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Quarterly Progress Report for the
Chemical Development Section of the
Chemical Technology Division:
April-June 1996

R. T. Jubin

MASTER

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ORNL-27 (3-96)

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Chemical Technology Division

QUARTERLY PROGRESS REPORT FOR THE
CHEMICAL DEVELOPMENT SECTION OF THE
CHEMICAL TECHNOLOGY DIVISION:
APRIL-JUNE 1996

R. T. Jubin

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CONTENTS

EXECUTIVE SUMMARY	v
1. CHEMICAL PROCESSES FOR WASTE MANAGEMENT	1
1.1 COMPREHENSIVE SUPERNATE TREATMENT	1
1.1.1 Purpose and Scope	1
1.1.2 Progress	1
1.2 PARTITIONING OF SLUDGE COMPONENTS BY CAUSTIC LEACHING	3
1.2.1 Purpose and Scope	3
1.2.2 Progress	4
1.3 STUDIES ON TREATMENT OF DISSOLVED MVST SLUDGE USING TRUEX PROCESS	5
1.3.1 Purpose and Scope	5
1.3.2 Progress	6
1.4 ACT*DE*CON SM PROCESS TEST PROGRAM	6
1.4.1 Purpose and Scope	6
1.4.2 Progress	6
1.5 HOT DEMONSTRATION OF PROPOSED COMMERCIAL NUCLIDE REMOVAL TECHNOLOGY	7
1.5.1 Purpose and Scope	7
1.5.2 Progress	8
1.5.2.1 Superlig® 644C at 1 N Hydroxide and 3.5 CV/h	8
1.5.2.2 RF Resin at 1 N Hydroxide and 3.5 CV/h	11
1.5.2.3 Batch Tests of the UPO IONSIV IE-911 CST	12
1.6 SLUDGE TREATMENT STUDIES	15
1.6.1 Purpose and Scope	15
1.6.2 Progress	15
1.7 DEVELOPMENT AND TESTING OF INORGANIC SORBENTS	16
1.7.1 Purpose and Scope	16
1.7.2 Progress	17
2. REACTOR FUEL CHEMISTRY—TECHNICAL ASSISTANCE IN REVIEW OF ADVANCED REACTORS	18
2.1 PURPOSE AND SCOPE	18
2.2 PROGRESS	18
3. THERMODYNAMICS—THERMODYNAMICS AND KINETICS OF ENERGY- RELATED MATERIALS	19
3.1 PURPOSE AND SCOPE	19
3.2 PROGRESS	19

4.	PROCESSES FOR WASTE MANAGEMENT	21
4.1	ION-EXCHANGE PROCESS FOR HEAVY METALS REMOVAL	21
4.1.1	Purpose and Scope	21
4.2.2	Progress	21
4.2	HOT CELL CROSS-FLOW FILTRATION STUDIES OF GUNITE TANK SLUDGES	22
4.2.1	Purpose and Scope	22
4.2.2	Progress	22
4.3	CHEMICAL CONVERSION OF NITRATE DIRECTLY TO NITROGEN GAS: A FEASIBILITY STUDY	23
4.3.1	Purpose and Scope	23
4.3.2	Progress	23

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 April–June 1996. The report describes 12 tasks conducted in 4 major areas of research and development within the section.

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 was conducted using Reillex HPQ anion-exchange resin to measure the removal of pertechnetate from ORNL Melton Valley Storage Tank (MVST) W-27 supernatant. The fractions from the small-column test were analyzed by inductively coupled plasma–mass spectroscopy (ICP-MS) to determine technetium content. The 50% technetium breakthrough occurred at about 45 bed volumes. The technetium was eluted in about 7 bed volumes of eluent using a solution containing 0.017 *M* stannous chloride, 0.1 *M* ethylenediamine, and 0.075 *M* sodium hydroxide.

A second small-column test using Eichrom ABEC-5000-XL anion-exchange resin to remove pertechnetate from ORNL MVST W-27 supernatant was also completed. Samples from this test are being analyzed for technetium using ICP-MS.

