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**Quarterly Progress Report for the
Chemical Development Section of the
Chemical Technology Division:
July–September 1996**

R. T. Jubin

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Chemical Technology Division

QUARTERLY PROGRESS REPORT FOR THE
CHEMICAL DEVELOPMENT SECTION OF THE
CHEMICAL TECHNOLOGY DIVISION:
JULY-SEPTEMBER 1996

R. T. Jubin

Date Published-March 1997

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 July–September 1996. The report describes 12 tasks conducted in 4 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, Studies on Treatment of Dissolved MVST Sludge Using TRUEX Process, ACT*DE*CONSM Test Program, Hot Demonstration of Proposed Commercial Nuclide Removal Technology, Sludge Treatment Studies, and Development and Testing of Inorganic Sorbents.

As part of the Comprehensive Supernate Treatment task, a small-column test using Eichrom ABEC-5000-XL anion-exchange resin to remove pertechnetate from ORNL Melton Valley Storage Tank (MVST) W-27 supernatant was completed. Samples from the test were analyzed for technetium using inductively coupled plasma–mass spectroscopy. Additional batch tests were made to determine the effects of sorbent pretreatment and analytical procedures on the results. Preparations are under way for conducting column chromatographic tests to remove strontium from an ORNL MVST supernatant.

Caustic dissolution tests on surrogate Hanford sludges, as well as hot-cell tests to measure the dissolution behavior of ORNL MVST W-25 sludge at different temperatures and NaOH concentrations, were completed as part of the Partitioning of Sludge Components by Caustic Leaching task. Chemical analyses of residues, leachates, and rinses from the caustic leach tests on sludge samples from Hanford tanks S-104 and SX-113 were performed. The samples were leached with 6.33 M NaOH at 70°C for 21 h. The higher NaOH concentration (6.33 M compared with 3.99 M) increased the aluminum removal from the S-104 sludge slightly, from 21 to 27%. At the higher NaOH concentration, 51% of the aluminum was removed from the SX-113 sludge. Two additional caustic leaching tests on sludges from Hanford tanks C-105 and C-107 were initiated. The samples were leached with 6.33 M NaOH at 70°C for 22 h. Chemical analyses have not been completed.

Efforts in the Studies on Treatment of Dissolved MVST Sludge Using TRUEX Process task have been discontinued. A paper entitled “Thermodynamics of Extraction Equilibria Between OφD(iB)CMPO–*n*-Dodecane and Aqueous Nitric Acid Media. I. Nitric Acid” was completed and accepted for publication in *AIChE Journal*.

Work on the ACT*DE*CONSM Test Program task, which included development of a sludge-processing flow sheet and publication of an ORNL/TM report, has been completed.

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 test 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 used to test the materials in columns or modules using the same batch of supernatant so that they can all be compared on the same basis. During the last quarter, UOP's IE-911 crystalline silicotitanate and the resorcinol/formaldehyde (RF) resins (from AEA Technologies, United Kingdom) were tested. The RF resin was tested at a feed concentration of 5.0 M sodium, 0.1 M hydroxide, and 1×10^{-5} M cesium. The Electrochemical Ion-Exchange test rig developed by AEA Technologies was received, installed into the hot-cell system, and tested using the MVST W-27 feed (the same material used in most of the previous tests).

Within the Sludge Treatment Studies task, Enhanced Sludge Washing tests have been conducted with sludge from Hanford tanks C-105, C-107, C-108, and SX-113, and the filtered process solutions were examined for solid formation. Solids formed in 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 solid formation in all of the leachates after filtration.

Several composite microspheres containing sodium titanate embedded in hydrous titanium oxide were prepared using the internal gelation process as part of the Development and Testing of Inorganic Sorbents task. Batch tests are under way to measure the effectiveness of these sorbents for removing strontium from simulated waste tank supernatants. Several types of composite microspheres containing sodium titanate embedded in hydrous titanium oxide were tested to measure the effectiveness of these sorbents for removing strontium from simulated waste tank supernatants. The strontium distribution ratios ranged from 3500 mL/g (95% removal) to 137,000 mL/g (99.9% removal). Composite microspheres containing sodium titanate embedded in hydrous titanium oxide were tested to measure the effectiveness of these sorbents in removing strontium from simulated waste tank supernatants. The strontium distribution ratios ranged from 2000 mL/g (90% removal) to 136,000 mL/g (99.8% removal).

Within the *second research area—Reactor Fuel Chemistry*—a new scope of work for the Technical Assistance in Review of Advanced Reactors task has been established to include assessments of iodine behavior and pH control in operating nuclear reactor containments as well as

in advanced reactor systems. This task is on hold, awaiting receipt of the necessary information from Westinghouse to permit the start of the study.

Within the *third research area—Thermodynamics*—efforts continued in the Thermodynamics and Kinetics of Energy-Related Materials task. Manuscripts entitled “Nonstoichiometry and Decomposition of $\text{Pr}_{1+z}\text{Ba}_{2-z}\text{Cu}_3\text{O}_y$ and Comparison with Y123, La123, and Nd123” and “Oxygen Equilibration and Chemical Diffusion in Massive $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ” prepared by T. B. Lindemer prior to his retirement, were accepted for publication by *Physica C*. In addition, a two-year collaboration with Dr. Gennady Voronin of Moscow State University was initiated. The goal of this joint effort is to determine the solidification conditions of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (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} ; chemical composition of the melt; and phase and chemical composition of the growing solids. Differential thermal analysis/thermogravimetric analysis and hydrogen reduction are being used to determine the oxygen contents of melts from phase-pure Y123 at partial oxygen pressures ranging from 0.1 to 0.00001 MPa.

The *fourth major research area—Processes for Waste Management*—includes work on these tasks: Ion-Exchange Process for Heavy Metals Removal, Hot Cell Cross-Flow Filtration Studies of Gunit Tank Sludges, and Chemical Conversion of Nitrate Directly to Nitrogen Gas: A Feasibility Study.

The first of these tasks—Ion-Exchange Process for Heavy Metals Removal—involves the use of a transportable pilot-scale ion-exchange system to remove heavy metals from multiple sites using the most effective commercially available sorbent based on laboratory screening experiments. (This work is an extension of the Acid Mine Drainage Treatment Project.) The system will operate alongside three novel treatment systems and serve as baseline technology. The project is being run by the National Institute of Environmental Renewal. During the past quarter, the demonstration of the ion-exchange process at Tobyhanna Army Depot was initiated. There were two major unexpected difficulties with the waste stream used for the demonstration: (1) the waste stream had a very high suspended solids content, and (2) a significant fraction of the heavy metals was in the suspended solids. Despite these difficulties, the demonstration is under way and will continue into November.

