both stable and metastable phases will be made.

Earlier attempts to address this problem through steps 2 and 3 have failed due to the lack of experimental values for the thermodynamic functions of the four-component YBCO melts.

The hydrogen reduction procedures for the initial samples and the melts have been established after a series of tests. Six-gram samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ were prepared in the vacuum TGA, and the oxygen content was determined through hydrogen reductions at 925°C. Melts of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ samples have been prepared at different temperatures under partial oxygen pressures of 0.1, 0.01, 0.001, 0.0001, and 0.00006 MPa. After the melts have been allowed to equilibrate overnight, they are reduced with hydrogen. The DTA/TGA is then purged with nitrogen so the final weight loss due to the hydrogen reduction can be determined. It is assumed that the melt was reduced to Y_2O_3 , BaO, and copper and that the high-purity alumina sample holders did interact with the melts. Efforts are under way to determine the contributions from the sample holder.

4. PROCESSES FOR WASTE MANAGEMENT

4.1 ION-EXCHANGE PROCESS FOR HEAVY METALS REMOVAL (J. C. Rudolph)

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Summary: This project is the demonstration of a pilot-scale ion-exchange system to remove heavy metals from multiple sites (originally just from an acid mine site) using the most effective commercially available sorbent based on laboratory screening experiments. This system will operate alongside three novel treatment systems and serve as baseline technology. This project is run by the National Institute of Environmental Renewal. The ion-exchange system consists of a filter system to remove suspended solids followed by two 4-in.-diam by 5-ft-long ion-exchange columns in series to remove the metal-ion contaminants. The exiting water is periodically sampled and analyzed for breakthrough. The system is designed to flow up to 2.2 L/min of contaminated water and is also set up for regeneration and precipitation of the regenerant. The entire system is controlled by a programmable logic controller that is operated by a modem and located in a trailer.

In the past quarter, the demonstration of the ion-exchange process at Tobyhanna Army Depot was completed. The operation of the ion-exchange system was intermittent due to three operational problems; however, the system was still able to process 17,000 L, or 1130 CV, of wastewater without breakthrough. The columns were regenerated, and the sludge was disposed of. Samples of the sludge and supernatant from the regeneration were taken for later analysis. The system is packed and ready for transportation back to ORNL.

4.1.1 Purpose and Scope

The scope of this project has been modified. The original scope was to demonstrate the ability of a pilot-scale ion-exchange system to remove heavy metals from an acid mine drainage site. An initial screening of materials was to be performed to choose the most effective sorbent. This process would then serve as a baseline to compare the abilities of three new innovative technologies to treat the same stream. The project is now investigating heavy metals contamination at multiple sites, none of which are mine drainage sites. This expands the scope since each stream must be treated separately for the purpose of screening tests.

4.1.2 Progress

When the ion-exchange system was being set up at the Tobyhanna site, we learned that we were not going to be able to tap into the waste stream before the pH adjustment step was performed at the already existing waste treatment plant. This situation posed two major difficulties for the demonstration. The first is that the pH adjustment caused most of the metals to come out of solution, which meant that the majority of the heavy metals would be trapped by our filter system and very

little of the metal removal capacity of the ion-exchange system would be demonstrated. It also greatly increased the suspended solids content of the waste stream, which would cause the filters to plug very quickly. For this reason, the pH adjustment tank was added to the system. Its purpose was to lower the pH to 5 in an attempt to redissolve as much of the solids, especially the toxic metals, as possible.

The demonstration at Tobyhanna Army Depot was completed in the middle of November 1997. Unfortunately, however, the operation at Tobyhanna was on an intermittent basis due to several mechanical difficulties caused by the on-site conditions previously described. There were three primary problems: difficulty with pH measurement in the adjustment tank due to electrical current entering the tank through the mixer shaft (a problem that was fixed by the end of July); persistent clogging of the sump pump used to feed the pH adjustment tank; and clogging of cartridge filters, caused by the extremely high solids content of the waste stream. As a result, throughout the 16-week-long demonstration (1664 h of possible run time), only 17,000 L of wastewater at an operational flow rate of 1 L/min was processed (283 h of run time), which is equivalent to 83% downtime. Further loading could not be performed because winter temperatures made operation impossible.