Several tests to measure the caustic dissolution behavior of Hanford tank sludges were completed as part of the Partitioning of Sludge Components by Caustic Leaching task. Two samples of Hanford tank S-104 sludge were leached with 3.9 *M* NaOH at 70°C for 4 and 24 h to determine the effect of time on dissolution behavior. Two other samples were leached with 3.9 *M* NaOH at 70°C for 21 h using different leachant-to-sludge ratios to determine if the dissolution behavior is governed by limited solubility of specific components. Additional caustic leach tests were completed on sludge samples from Hanford tanks S-104 and SX-113 leached with 6 *M* NaOH at 70°C for 21 h.

Preliminary results from the S-104 sludge indicate a kinetic effect in the caustic leaching. Neither liquid-to-solid ratios greater than 5 or caustic concentrations that had been increased from 4 *M* to 6 *M* had a significant effect. Under identical conditions, the fraction of aluminum leached from SX-113 sludge was twice that leached from S-104 sludge.

Efforts in the Studies on Treatment of Dissolved MVST Sludge Using TRUEX Process task continued to focus on the preparation of an ORNL/TM report on the transuranium extraction (TRUEX)

tests performed with dissolved MVST sludge. The report was largely completed by the end of the quarter.

The major activity of the ACT*DE*CONSM Test Program task involved completion (and publication in May) of ORNL/TM-13201, *Evaluation of the ACT*DE*CONSM Process for Treating Gunite Tank Sludge*.

The Hot Demonstration of Proposed Commercial Nuclide Removal Technology task continued to address 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, SuperLig 644C and resorcinol/formaldehyde (RF) resins were tested. The RF resin was tested at a feed concentration of 5.5 M sodium, 1 M hydroxide, and 1×10^{-5} M cesium. The SuperLig resin was tested for one loading at the above concentrations and three loadings at a cesium concentration of 7×10^{-5} M. The same resin was loaded and eluted four times. Batch tests were also conducted to help decide the tank and adjustment requirements for the Cesium Removal Demonstration Project using the IONSIV 911 CST.

Within the Sludge Treatment Studies task, test results from two Enhanced Sludge Washing sequences run on sludge from Hanford underground storage tank T-104 provided direct evidence that phosphate reprecipitated into the sludge residue-leachate mixture when the temperature was decreased from 75°C to ambient. This resulted in the formation of a gelatinous material that sticks to the walls of the container. The results show that phosphate solids will form if the correct leaching temperature is not maintained throughout the process.

During the quarter, several batches of hydrous titanium oxide microspheres were prepared as part of the Development and Testing of Inorganic Sorbents task. Equipment modifications for converting hydrous titanium oxide microspheres to sodium titanate at elevated temperatures were completed. Three batches of hydrous titanium oxide microspheres embedded with fine particles of sodium titanate have been prepared using the internal gelation process.

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 finalization of the revised proposal and receipt of the necessary information from Westinghouse to permit the start of the study.

Within the *third research area—Thermodynamics*—the Thermodynamics and Kinetics of Energy-Related Materials task has used a differential thermal analysis (DTA)/thermogravimetric analysis (TGA) to study the phase transitions of phase-pure $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ (123) at partial oxygen pressures ranging from 1 to $10^{-4.3}$ atm. Each sample of sintered 123 was allowed to equilibrate for 2 h at a temperature slightly below that of the first phase transition. The temperature of the 123 sample was increased at a rate of $1^\circ\text{C}/\text{min}$ until a temperature of 1295°C was reached. The temperatures (based on DTA results) of the two phase transitions—(1) $123 \rightarrow \text{Y}_2\text{BaCuO}_5$ (211) + liquid and (2) $211 + \text{liquid} \rightarrow \text{liquid}$ —were determined. Our current results for the $123 \rightarrow 211 + \text{liquid}$ transition are in excellent agreement with K. W. Lay's earlier study with a DTA/TGA system. Unfortunately, our results do not agree with those obtained by T. B. Lindemer in an earlier study. Efforts are under way to account for these discrepancies.