The mobilization of Gunit tank sludges and future MVST sludges requires reliable filtration as a first step in volume reduction. In the Hot Cell Cross-Flow Filtration Studies of Gunit Tank Sludges task, a small cross-flow filter was evaluated for this application using the Cell Unit Facility (CUF) unit with actual tank sludges in a hot cell. The CUF is a bench-scale apparatus fabricated at Savannah River. After several minor modifications, the unit worked well. Cross-flow filtration tests

of all Gunitite and associated tanks composites and sludge from MVST W-25 were completed and generally showed that cross-flow filtration is well suited to the dewatering of such sludges. All work with the CUF has been completed, and the unit is in the process of being decontaminated for storage and eventual disposal. Settling tests of the sludges in process water, and in one case 4 M NaNO₃ solution, revealed that the MVST sludge might present filtration problems, judging from the amount of suspended fines observed.

As part of the final task within this area—Chemical Conversion of Nitrate Directly to Nitrogen Gas—a bench-top feasibility study to prove the viability of converting the nitrate anion directly to nitrogen from a near-neutral solution using aluminum metal in the presence of a minimal amount of mercury has been partially successful. While it is believed that nitrogen was produced, it is also believed that an undesirable rise in pH, due to the formation of some amount of hydrogen, resulted in a cessation of nitrogen production in one test.

1. CHEMICAL PROCESSES FOR WASTE MANAGEMENT

B. Z. Egan

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

Contact: B. Zane Egan
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Summary: A small-column test using Eichrom ABEC-5000-XL anion-exchange resin to remove pertechnetate from Oak Ridge National Laboratory (ORNL) Melton Valley Storage Tank (MVST) W-27 supernatant was completed. Samples from the test were analyzed for technetium using inductively coupled plasma-mass spectroscopy (ICP-MS). Additional batch tests were made to determine the effects of sorbent pretreatment and analytical procedures on the results. Preparations are under way for conducting column chromatographic tests to remove strontium from an ORNL MVST supernatant. A draft letter report summarizing the results for the past year was prepared.

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 for recovering the radionuclides from the sorbents will be evaluated.

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

1.1.2 Progress

Fractions derived from a small-column test using Eichrom ABEC-5000-XL resin to measure the removal of pertechnetate from ORNL MVST W-27 supernatant were analyzed by ICP-MS. MVST supernatant from tank W-27 had been processed previously to remove most of the cesium, and the remaining cesium was removed by further batch treatments with crystalline silicotitanate and potassium cobalt hexacyanoferrate. The resulting supernatant was then filtered through a 0.2- μ m filter. Because of the relatively low technetium content of the supernatant (0.43 mg/L), 65 μ Ci of ^{99}Tc was added to 2 L of the treated supernatant to adjust the concentration to 3.0 mg/L. The glass column had an inside diameter of 1.45 cm. The resin, slurried in water, was added to give a bed

height of 10.5 cm. The resin was washed with 4 M NaOH, and a simulated feed solution was added to the column. Once the treated MVST W-27 supernatant was added to the resin bed, the final bed height was 6.2 cm. Results from analysis of the eluate fractions indicated that the resin did not remove appreciable amounts of the pertechnetate. Column breakthrough occurred at less than 5 column volumes, which was much earlier than expected based on previous batch tests with a similar supernatant solution. Consequently, additional batch tests were conducted to determine whether the differences were due to pretreatment of the sorbent, differences in the supernatants, or analytical procedures.

The resin was pretreated before contact with the MVST supernatant by several methods: (1) washing with a solution containing 4.5 M NaNO₃ and 0.16 M NaOH, (2) washing with the same solution followed by mixing with 4 M NaOH, (3) treating with 4 M NaOH only, and (4) no pretreatment. Also, a sample of the Eichrom resin from a different batch was tested "as received" with no pretreatment. The ratio of supernatant to sorbent was 200 with a contact time of 24 h. Results from these tests showed no significant differences and were inconclusive.

Several tests were also designed to examine whether the counting procedure, particularly the liquid scintillation cocktail, was the limiting factor in the analysis. For these tests the pertechnetate distribution on three sorbents, Purolite A520E, Reillex HPQ, and Eichrom ABEC-5000-XL, was measured. Solutions were analyzed using three different scintillation fluids. Results from these tests were also inconclusive. Reasons for the unexpected behavior of the ABEC-5000-XL are still being investigated.

Preparations are under way to conduct column tests on strontium removal from MVST supernatant. Additional batch tests using Duolite C467, Chelex 100, Amberlite IRC-718, and microspheres synthesized at ORNL will be used to select the best sorbent for column tests. Preparations are under way for the batch and column tests. Elution of the strontium from the sorbents will also be evaluated as appropriate.

In response to a request by Dr. K. Gerdes, information was provided to JoAnne Jackson of SAIC for use in preparation of an Innovative Technology Summary Report. Technical Task Plans for FY 1997 were prepared.

A draft letter report describing the results obtained during FY 1996 was prepared. The report summarized both batch tests and small chromatographic column tests using various sorbents to remove cesium, strontium, and technetium from ORNL MVST supernatant. Sorbents that were

identified from batch tests as being the most effective for removing cesium were further evaluated in a hot cell as part of another Efficient Separations and Processing Crosscutting Program (ESP).

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)

Contact: B. Zane Egan
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Summary: Results from tasks completed in FY1996 were summarized in a draft letter report. Caustic dissolution tests on surrogate Hanford sludges were completed. Hot-cell tests to measure the dissolution behavior of ORNL MVST W-25 sludge at different temperatures and NaOH concentrations were completed.

Chemical analyses of residues, leachates, and rinses from the caustic leach tests on sludge samples from Hanford tanks S-104 and SX-113 were completed. The samples were leached with 6.33 M NaOH at 70°C for 21 h. The higher NaOH concentration (6.33 M compared with 3.99 M) increased the aluminum removal from the S-104 sludge slightly, from 21 to 27%. At the higher NaOH concentration, 51% of the aluminum was removed from the SX-113 sludge.

Two additional caustic leaching tests on sludges from Hanford tanks C-105 and C-107 were initiated. The samples were leached with 6.33 M NaOH at 70°C for 22 h. Chemical analyses have not been completed.

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) for disposal. There is increasing emphasis on removing these materials through "Enhanced Sludge Washing," for example, taking advantage of the solubility 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.

*Robotics and Process Systems Division, ORNL.

**Tennessee Technological University, Cookeville, Tennessee.

1.2.2 Progress

Chemical analyses of the liquid and solid samples derived from the additional caustic leaching tests using samples of Hanford sludge from tanks S-104 and SX-113 were completed. About 1.5 g of each sludge sample was mixed with 15-mL volumes of 6.33 *M* NaOH for 21 h at 70°C. These conditions were chosen to try to increase the removal of aluminum and other nonradioactive components from the sludge.