Prior to shutdown, the columns were regenerated, and the eluant from each column was collected separately. The acid used for regeneration was 2 M HCl and the base used was 2 M NaOH. The columns were regenerated by first using 3 CV of acid, then 2 CV of water, then 3 CV of base, and finally 3 CV of water. The eluant stream was then adjusted to a pH of 10 to precipitate the metal hydroxides. Column 1 was regenerated in place using a programmed cycle; however, due to system damage caused by freezing conditions, Column 2 had to be regenerated in batches. Equivalent amounts of acid base and water were used, but the regeneration was performed in batches. Samples of the sludge and supernatant from each column eluant were taken for analysis. The supernatant was discharged back to the plant's process treatment system, and the sludge went to the plant's sludge disposal.

A final weight of the sludge was supposed to be obtained by personnel at the army base prior to sludge disposal. However, the sludge was disposed of without these measurements being made. This clearly causes large errors in final material balances, since the amount of sludge has to be estimated from approximate volumes and densities. It was also discovered that what was believed to be nickel breakthrough was actually silicon. Without heavy metals breakthrough, an overall capacity of the resin for the waste stream cannot be calculated. However, conservative estimates can

be made using the amount of metals that had already been loaded on the columns. A final report on the demonstration will be issued by the end of May 1997.

4.2 SEARCH FOR TECHNETIUM IN NATURAL METALLURGICAL RESIDUES (A. J. Mattus, G. W. Parker,^{*} G. D. DelCul,[†] Y. Kamyshkov,[‡] Y. Efremenko[§])

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Summary: Work is in progress to search for naturally occurring technetium isotopes at a depth of 2000 m below the earth in tin minerals, where they are theorized to be forming from solar radiation at the proper energy. If successful, this work may resolve a modern-day physics question regarding a long debate over baryon instability.

4.2.1 Purpose and Scope

This multidivisional and university Seed Money project is directed at establishing the feasibility of a joint DOE and mining industry project to prove the existence of $^{97,98,99}\text{Tc}$ in tin minerals at a great depth below the earth. Normally, such isotopes originate only from above-ground nuclear tests reactors or fission of some uranium isotopes in the earth by solar radiation. This work is a supplement to well-funded, ongoing international efforts in the physics community to prove nucleon instability by experimental observation of baryon instability and remains among the most essential problems of modern-day physics. It is theorized and shown by calculation that cosmic energy as muons or neutrinos may cause natural isotopes of tin to form a distribution of technetium isotopes in sufficiently deep mines where the energy is properly attenuated. Ideally, at 2000 m below the earth in tin mines, multiton quantities of tin ore (cassiterite) would be recovered and carefully concentrated, roasted, and smelted, avoiding surface contamination that produces an ash residue. It is thought that the technetium, as well as any rhenium present, will deposit in the resulting ash. The ash, once washed with water, would be concentrated and the technetium present analyzed by laser

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photo ionization spectrometers from the concentrated aqueous solution. A lower analytical detection limit of 10^6 atoms of technetium will be necessary to establish the presence of technetium isotopes.

4.2.2 Progress

Considerable effort was spent this quarter contacting mining operations around the globe that are still recovering tin. The market price of this metal is very low, and many mining companies have stopped recovering it, especially when the grade is low. The U.S. Geological Survey in Denver aided us in locating mines that are known to be approximately 2000 m deep. (Many of the world's mines are shallow, and many dredge from rivers and mountainsides.) The search has found a few prospects in Australia and one good prospect in Sudbury, Ontario, at the Kidd Creek Mine that is deeper than 2000 m.

The Kidd Creek Mine has stopped mining tin because their grade is low and the market price is very low. Some flotation equipment, used to make a concentrate from the crushed ore, was even removed for the company concentrates on the recovery of Zn, Cu, Ag, Pb, and some Au. Kidd personnel have tentatively said they will aid us in costing a flotation circuit and associated costs of working with the DOE to remove and concentrate 100,000 tonnes for our use. Such an ambitious project will be costed and submitted in our year-end report.