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 Gunitite 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. Construction of the systems was completed the first week of June, with equipment checkout and programming completed near the end of June. All instrumentation functioned properly, and modem communication with the machine was tested and confirmed. The demonstration trailer was shipped to the Tobyhanna Army Depot on June 26, 1996.

The mobilization of Gunitite 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 Gunitite Tank Sludges task, a bench-top, cross-flow filtration apparatus, placed in a hot cell, will filter actual Gunitite tank sludges as part of an effort designed to study filtration and operational reliability. The Cell Unit Facility unit was received from Savannah River and tested with surrogate sludge outside the hot cell. Following a number of modifications to the unit, it was placed inside the hot cell; a final operational check is in progress. Operational tests with Gunitite sludge composites are expected to be completed next quarter.

As part of the final task within this area—Chemical Conversion of Nitrate Directly to Nitrogen Gas—a bench-top feasibility study to convert nitrate directly to nitrogen gas utilizing aluminum metal with amalgamated surfaces is in preparation. The experimental equipment for processing 200 mL of 4 M nitrate-based solution has been set up and a safety review completed. Tests of the principle involved are expected to be conducted next quarter.

1. CHEMICAL PROCESSES FOR WASTE MANAGEMENT

B. Z. Egan

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

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Summary: A small-column test was conducted using Reillex HPQ anion-exchange resin to measure the removal of pertechnetate from Oak Ridge National Laboratory (ORNL) Melton Valley Storage Tank (MVST) W-27 supernatant. The fractions from the small-column test were analyzed by inductively coupled plasma-mass spectroscopy ICP-MS to determine technetium content. The 50% technetium breakthrough occurred at about 45 bed volumes (BV). The technetium was eluted in about 7 BV of eluent using a solution containing 0.017 M stannous chloride, 0.1 M ethylenediamine, and 0.075 M sodium hydroxide.

A second small-column test using Eichrom ABEC-5000-XL anion-exchange resin to remove pertechnetate from ORNL MVST W-27 supernatant was also completed. Samples from this test are being analyzed for technetium using ICP-MS.

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 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

Reillex HPQ was selected for the first column run to measure the removal of pertechnetate from ORNL MVST W-27 supernatant. The supernatant was column effluent from which a large portion of the cesium had been removed. The supernatant was also filtered through a 0.45- μ m filter. The pH was 12.86. Because of the relatively low technetium content of the supernatant (0.43 mg/L), ammonium pertechnetate was added to the feed to adjust the concentration to 3.0 mg/L. The 1.45 cm (ID) $\times$ 15 cm ion-exchange column containing Reillex HPQ was conditioned with a solution of 5.0 M sodium nitrate and 0.16 M sodium hydroxide prior to beginning the run.

The height of the preconditioned resin bed was 6.3 cm, providing a packed bed of about 10.4 cm³. Supernatant solution was passed through the column at a rate of about 6 BV/h. Eluate fractions were collected, and selected fractions were analyzed by ICP-MS to determine the technetium concentration. Results indicated a 50% technetium breakthrough at about 45 BV. This corresponds to approximately 1.4 mg of technetium loaded on the 6.97 g of resin at 50% breakthrough.

The column was washed with about 7 BV of water before eluting the resin bed at a flow rate of ~4 BV/h using an eluent solution containing 0.017 *M* stannous chloride, 0.1 *M* ethylenediamine, and 0.075 *M* sodium hydroxide. This eluent was developed and used successfully by N. C. Schroeder of Los Alamos National Laboratory for eluting technetium from Reillex HPQ. The technetium was readily removed from the column using this eluent. Approximately 1.2 mg of technetium was eluted in 7 BV of eluent. In one fraction, the technetium concentration was more than 40 times the concentration in the supernatant feed.