The leachates and cumulative washes, along with the residues, were analyzed for both radioactive and nonradioactive components. The percentage removal of several components was calculated by comparing the residue analysis with the original sludge analysis. On this basis, increasing the NaOH concentration from 3.99 *M* to 6.33 *M* increased the aluminum removal from 21 to 27% for the S-104 sample. Other components that showed significant removal from the S-104 sludge included Cr (97%), P (49%), Cs (99%), and Pu (34%). Under similar conditions, components removed from the SX-113 sludge included Al (51%), Cr (53%), P (99%), Cs (60%), and Pu (41%).

Material balances for some species, such as silicon and phosphorus, were poor and indicated either difficulty in their analysis or reprecipitation prior to sampling for analysis. For other materials, such as aluminum and chromium, the material balances were better, so the effect of caustic leaching of these components can be described with more confidence. Preliminary results indicated that (1) increasing contact time from 4 to 24 h increased the amount of aluminum removed from the sludge; (2) the leachant-to-sludge ratio, over the range tested, did not significantly affect the removal of metals from the sludge; and (3) increasing the NaOH concentration from 4 *M* to 6 *M* increased the aluminum removal slightly. As expected, different sludges have been shown to react to treatment very differently. For example, under identical conditions the fraction of aluminum leached from SX-113 sludge was twice that leached from S-104 sludge, while twice as much chromium was leached from the S-104 sludge, as from the SX-113 sludge. Additional experiments are planned, and data analysis is continuing. Analytical procedures have been modified in attempts to improve the material balance values.

Two caustic leaching tests were initiated on sludge samples from Hanford tanks C-105 and C-107. Each sludge sample was mixed with about 15-mL volumes of 6.33 *M* NaOH for 21.7 h at 70°C. As before, these conditions were chosen to try to increase the removal of aluminum and other nonradioactive components from the sludge. After the leach step, the residues were rinsed with three 15-mL portions of a solution containing 0.01 *M* NaNO₂ and 0.01 *M* NaOH.

The C-105 sample was a relatively dry material; therefore, a mass of 1.51 g was used. After the leach and rinse, the wet residue weighed 0.53 g. The NaOH concentration in the leachate, determined by titration, was 6.2 M. The leachate contained about 18.5 μCi of cesium per gram, for a total of 357 μCi . The combined rinse solutions contained an additional 10 μCi of cesium.

The C-107 sample was a wet, gooey material. Consequently, a larger mass, 4.37 g, was used for the leach test. The wet residue from the leach weighed 3.67 g. The final NaOH concentration in the leachate from this sample was 5.6 M. The leachate contained 4.74 μCi of cesium per gram, for a total of 88 μCi , while the combined rinse solutions contained an additional 11 μCi of cesium.

Chemical analyses of the leachates and residues have been delayed until FY 1997, when additional funding will become available. Samples of the leachates were provided to the program on Sludge Treatment Studies (Task C) for turbidity and gel-formation studies.

Technical Task Plans for FY 1997 were prepared.

1.3 STUDIES ON TREATMENT OF DISSOLVED MVST SLUDGE USING TRUEX PROCESS (B. B. Spencer* and C. W. Chase)

Contact: Barry B. Spencer
Telephone: (423) 574-7143
Internet: spencerbb@ornl.gov

Summary: Work on this program has been discontinued. A paper entitled "Thermodynamics of Extraction Equilibria Between $\text{O}\phi\text{D}(\text{iB})\text{CMPO}-n\text{-Dodecane}$ and Aqueous Nitric Acid Media. I. Nitric Acid" was completed and accepted for publication in *AIChE Journal*.

1.3.1 Purpose and Scope

The focus of this experimental program is to evaluate the transuranium extraction (TRUEX) solvent extraction process for partitioning actinides from actual HLW sludge dissolved in HNO_3 . A large sludge sample was previously removed from MVST W-25, has been well characterized, and was available for the test program. The experimental phase of the evaluation program included dissolving portions of this sludge in HNO_3 , followed by batch liquid-liquid equilibrium tests of both the extraction and stripping operations. Chemical analyses of both phases are used to evaluate the process. Evaluation is based on two metrics: the fraction of transuranic elements removed from the dissolved sludge, and comparison of the results with predictions made with the Generic TRUEX Model.

*Robotics and Process Systems Division, ORNL.

1.3.2 Progress

Experimental work on this program has been discontinued. A paper entitled "Thermodynamics of Extraction Equilibria Between O ϕ D(iB)CMPO-*n*-Dodecane and Aqueous Nitric Acid Media. I. Nitric Acid" was completed and accepted for publication in *AIChE Journal*.

1.4 ACT*DE*CONSM PROCESS TEST PROGRAM (B. B. Spencer and C. W. Chase)

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Summary: Work on this program has been completed.

1.4.1 Purpose and Scope

The ACT*DE*CONSM process, a proprietary process of Selective Environmental Technologies, Inc. (Selentec), is designed to remove actinides from soils or soil-like media. The process is proposed as an alternative for removal of actinides from tank-stored HLW sludges. The ACT*DE*CONSM solvent is an aqueous carbonate solution containing a chelating agent and an oxidant. This combination of chemicals is rather benign and is intended to leach specific metal species from a soil matrix without destroying the bulk of the soil. The objective of the test program is to evaluate the ACT*DE*CONSM process for pretreating Gunite and associated tanks sludge as part of the sludge-processing flow-sheet development effort.

1.4.2 Progress

Evaluation of the ACT*DE*CONSM process for pretreating ORNL Gunite and associated tanks sludge as part of a sludge-processing flow-sheet development effort was completed. The results were summarized in a report, *Evaluation of the ACT*DE*CONSM Process for Treating Gunite Tank Sludge*, ORNL/TM-13201. No further work is planned.

1.5 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 from supernatants at the various DOE sites. The primary objective is to test 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 used to test the materials in columns or modules using the same batch of supernatant so that they can all be compared on the same basis. During the last quarter, UOP's IE-911 crystalline silicotitanate (CST) and the resorcinol/formaldehyde (RF) resins (from AEA Technologies, United Kingdom) were tested. The RF resin was tested at a feed concentration of 5.0 M sodium, 0.1 M hydroxide, and 1×10^{-5} M cesium. The Electrochemical Ion-Exchange (EIX) test rig developed by AEA Technologies was received, installed into the hot-cell system, and tested using the MVST W-27 feed (the same feed material used in most of the previous tests).