A second aspect of this project has been to extract technetium from small samples of tin that were irradiated at the Stanford Linear Accelerator Center facility in California to produce a distribution of technetium isotopes. The energy imparted to the tin was approximately what might be expected at depth in a deep tin mine. A series of laboratory experiments is currently being planned to recover all the technetium in the tin, which is estimated to be 10^{10} atoms. The recovered technetium will be electroplated onto a platinum cathode, over a 1-mm-diam circle. This cathode will be analyzed by Atom Sciences, Inc., of Oak Ridge using a laser photoionization time-of-flight mass spectrometry to determine the distribution of the various technetium isotopes and the total technetium mass. These data are expected to yield a technetium distribution with the isotopic distribution skewed toward a larger amount of ^{99}Tc , a ratio expected 2000 m below the earth.

The tin samples will be melted in a tube furnace, and high-purity oxygen and argon will pass over the molten tin inside a quartz tube. The metal in quartz boats will be oxidized to tin oxide, and the technetium will be made to sublime at temperatures above 850°C as Tc_2O_7 and will be captured in an alkaline solution outside the furnace. This solution will then be used to plate the technetium

as TcO_2 hydrate onto the platinum cathode between 3 and 6 V and at approximately 300 mA/cm² cathode current density at room temperature.

4.3 WASTE FORM DEVELOPMENT AND TESTING OF A GLASS- AND CEMENT-BASED DEDICATED HOT-CELL FACILITY (A. J. Mattus, and R. D. Spence*)

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Summary: A dedicated hot-cell facility at ORNL has been modified and equipped to produce glass- and cement-based waste forms for comparative, waste form performance testing. The test work will employ actual transuranic waste and surrogate waste representing typical sludge from the ORNL MVSTs.

4.3.1 Purpose and Scope

This task is part of a joint effort with the Savannah River Technology Center and the Engineering Development Section of the Chemical Technology Division to evaluate the tailored grout and glass formulas using actual radioactive waste sludges. The initial sludge sample for testing is from MVST W-25. The work will be performed in a dedicated hot cell where equipment is available for making a borosilicate-based glass and a cement-based grout from both the surrogate and actual radioactive sludge. Testing will include the Product Consistency Test for glass-forming elements and select radioelements as well as the TCLP test for the cement-based grout. Grout testing will also include the unconfined compressive strength as well as an investigation of potential bleed-water problems during the curing stage. Data from the comparisons of test results from both the surrogate and actual average waste sludge will be used as a benchmark of potential performance to gage private-sector proposals and data as well as prove the viability of using a surrogate to represent the typical tank sludge. This will also provide support to future requests for proposals by DOE to the private sector to immobilize transuranic sludges in the MVSTs.

4.3.2 Progress

Sludge from MVST W-25 was chosen for the initial series of tests. Samples of W-25 sludge have been analyzed, and a surrogate waste has been prepared. Sufficient quantities of the actual sludge are currently available for use in this test work, thus avoiding the need for additional sampling. Most

*ORNL Chemical Technology Division, Engineering Development Section.

of the effort on this project this quarter has centered around formulation of a surrogate waste based on analytical data on W-25 transuranic sludge. The surrogate was also tested using a dry solid formula composed of portland cement, perlite, fly ash, blast-furnace slag, and Indian Red Pottery clay. A number of tests with various ratios of sludge to dry blend were investigated to observe the leachability by the TCLP test, unconfined compressive strength, bleed-water formation, and fluidity of the wet sludge. After this series of tests were performed, a final mix ratio was established for in-cell work. Concurrently, the Savannah River Laboratory is formulating and testing a borosilicate-based glass developed at Oak Ridge for this waste sludge.

A hot cell in Building 4501 is being decontaminated for dedicated use for producing glasses and cement-based grouts to support the various tests with final products. A number of special tools and other equipment were built to allow performance of the complex in-cell tasks associated with this project. Work with surrogate waste representing W-25 sludge is expected to commence in mid-April. Initial work will center on forming the cement-based waste forms with the surrogate and the actual waste. Later in the year, following tests currently in progress at Savannah River to confirm that our glass formulation will perform as expected, work will be conducted on forming a borosilicate glass from the surrogate and actual waste.

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