A small-column test using Eichrom ABEC-5000-XL resin to measure the removal of pertechnetate from ORNL MVST W-27 supernatant was also run. For preparation of a feed solution, an additional 5 L of MVST supernatant from tank W-27 that had been processed previously by D. D. Lee to remove most of the cesium was obtained. Most of 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), feed solution for the ABEC-5000 column test was then prepared by adding 65 μ Ci of ⁹⁹Tc to 2 L of the treated supernatant to adjust the concentration to 3.0 mg/L.

A Kontes glass column with an inside diameter of 1.45 cm was used. The resin, slurried in water, was added to give a bed height of 10.5 cm, corresponding to a bed volume of 17.3 mL. The resin was then washed with 3 BV of 4 *M* NaOH. This caused the bed height to shrink to 5.1 cm. A solution containing 0.16 *M* NaOH and 4.5 *M* sodium nitrate, simulating the feed solution, was added to the column, resulting in an increase in the bed height to 8.55 cm. Once the treated MVST W-27 supernatant was added to the resin bed, the final bed height was 6.2 cm, providing a packed bed of about 10.4 cm³. Supernatant solution was passed through the column at a rate of about 6.8 BV/h. The ABEC-5000-XL resin floated in all the solutions except water. A special apparatus was used to maintain the bed during swelling and shrinkage.

About 1200 mL of supernatant was passed through the column, and 120 fractions were collected. The column was then washed with about 3 BV of 2 *M* NaOH. To elute the technetium from the column, about 100 mL of water was passed through the column at an average flow rate of 5 BV/h. Eluate

fractions were collected, and selected fractions are currently being analyzed by ICP-MS to determine the technetium concentration.

The principal investigator participated in the Efficient Separations Processes Crosscutting Program (ESP) Midyear Review in Gaithersburg, Maryland, April 16-18, 1996.

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: Several tests to measure the caustic dissolution behavior of Hanford tank sludges have been completed. Two samples of Hanford tank S-104 sludge were leached with 3.9 M NaOH at 70°C for 4 and 24 h to determine the effect of time on the dissolution behavior. Two other samples were leached with 3.9 M NaOH at 70°C for 21 h using different leachant-to-sludge ratios to determine if the dissolution behavior is governed by limited solubility of specific components. Additional caustic leach tests were completed on sludge samples from Hanford tanks S-104 and SX-113 leached with 6 M NaOH at 70°C for 21 h.

Preliminary results from the S-104 sludge indicate a kinetic effect in the caustic leaching. Neither liquid-to-solid ratios greater than 5 or caustic concentrations that had been increased from 4 M to 6 M had a significant effect. Under identical conditions, the fraction of aluminum leached from SX-113 sludge was twice that leached from S-104 sludge.

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 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.

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**Tennessee Technological University, Cookeville, Tennessee.

1.2.2 Progress

Several additional caustic washing or leaching tests on Hanford tank sludges have been completed. The tests were performed at an operating temperature of 70°C with a 24-h contact time. Three tests on sludge from tank S-104 were done with ~4 M NaOH at liquid-to-solid ratios of approximately 5, 7.5, and 10 mL/g. A previous test using a liquid-to-solid ratio of 7.5 also provided data for a 4-h contact time. A fourth test on S-104 sludge was completed using a liquid-to-solid ratio of 10 and a caustic concentration of ~6 M NaOH. One test was performed with SX-113 sludge at a liquid-to-solid ratio of 10 and a caustic concentration of ~6 M NaOH. The residual solids, leachates, and rinse solutions from each test were analyzed for the constituents found in the original sludge.

Analyses were completed of the liquid and solid samples derived from leaching tests in which two 3-g samples of Hanford sludge from tank S-104 were mixed with 24 mL of 3.9 M NaOH at 70°C for 4 and 24 h. In these tests the leached sludge solids were also washed three times with a solution containing 0.01 M sodium hydroxide and 0.01 M sodium nitrite. Analyses of the residues, leachates, and wash solutions showed that both of the tests removed about 98% of the ^{137}Cs , 98–99% of the chromium, and > 80% of the sodium. These components, along with aluminum, are the major constituents in the sludge. Increasing the mixing time from 4 to 24 h increased the removal of aluminum from 35 to 51%. Based upon residue analysis, other components that showed significant solubility included Cu, K, Mn, and Fe. Smaller amounts of Ca, Mg, Bi, and Ni were removed. Since Fe, Mn, Ni, and Cu were present in relatively small amounts in the sludge, those results are being evaluated further.