1.5.1 Purpose and Scope

This task involves 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 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. This unit provides a test bed for investigating new technologies that become available during this program and complements the comprehensive supernatant task by using larger engineering-scale, continuous equipment to verify and expand the batch studies. It also complements the Tank Focus Area's (TFA's) Cesium Removal Demonstration (CsRD) at Oak Ridge by providing sorbent-selection information, evaluation and testing of proposed sorbents, and operational experience and characteristics using the sorbent and supernatant to be used in the demonstration.

There is close cooperation with the ESP and the TFA in order ultimately to transfer the technologies being developed to the end user. The TFA requested (through ESP) that ORNL test AEA Technology's electrodialysis/ion-exchange (ED/IX) system as part of this ESP project because ORNL was the only site with sufficient supernatant available for testing the multiple-cycle ED/IX system.

Initial candidate sorbents for cesium removal were the RF resin, CSTs, SuperLig® 644C resin, 3M WWL 644 WEB material with SuperLig® 644 embedded, Rohm & Haas CS-100 resin,

and granular potassium cobalt hexacyanoferrate. The results of these tests will be compared with batch results and small-column tests results obtained in the Comprehensive Supernatant Treatment Task (B. Z. Egan). The results are being used to supply the CsRD (J. F. Walker) with the information to determine the design parameters and sorbent 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.

1.5.2 Progress

Two ion-exchange material tests were completed in Hot Cell C during the fourth quarter of FY1996. The feed supernatant for the tests of RF resin supplied by AEA Technologies was obtained from MVST W-27 in April 1995. Tank W-27 contains supernatant at pH 7.2 and has the lowest potassium and ^{137}Cs levels of the available tanks. This supernatant was adjusted to pH 13.3 ($\sim 0.1\text{ M}$ hydroxide concentration), and runs were completed with total cesium concentration of $1 \times 10^{-5}\text{ M}$. The RF resin was first tested in a standard column and then by using the EIX rig supplied by AEA Technologies. The EIX rig cells were first loaded with cesium from W-27 supernatant and then eluted using the electrochemical elution process developed by AEA. Three loadings were completed using the two separate cells in the rig. Two electrochemical elutions were completed, and one was checked using a standard acid elution.

1.5.2.1 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 to 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 planned operating conditions were as follows: flow rate was 6 column volumes (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 approximately each 50 CV for analytical determinations; the feed supernatant was to be filtered through the 25- μm filter (supplied by the CsRD) before passing through the column; and the column loading would be continued until at least 50% breakthrough of the cesium occurred.

Experimental results

Preparation of the MVST supernatant. The supernatant was obtained on August 8, 1996, by ORNL Waste Operations and CsRD personnel, in three 2-gal polypropylene containers. The container selected for this test, Container No. 2, was sampled for pH and for radioactive cesium content. A portion was also transferred to Building 2026 for chemical and radiological analysis.

The pH of the sample was measured by titration using 0.02 *N* HCl to the phenolphthalein end point (pH 8.2–8.4) followed by titration to the methyl orange end point (pH 4.0–4.3). The hydroxide concentration was determined to be 0.08 *N*, which represents a pH of 12.9. The carbonate content was measured by the amount of acid required to reach the methyl orange end point. This yielded a 0.08 *N* carbonate concentration. There was quite a lot of buffering capacity in the supernatant solution during the titration.

The radioactive cesium was determined using an Aptec intrinsic germanium detector and a Nuclear Data multichannel analyzer system. The cesium content was about 12.3 $\mu\text{Ci/mL}$ of ^{137}Cs and 0.21 $\mu\text{Ci/mL}$ of ^{134}Cs , for a ^{137}Cs -to- ^{134}Cs ratio of 57.

Column preparation. The ion-exchange column was prepared on the day the run was started. The CST was in slurry form and was pipetted directly from the plastic bottle to the column. A total of 6.3 cm of CST was added to the column and tapped to at least a volume of 10.4 mL. The packed bed was then fluidized to remove fines using a simulant containing 4.5 *M* NaNO_3 and 0.1 *N* NaOH. The initial flow was milky and left a lot of fines in the catch bottle. A total of 100 mL of simulant was pumped through the column, and the bed was tapped to the most settled position of 6.3 cm. The level of simulant was lowered to about 1 cm above the bed by allowing the simulant to pass downward through the bed, and the column was secured for transfer to the cell after adding the top tubing connections and clamping the inlet and outlet tubes with pinch clamps. A total of between 0.33 and 0.5 mL of fine solids was collected from the 10.4-mL column bed during washing with the simulant.

Conduct of CST loading. As the feed entered the column and mixed with the simulant present above the bed, some turbidity was noted. This disappeared as the feeding continued over the next several minutes. Also, after about 15 min of feeding, some brown specks could be seen on the top of the bed in the column. No problems were encountered until about 7 h after the feed was started. At this point in the run, the feed pump was not restarted after the flow rate of supernatant through the column was checked; this resulted in the column being drained of liquid. The feed pump was restarted, and the column refilled with supernatant with the column pump off. The column pump

was restarted at its normal rate, but due to pressure drop caused by air in the effluent filter, the pump rate had to be increased slightly to compensate.

Once flow had been completely reestablished through the column, pump, and filter at the desired flow rate (the feed pump was set at the flow rate used before the problem had occurred, and the column pump was adjusted to match it during the air-purging process), attempts were made to remove the bubbles of air that had formed in the bed. This was done by reversing the pump flow momentarily (about 10 s) to try to make the bubbles rise through the bed and leave through the vent. This was done twice and did not fluidize the bed but did discharge several large and small bubbles. After the upset, the settled bed was at 6.4 cm instead of the original 6.3 cm, but the 6.3 level was used for bed volume calculations for the whole run. Several small and very small bubbles remained visible in the bed, but, over the next several hours of feeding, they gradually disappeared, although the bed height did not change. Total flow was off for approximately 30 to 35 min; consequently, this time was subtracted from the elapsed time of the run in the data analysis. The detector was watched carefully for indications of channeling or any other problem, but none was seen. As a result, the run was continued and was completed uneventfully during the next 500 CV.

The loading was shut down by stopping feed to the column, emptying the lines back to the feed tank, and adding 100 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. Following the simulant rinse, the system was rinsed with deionized (DI) water, and the detector counts decreased as expected, going from about 55% breakthrough level to about 5% breakthrough in about 1 h.

Results of loading. The eluant samples from the column were collected and sampled. Samples of the eluant from about every 55 CV, starting at 26 CV, were sent for analyses for both radiochemical and chemical species present. The loading curve for the CST with W-29 is shown in Fig. 1 for the ¹³⁷Cs and other selected materials.

1.5.2.2 AEA Technologies EIX System

The laboratory-scale EIX rig was built at AEA Technologies at Harwell, United Kingdom, and delivered to ORNL, where it was installed into the hot-cell system that had been used to test various ion-exchange materials with actual radioactive liquid waste from the MVSTs. The EIX process uses the electrolysis of water as the electrochemical driving force. Water is oxidized at the anode producing acid and oxygen and is reduced at the cathode yielding base and hydrogen. The

Fig. 1. Loading curves for cesium and other materials from W-29 on CST.

electrogenerated protons produced are used to elute the cesium that has been previously loaded onto an ion-exchange resin.

Experimental operation

The EIX technology replaces the acid-elution step in ion exchange with an electrochemical elution that preliminary studies suggest has the potential to reduce the volume of elution waste by more than 90%, compared with the acid elution. The EIX process also eliminates the use of chemical reagents for elution because the acid needed for elution is produced via the electrolytic dissociation of water. The EIX equipment was installed in place of a cesium-removal module, and the two cells were filled with RF resin. It was intended to be studied over repetitive loading/eluting cycles to obtain information on fouling, improvement in efficiency and volume reduction over conventional acid elution, and to discover any design considerations to accommodate resin swelling or shrinkage.

Three members of the AEA Technologies team that developed the EIX concept and the experimental rig came to ORNL to help commission and operate the equipment for the first series of runs. The system was cold tested for commissioning, and several minor changes were made. These consisted of adding hand valves for controlling flow from the cells to the detector, replacing some tubing with smaller-diameter tubing to reduce dead volume between the bubble traps and the cells and between the cells and the hand valves, and adding quick-connect fittings to tube ends to allow connection to the fill lines to the various tanks in the EIX rig.

When the system was ready to be placed inside the hot cell, RF resin supplied by AEA Technologies from batch BSC-187 was prepared for addition to the two EIX cells on the rig. This resin had been tested in the United Kingdom on simulant and at ORNL on the W-27 supernatant with results showing that it was far superior (5 to 10 times more CV to 50% breakthrough) to the RF resin that had been used in previous tests at ORNL. This resin had been stored at AEA Technologies in a closed bottle on a shelf for several years and just recently was tested when the newer batch proved to have deteriorated significantly in performance. Approximately 9 mL of dry RF resin was prepared by treating with 50 mL of 0.5 *N* HNO₃, which produced a large quantity of gas at first contact. The acid was removed, and another 50 mL of the acid was added, with a slight amount of gas produced this time. The resin was then rinsed with 100 mL of distilled/DI water in 50-mL increments. It was converted to the sodium form by treatment with 25 mL of 1 *N* NaOH and allowed to stand for 10 min before the caustic was removed and another 25 mL added. After 10 min, it was removed and the

resin rinsed with 50 mL of DI water, followed by 100 mL of DI water. Each of the two cells was then filled with 5 mL of resin and secured in preparation for placement in the hot cell.

The EIX rig was placed in the hot cell, and all tubing, electrical connections, and power supply cables were attached and tested. The feed supernatant for the tests was obtained from MVST W-27 in April 1995. Tank W-27 contains supernatant at pH 7.2 and has the lowest potassium and ^{137}Cs levels of the available tanks. The supernatant was adjusted to pH 13.3 (0.11 M hydroxide) using solid NaOH pellets. The feed was filtered through a 0.45- μm filter.

The system was readied for operation by filling Tank B with 250 mL of DI water to check flow through the EIX cells. Water was pumped to the bubble traps of both cells and then allowed to flow through the EIX cells. When water left the cells, color could be seen in the exit tubing. The feed pump was started at a rate of about 6.6 CV/h to load the cell resin with cesium. The feed was allowed to flow for 16 h (about 106 CV). At this point, the cesium breakthrough was about 1–2% as measured by the in-cell detector. Then, the lines were emptied back to the feed tank, and DI water was pumped to the bubble trap to rinse the cell and reduce the conductivity to prepare for the elution.

The electrochemical elution was begun by first filling the catholyte tank with 250 mL of 0.1 M NaOH and the anolyte tank with 250 mL 0.1 N HNO_3 . Next, the solutions were pumped through the cell chambers and tubing at 800 mL/h for the duration of the elution. The power supply was set at 150 mA, which resulted in a voltage of about 20 V when the power was directed to the cell. During the elution, the voltage increased to the maximum setting of 60 V over a 30-min period, and then the current gradually dropped to about 40 mA. After 5 h the elution was discontinued and the lines emptied back to their tanks. The system was then prepared for the loading of cesium onto the resin again by passing 25 mL of 1 M NaOH through the cell resin. This was followed by the next batch of W-27 feed.

When the feed material reached the detector after passing through the resin, the cesium level was higher than before the elution. This suggested that either the resin had developed a channel or it had not been eluted. After finding that the catholyte did not contain the expected amount of cesium when it was analyzed, it was decided to go ahead and load the resin for about 60–70 CV and then try again to electrochemically elute it. The cesium breakthrough after the loading was about 15%.

The second elution was started after the cell had been rinsed with 20 mL of DI water and the catholyte tank filled with 250 mL of fresh 0.1 M NaOH. The elution followed the same course as the first, with the only difference being that the current remained at 150 mA for slightly longer. Again, the elution was carried out for 5 h before stopping. When the catholyte had been emptied and

sampled, it was again found that very little cesium had been eluted. It was also verified that the electrocells were correctly installed.

It was then decided to load Cell 2 with about 45–50 CV of W-27 supernatant and try the elution again, but this time pass the catholyte through the cesium-detection circuit during the elution. The cesium coming off the resin could thus be monitored and the elution continued if cesium began to come off. The elution was run as before, and the current started at 150 mA. During the first 5 h, very small amounts of cesium began to enter the catholyte stream and gradually increased. When the increase was noted, it was determined that the elution should be continued to see if the cesium would eventually be removed. After the first 5 h, a curve of the cesium content in the catholyte versus time began to increase sharply and rose to a level close to what the feed level was projected to be. When the curve flattened out, the elution was stopped and the catholyte pumped back to the catholyte tank and then sampled. As the cell detector indicated, the level of cesium in the catholyte was about 70% of the predicted level for the volumes used. In addition, the bed volume decreased slightly, which would be expected if the resin were converted to the hydrogen form from the sodium form.

In order to check the extent of elution, the bed was next subjected to a normal acid elution by passing 0.5 N HNO₃ through the bed and collecting the effluent for counting. The analysis showed that about 9% of the cesium loaded was recovered during the acid elution and another 89% was recovered during the EIX elution.

Based on the success of the elution of Cell 2, Cell 1 was again set up for elution where it had been left after the previous tries. A total of 92% of the cesium loaded was recovered during the electrochemical elution.