Also, caustic leaching tests with samples of Hanford sludge from tank S-104 were completed in which 1.5 and 3.0 g were mixed with 16-mL volumes of 3.98 M NaOH for 21 h at 70°C. The solid residues were washed four times with 16-mL volumes of a solution containing 0.01 M sodium hydroxide and 0.01 M sodium nitrite to remove the interstitial leachate. The leachates and cumulative washes along with the residues were analyzed for both radioactive and nonradioactive components. Good mass balances were not obtained with some components, and the reasons for this behavior are being studied. Similar behavior has been noted in sludge dissolution studies at other sites.

Two additional caustic leaching tests with 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 6.27 M NaOH at 70°C for 21 h. These conditions were chosen to increase the removal of components from the sludge. The solid residues were washed three times with an "inhibited water" solution containing 0.01 M sodium hydroxide and 0.01 M sodium nitrite to remove the interstitial leachate. The weights of the leachates, wash solutions, and residues were determined. The leachates and cumulative washes, along

with the residues, are being analyzed for radioactive and nonradioactive components. Preliminary gamma-counting data indicated that much less cesium was removed from the SX-113 sample, possibly due to sorption on the diatomaceous earth in this tank.

Material balances for some species, such as silicon and phosphorus, are poor and indicate either difficulty in analysis or reprecipitation prior to sampling. For other materials, such as aluminum and chromium, the material balances are much better, and the effect of caustic leaching may be described with more confidence. Preliminary results indicate that (1) increasing contact time increases the amounts of aluminum removed from the sludge; (2) the liquid-to-solid ratio, over the range tested, does not significantly affect the removal of metals from the sludge; and (3) increasing the caustic concentration from 4 M to 6 M has no significant effect. Different sludges have been shown to react to treatment much differently. For example, under identical conditions the fraction of aluminum leached from SX-113 sludge is twice that leached from S-104 sludge. Additional experiments are planned, and data analysis is continuing. Analytical procedures have been modified in attempts to improve the material balance values.

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

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Summary: Preparation of an ORNL/TM report on the transuranium extraction (TRUEX) tests performed with dissolved MVST sludge continued as a low-priority effort. The report is about 85% complete.

1.3.1 Purpose and Scope

The focus of this experimental program is to evaluate the TRUEX solvent extraction process for partitioning actinides from actual HLW sludge dissolved in nitric acid. A large sludge sample, 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 nitric acid, 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:

*Robotics and Process Systems Division, ORNL.

the fraction of transuranic elements removed from the dissolved sludge and comparison of the results with predictions made with the Generic TRUEX Model (GTM).

1.3.2 Progress

Work to document the TRUEX tests performed with dissolved MVST sludge continued as a low-priority effort. The GTM was used to simulate the experiments that were performed in the laboratory. The calculations were compared with the experimental results. The resulting report is about 85% complete.

A paper entitled "Thermodynamics of Extraction Equilibria Between $\text{O}\phi\text{D}(\text{iB})\text{CMPO}-n$ -Dodecane and Aqueous Nitric Acid Media. I. Nitric Acid" was completed and submitted for publication in the open literature.

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

Contact: Barry B. Spencer
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Summary: The report *Evaluation of the ACT*DE*CONSM Process for Treating Gunite Tank Sludge*, ORNL/TM-13201, was completed and published in May.

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 tank sludge as part of the sludge-processing flow-sheet development effort.

1.4.2 Progress

A report describing the results of a test to evaluate the proprietary ACT*DE*CONSM process for selectively removing actinides from Gunite tank sludge was completed. *Evaluation of the ACT*DE*CONSM Process for Treating Gunite Tank Sludge*, ORNL/TM-13201, was published in May.