1.6 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 have been run with sludge from Hanford tanks C-105, C-107, C-108, and SX-113, and the filtered process solutions were examined for solid formation. Solids formed in 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 solid formation in all of the leachates after filtration.

1.6.1 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.

1.6.2 Progress

In Enhanced Sludge Washing it is very important to prevent the uncontrolled formation of solids in process solutions. Failure to do so will result in the formation of crystalline solids and gels that are unacceptable because they will (1) prevent mixing; (2) prevent pumping; (3) retard separations; (4) coat surfaces; and (5) clog pipes, equipment, and filters. Tests of Enhanced Sludge Washing of Hanford T-104 sludge, reported previously, demonstrated that solid formation in filtered process solutions takes a variety of forms: very fine particles, larger particulates, solids floating in solution like egg whites, gels, crystals, and coatings on sample containers.

Enhanced Sludge Washing tests have been run on sludge from Hanford tanks C-105, C-107, C-108, and SX-113, and the filtered process solutions were examined for solid formation. The C-108 and SX-113 sludge was leached with 3 M NaOH and washed three times with inhibited water. The temperature throughout the leaching, settling, washing, and filtration was 75°C. The ratio of leachate or wash solution to sludge weight was 10 based on the original mass of sludge. The C-105 and C-107 sludge was leached at 70°C in 6 M NaOH as part of the Sludge Partitioning Chemistry program (3TFA) under B. Z. Egan. After leaching, the sludge residue was washed three times at ambient temperature. In the tests with C-108 and SX-113 sludge, the process solutions were first examined for solids ~ 30 min after filtration. The tests with the material from C-105 and C-107 were run in a hot cell, and there was a 2-d delay before the first examination could be carried out.

Solids formed in filtered process solutions from each of these sludges. With C-105 and C-107 a clear gel-like material formed in the leachates. Wash solutions from the C-105 and C-107 tests also had some clear masses. The leachate from the C-108 test developed a mass of gel-like material as well as some material that appeared to be more crystalline. The wash solutions from the C-108 test developed a small amount of a filmy fibrous material. The filtered leachate from the SX-113 test produced a significant amount of particulate material, which when suspended appeared to be semigelatinous. The wash solutions formed a small amount of filmy material as well as small

clear masses that adhered to the bottom of the sample tubes. At this time, sludge from six Hanford storage tanks has been tested by Enhanced Sludge Washing to evaluate the formation of solids in process solutions. Of these six different sludges, only the material from tank S-104 failed to produce solids in filtered process solutions. Tests with material from tanks T-104, C-105, C-107, C-108, and SX-113 all resulted in formation of solids in leachates and wash solutions.

The aim of both Enhanced Sludge Washing and acid treatment is to obtain a low-volume high-activity waste stream and a high-volume low-activity waste stream. In acid treatment the initial goal is total dissolution of sludge. Subsequent to dissolution, the acidic leachate and wash solutions would be subjected to separations processes such as TRUEX and ion exchange to remove radionuclides.

Acidic treatment of sludge from Hanford underground storage tank B-202 was carried out. This material was selected for testing because it contains a relatively high fraction of transition metals in the sludge solids and because Enhanced Sludge Washing tests run at Pacific Northwest National Laboratory and at Los Alamos National Laboratory showed that only a small fraction of aluminum dissolved in the caustic treatment. Two test sequences were run with the B-202 sludge. In both test sequences the sludge was leached successively with 1 M HNO₃, 3 M HNO₃, and 6 M HNO₃ and then washed three times with water. In one case the entire sequence was carried out at 75°C, and, in the other case, it was performed at ambient temperature. This test plan enabled an evaluation of both acid concentration and temperature on sludge dissolution. The initial sludge looked like a dark shoe polish. The ratio of leachate or wash to sludge weight was 10 based on the original weight of sludge.

In the sequence at 75°C, sludge solids remained after leaching with 1 M HNO₃ and 3 M HNO₃. However, the sludge was completely dissolved by the 6 M HNO₃ step in the sequence. This was not the case in the sequence run at ambient temperature. In that case sludge solids remained at all times. Thus, the temperature difference between 75°C and ambient was the important factor in the complete dissolution of this material.

The leachates and wash solutions were all filtered through 0.45-μm Teflon syringe filters. There was some indication of solid formation in all of the leachates after filtration. This varied from a halo-like deposit on the sample tube in the 1 M HNO₃ leachate from the ambient temperature test to particles settled at the bottom of the 1 M HNO₃ leachate in the 75°C test. Although solid formation occurred in the leachates, the amount of solids was small in comparison to the gel formation that was observed previously in acid treatment of Oak Ridge MVST W-25 sludge.

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

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Summary: Several composite microspheres containing sodium titanate embedded in hydrous titanium oxide were prepared using the internal gelation process. Batch tests are under way to measure the effectiveness of these sorbents for removing strontium from simulated waste tank supernatants.

Several types of composite microspheres containing sodium titanate embedded in hydrous titanium oxide were tested to measure the effectiveness of these sorbents for removing strontium from simulated waste tank supernatants. The strontium distribution ratios ranged from 3500 mL/g (95% removal) to 137,000 mL/g (99.9% removal).

Composite microspheres containing sodium titanate embedded in hydrous titanium oxide were tested to measure the effectiveness of these sorbents in removing strontium from simulated waste tank supernatants. The strontium distribution ratios ranged from 2000 mL/g (90% removal) to 136,000 mL/g (99.8% removal).

1.7.1 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 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 NaOH at elevated temperatures in a sealed reactor vessel. The other method involves an alkoxide conversion of the hydrous titanium oxide microspheres.

1.7.2 Progress

An effort is being made to make more column-usable inorganic ion exchangers for removing strontium from alkaline saline solutions such as the Hanford supernatants. The internal gelation process is being employed to make inorganic ion exchangers as microspheres with controlled sizes. The formulations and procedures for making hydrous titanium oxide and titanium monohydrogen

phosphate microspheres have been developed. Composite microspheres of these materials that contain varying amounts of sodium titanate homogeneously embedded in microspheres of hydrous titanium oxide have been prepared utilizing the internal gelation process.

One goal is to determine the optimum amount of sodium titanate that can be added to maximize the removal of strontium from aqueous waste. To that end, a number of composite hydrous titanium oxide microspheres containing different amounts of sodium titanate powder were prepared. An additional preparation of composite microspheres was also made in which the hydrous titanium oxide matrix material was converted to the titanium monohydrogen phosphate form.

To test the effectiveness of these composite microspheres for removing strontium, batch tests are currently being conducted. A simulated supernatant of the following composition is being used: 3.9 *M* NaNO₃, 1.0 *M* NaOH, 0.14 *M* Na₂CO₃, 0.1 *M* NaCl, 0.25 *M* KNO₃, 0.0001 *M* CaCO₃, and 1 ppm strontium. The strontium was added as SrNO₃ which was traced with ⁸⁵Sr. After the strontium was added, the solution was equilibrated for about 24 h, filtered, and counted. This step was repeated after several days to verify that the strontium remained in solution.

Duplicate batch tests using a supernatant-to-sorbent ratio of 200/1 were conducted with a mixing time of 24 h. Some of the sorbent samples were dried at 110°C before testing. The strontium distribution ratios were 3500 mL/g for the hydrous titanium oxide microspheres and 3600 mL/g for the hydrous titanium phosphate microspheres. When sodium titanate was incorporated into these materials, the strontium distribution ratios increased to 6600 mL/g for hydrous titanium oxide containing 13% sodium titanate and to 137,000 mL/g for hydrous titanium phosphate containing 13% sodium titanate.

Additional batch tests were conducted on both air-dried and wet composite microspheres containing different amounts of sodium titanate. Both types of materials contained 9.2, 13.2, 16.8, 20.2, and 23.3 wt % sodium titanate (dry basis). The strontium distribution ratios ranged from 7000 mL/g (97.1% strontium removal) to 18,100 mL/g (98.9% strontium removal) for the nondried sorbents. The air-dried sorbents gave lower strontium distribution ratios, ranging from 2000 mL/g (90.0% strontium removal) to 5000 mL/g (96.9% strontium removal). In a series of 24-h batch tests with the composite microspheres that were not dried, the average values for the strontium distribution ratios and percentages of strontium removed ranged from 41,000 mL/g (99.5%) to 136,000 mL/g (99.8%). For comparison, an average strontium distribution ratio of 8000 mL/g (95.5% removal) was obtained for 1-h batch tests using granular sodium titanate that was obtained from Allied Signal; in 24-h tests, an average value of 19,000 mL/g (98.9% removal) was obtained. In each batch test using

the Allied Signal granular material, there was some powder erosion. There was no noticeable powder erosion from the composite microspheres.

Additional materials will be prepared and tested. Additional tests are also planned to determine the sorption rate.

In response to a request by Dr. Kurt Gerdes, information was provided to JoAnne Jackson of SAIC for use in preparing an Innovative Technology Summary Report.

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: A new scope of work for this task has been established to include assessments of iodine behavior and pH control in operating nuclear reactor containments as well as in advanced reactor systems. This task remains on hold, awaiting receipt of the necessary information from Westinghouse to permit the start of the study.

2.1 PURPOSE AND SCOPE

The objective of this project is to provide assistance to the U.S. Nuclear Regulatory Commission (NRC) 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 HNO₃ 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

A new statement of work for this project has been received from the NRC. This work will include assessments of iodine behavior and pH control in operating nuclear reactor containments as well as in advanced reactor systems. This task is on hold, awaiting receipt of the necessary information from Westinghouse to permit the start of the study.

3. THERMODYNAMICS

E. C. Beahm

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

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Summary: Manuscripts entitled "Nonstoichiometry and Decomposition of $\text{Pr}_{1+z}\text{Ba}_{2-z}\text{Cu}_3\text{O}_y$ and Comparison with Y123, La123, and Nd123" and "Oxygen Equilibration and Chemical Diffusion in Massive $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$," prepared by T. B. Lindemer prior to his retirement, were accepted for publication by *Physica C*. In addition, a two-year collaboration with Dr. Gennady Voronin of Moscow State University was initiated. The goal of this joint effort is to determine the solidification conditions of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (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} ; chemical composition of the melt; and phase and chemical composition of the growing solids. Differential thermal analysis (DTA)/thermogravimetric analysis (TGA) and hydrogen reduction are being used to determine the oxygen contents of melts from phase-pure Y123 at partial oxygen pressures ranging from 0.1 to 0.00001 MPa.

3.1 PURPOSE AND SCOPE

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

3.2 PROGRESS

Two revised manuscripts on the thermodynamics of the R-Ba-Cu-O system were reviewed and accepted for publication in *Physica C*: "Nonstoichiometry and Decomposition of $\text{Pr}_{1+z}\text{Ba}_{2-z}\text{Cu}_3\text{O}_y$ and Comparison with Y123, La123, and Nd123" by T. B. Lindemer and E. D. Specht and "Oxygen Equilibration and Chemical Diffusion in Massive $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ " by T. B. Lindemer.

A two-year collaboration with Dr. Gennady Voronin of Moscow State University was initiated. 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} ; 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 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 upon the experimental results, and thermodynamic properties of the liquid and solid phases can then be determined. Therefore, the task includes the following 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 0.00001 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. A large sample of $\text{YBa}_2\text{Cu}_3\text{O}_{6.829}$ was prepared in the vacuum TGA, and the oxygen content was determined through hydrogen reductions at 925°C. Melts of $\text{YBa}_2\text{Cu}_3\text{O}_{6.829}$ sample have been prepared at different temperatures under a partial oxygen pressure of 0.1 MPa. After the melts have reached equilibrium, 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. This series of experiments will be repeated at partial oxygen pressures of 0.01, 0.001, 0.0001 and 0.00001 MPa.

4. PROCESSES FOR WASTE MANAGEMENT

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

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Summary: This project provides a transportable pilot-scale ion-exchange system to remove heavy metals from multiple sites using the most effective commercially available sorbent based on laboratory screening experiments. (This work is an extension of the Acid Mine Drainage Treatment Project.) This system will operate alongside three novel treatment systems and serve as baseline technology. The project is being run by the National Institute of Environmental Renewal. In the past quarter the demonstration of the ion-exchange process at Tobyhanna Army Depot was initiated. There were two major unexpected difficulties with the waste stream used for the demonstration. The first problem was that the waste stream had a very high suspended solids content. The second problem was that a significant fraction of the heavy metals was in the suspended solids. Despite these difficulties, the demonstration is under way and will continue into November.

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

Tobyhanna Army Depot was chosen as the first site to demonstrate the heavy metals removal systems. Project staff were given minimal data on the streams, consisting only of heavy metal content. No data on suspended solids content, pH, other competitive ions, organics, or other complexing agents were supplied. From the available data, it appears that the site does have Cd, Cu, Ni, and Zn in the range of 1 to 3 ppm.

The ion-exchange system consists of a filter system to remove suspended solids followed by ion-exchange columns to remove the metal ion constituents. The exiting water will be periodically sampled and analyzed for breakthrough. The system is also set up for regeneration and precipitation of the regenerant. The entire system is controlled by a programmable logic controller, which is

operated by modem. The system is designed to allow up to 2.2 L/min of contaminated water to flow. The entire system is located in a trailer.