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, SuperLig 644C and the resorcinol/formaldehyde (RF) resins were tested. The RF resin was tested at a feed concentration of 5.5 M sodium, 1 M hydroxide, and 1×10^{-5} M cesium. The SuperLig resin was tested for one loading at the above concentrations and for three loadings at a cesium concentration of 7×10^{-5} M. The same resin was loaded and eluted four times. Batch tests were also conducted to help determine the tank and adjustment requirements for the Cesium Removal Demonstration Project (CsRD) using the IONSIV 911 crystalline silicotitanate (CST).

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) 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. 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 third quarter of FY 1996. 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. This supernatant was adjusted to pH 14.0 (1 *M* hydroxide concentration), and runs were completed with and without cold cesium added to provide a total cesium concentration of either 1×10^{-5} or 7×10^{-5} *M*.

1.5.2.1 SuperLig® 644C at 1 *N* Hydroxide and 3.5 CV/h

The SuperLig® for this run was prepared by measuring 4.657 g of dry resin into a column (6.2 mL packed dry), treating as in the previous run (wetting with deionized water, followed by 2 *N* NaOH), and then treating with a feed surrogate made to 5 *N* NaNO₃ and 1 *N* NaOH. This run used the W-27 feed made to pH 14 and was planned to be a multiple load and elute experiment in which the cesium was loaded and then eluted with 0.5 *N* HNO₃ and the resin regenerated with 2 *N* NaOH and then reloaded with the cesium in the W-27 feed. For this set of runs, the first loading was done with the normal amount of cesium in the feed (1.1×10^{-5} *M*), and the following three were done with approximately seven times as much cesium (in the form of cold cesium added as cesium nitrate), giving a measured total of about 7.5×10^{-5} *M* cesium in the feed. The loading was done at a flow rate of 3.5 column volumes (CV)/h in downflow. The flow rate was determined by measuring the resin bed volume during the loading process after several column volumes of supernatant had passed through the bed and the volume had stabilized. Because of the low density of the SuperLig® 644 in the 5 *M* salt solution, a special weighted bed follower, developed by J. L. Collins, was used to keep the bed packed during loading, elution, and regeneration, when the bed volume changed by up to 40–50%. For example, the loading took place with the bed at 10.3 cm³, the water rinse of the bed after loading increased the volume to 13.0 cm³, and elution of the bed reduced the volume to 8.6 cm³.

The first loading used pH 14 feed with 1.1×10^{-5} *M* cesium and a flow rate of 3.5 CV/h with a column volume of 10.2 cm³ and an ambient temperature of 28°C. The initial flow of supernatant through the column produced a reddish-brown color that gradually decreased over about 2 CV. The color could

be followed all the way to the fraction collector. Some discoloration of the downstream filter with a pink-colored material was also noted, but no plugging occurred. The cesium breakthrough was first seen when less than 10 CV had passed through the bed. The loading continued until about 60% breakthrough was indicated by the on-line detector with 50% breakthrough occurring at about 167 CV. The column was then rinsed with deionized water and prepared for the elution. The rinse expanded the bed to a volume of 12.9 cm³ and also resulted in some color being released from the column.

The elution was completed using downflow through the bed with 0.5 N HNO₃ at approximately the same flow rate as the loading and based on the loading volume. As soon as acid began flowing through the bed, it began to shrink. After about 3 CV passed through the bed, the volume had decreased to 10 cm³ and finally decreased to 9.5 cm³ by the end of the elution. A total of 90 mL of acid was used in the elution. The in-line detector curve flattened at about 5 C/C₀, where the detector is completely saturated and will not record higher readings. Fractions collected during the elution were analyzed to develop the total elution curve, with the peak occurring at about 36 C/C₀ at 4 CV of acid. The column was rinsed with deionized water following the elution, with the water remaining in the column until the regeneration.