As noted last quarter, the demonstration trailer was shipped to the Tobyhanna Army Depot on June 26, 1996. As part of the equipment startup, samples of the inlet stream were obtained for analysis. There were two major unexpected difficulties with the waste stream used for the demonstration. The first problem was that the waste stream had a very high suspended solids content. The second problem was that a significant fraction of the heavy metals was in the suspended solids. An analysis performed by Lehigh University showed that after setting out the suspended solids, the supernatant contained only Cu in significant quantity (500–1000 ppb), while our samples of the inlet with the suspended solids dissolved showed several parts per million of Cd and Zn and several hundred parts per billion of Ni. This meant that a large portion of the contaminants would be removed by the cartridge filters and would not demonstrate the capabilities of the ion-exchange process. To help solve this problem, a surge tank was added to the inlet of our system so that the pH could be lowered to around 5 and some of the suspended solids could be dissolved. This added several days to the system setup. Unfortunately, it also takes away from the purpose of treating a real waste stream, since in reality one would rarely, if ever, attempt to redissolve heavy metals in a waste stream.

After setup was completed in mid-July, the demonstration began. Operation was intermittent at first because of difficulties with the pH adjustment tank, which we were not able to fully test because of the hurried installation. Even with the pH adjustment tank, there was still a high concentration of suspended solids in the waste stream. This caused us to change the cartridge filters frequently. Approximately 12,000 L of wastewater has been processed to date. The only metal that appears to be breaking through is nickel. It has reached an outlet concentration of approximately 0.7 ppm.

The demonstration will continue to run into November with further samples being taken. The system will be regenerated, and mass balances will be calculated to determine the overall efficiency of the resin.

4.2 HOT CELL CROSS-FLOW FILTRATION STUDIES OF GUNITE TANK SLUDGES (A. J. Mattus)

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Summary: The mobilization of Gunite tank sludges and future MVST sludges requires reliable filtration as a first step in volume reduction. A small cross-flow filter was evaluated for this application using the Cell Unit Facility (CUF) unit with actual tank sludges in a hot cell. The CUF is a bench-scale apparatus fabricated at Savannah River. After several minor modifications, the unit worked well. Cross-flow filtration tests of all Gunite and associated tanks composites and sludge from MVST tank W-25 were completed and generally showed that cross-flow filtration is well suited to the dewatering of such sludges. All work with the CUF has been completed, and the unit is in the process of being decontaminated for storage and eventual disposal.

Settling tests of the sludges in process water, and in one case 4 M NaNO₃ solution, revealed that the MVST sludge might present filtration problems, judging from the amount of suspended fines observed.

4.2.1 Purpose and Scope

The mobilization of Gunite tank sludges and future MVST sludges requires reliable filtration as a first step in volume reduction. A bench-top cross-flow filtration apparatus, placed in a hot cell, will filter actual Gunite tank sludges as part of an effort designed to study filtration and operational reliability. With the CUF, sludge is pumped at high tangential velocity over the surface of a sintered metal tube. Solid-free filtrate passes through the tube, while the sludge can be concentrated on the other side. Periodic back-pressure pulses are employed to maintain the filtration rate by unplugging solids in the sintered tube.

4.2.2 Progress

All work with the CUF unit from Savannah River has been completed, and the unit is in the process of being decontaminated for storage and eventual disposal. The unit was modified by adding a larger-diameter suction line from the makeup tank to the pump to avoid cavitation. Additionally, a larger-diameter pipe was added in the return line to the makeup tank to avoid short-circuiting of the filtrate and slurry. After these modifications, the unit worked well with no observable vortexing in the makeup tank, which could result in short-circuiting. Cross-flow filtration tests of all Gunite and associated tanks composites and sludge from MVST tank W-25 were completed and generally showed that cross-flow filtration is well suited to the dewatering of such sludges when used with proper back-pulsing of the Mott filter to avoid possible fouling.

Settling tests of the sludges in process water, and in one case 4 M NaNO₃ solution, revealed that the MVST sludge might present filtration problems, judging from the amount of suspended fines observed. Surprisingly, this sludge was most amenable to filtration, producing the largest filtrate flux rates under all conditions.

A large number of samples of filtrate as well as raw sludge and settling test solutions were submitted to the Analytical Chemistry Division for analyses of suspended solids and water content. Select samples of raw sludge and sludge obtained following filtration are presently being analyzed for their particle size distribution to observe the effects of the filtration process on particle breakdown during continuous recycle. The data obtained with these actual sludges from the tanks are still being correlated for use in a scaled-up, cross-flow filtration unit.

4.3 CHEMICAL CONVERSION OF NITRATE DIRECTLY TO NITROGEN GAS: A FEASIBILITY STUDY (A. J. Mattus)

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Summary: A bench-top feasibility study to prove the viability of converting the nitrate anion directly to nitrogen from a near-neutral solution using aluminum metal in the presence of a minimal amount of mercury has been partially successful. While it is believed that nitrogen was produced, it is also believed that an undesirable rise in pH, due to the formation of some amount of hydrogen, resulted in a cessation of nitrogen production in one test.

4.3.1 Purpose and Scope

A bench-top feasibility study to convert nitrate directly to nitrogen gas utilizing aluminum metal with amalgamated surfaces is planned as part of an ORNL Seed Money proposal. A chemical process to convert this problematic anion to nitrogen, which could be discharged directly to the atmosphere, would save off-gas processing costs incurred with end products such as ammonia.

4.3.2 Progress

Experimental work to prove the viability of converting the nitrate anion directly to nitrogen from a near-neutral solution using aluminum metal in the presence of a minimal amount of mercury has been partially successful. It is believed that nitrogen was produced in the early part of an experiment when the pH was approximately 5. It is further believed that an undesirable rise in pH, due to the formation of some amount of hydrogen, resulted in a cessation of nitrogen production in

one test. This Seed Money-funded project was of a short duration, lasting only 3 months, and time and funding did not permit analysis of the gases produced.

The conclusions are based on the following observations.

1. Thermal conductivity measurements were made on the gaseous effluent. While using an argon blank and sweep gas in the experimental setup, only nitrogen or ammonia could have dropped the thermal conductivity. Hydrogen and argon are both good conductors and maintain a high thermal conductivity.
2. An acidic scrubber was placed in the off-gas line to remove any ammonia formed before the conductivity cell, and the exiting gases were mixed with HCl vapors to detect ammonium chloride. No reaction of the gas to HCl vapors was detected, which would have indicated that ammonia was present.