The column was regenerated with 50 mL (5 CV) of 2 N NaOH in upflow at a 0.5-mL/min flow rate. The bed was 9.2 cm³ at the start of regeneration. Color began coming off the bed as the first column volumes of regenerant passed through; this phenomenon continued for about 2 CV. The regeneration was continued with the final volume of the bed going to 11.9 cm³. The bed was then rinsed with 5 CV of the surrogate salt solution and readied for the next loading. During the salt rinse, it was noted that many small bubbles had formed throughout the bed; efforts were initiated to remove them. This was done by applying a vacuum to the bed and suddenly releasing it. A series of four cycles was completed, and the bed was reduced to a volume of 10.5 cm³ for the start of loading. No bubbles could be seen after the treatment.

The next loading was completed using feed that had cold cesium added to give a total cesium concentration of $7.5 \times 10^{-5} M$ with the pH still at 14 and other concentrations remaining the same. Feed to the column was again at 3.5 CV/h, and slight color was seen as the feed initially passed through the bed but disappeared after about 3 CV. Breakthrough of the cesium was almost immediate. Whether this was due to incomplete elution and regeneration or to flow distribution problems in the bed caused by the bubble removal process has not been determined. The loading curve was approximately parallel to the first curve, but the 50% breakthrough occurred at 77 CV. Deionized water was used for the rinse, and

the column was prepared for the elution. The bed volume at the end of the supernatant feed was 10.2 cm^3 and expanded to 12.7 cm^3 following the rinse.

The elution was conducted the same as the previous one, but a total of 12 CV (120 mL) acid was used. The elution curve was displaced about 2 CV to the right from the first elution curve, with the peak of $15 C/C_0$ occurring at about 5.5 CV. Some brown color came off the bed in the first few column volumes, and the bed shrank to 8.7 cm^3 by the end of the elution. Small bubbles were seen at the bottom of the bed after about 3 CV, and more bubbles began to appear on the sides and near the top as the elution continued. The bubbles increased in size and became more numerous until the elution was finished.

Before the regeneration was attempted, the bubbles were removed by again applying a vacuum/release sequence to the bed. When this was completed, the column volume was 8.4 cm^3 . The regeneration was started in upflow at about 3 CV/h with the 2 N NaOH. As in the first regeneration, a reddish-colored band that grew fainter and disappeared within the first two column volumes came off the column. During this time a few solids could be seen below the filter and in some of the lines. The final volume after regeneration was a false low reading. When the run was ended at about 25 % breakthrough, the curve was extrapolated to the 50 % point to give a 50% breakthrough of about 65 CV. The column was then rinsed with deionized water and the bed expanded to 13 cm^3 . No bubbles were seen during the loading or rinse.

The elution was preceded with a 5-CV rinse with deionized water to try to prevent bubble formation. A lot of color was seen during the first flow of the deionized water through the bed. The elution was completed with over 8 CV of 0.5 N HNO_3 and resulted in a peak of $14 C/C_0$ in the effluent at 3 CV of eluent. During the elution, the bed shrank from 13 to 8.4 cm^3 . After the elution was completed, the column was rinsed with deionized water, with no volume change in the column.

Regeneration prior to the fourth loading was completed in downflow (upflow was used in the first three regenerations) using ~10 CV of 2 N NaOH. Color left the bed almost immediately and continued for about 2 CV, and the bed expanded to 11.5 cm^3 . The salt surrogate was then pumped through the column and resulted in a bed volume of 10.9 cm^3 . No bubbles were seen during any of these operations, and no vacuum sequence was used before the fourth loading.

The fourth loading was begun at 3.5 CV/h and resulted in color leaving the column again but not as much as in previous loadings. The bed volume also decreased slightly to 10.5 cm^3 during the loading. The loading curve started up at a steep slope right away but gradually decreased in slope through the 5- to 10-CV range and became almost parallel to that of the second loading by the time the 50% breakthrough point was reached at about 50 CV. The column was rinsed with deionized water following

the loading, and the bed expanded to 13 cm³ during the rinse. The three loadings that exceeded 50% showed an increase in slope as the curves passed 40–45 % breakthrough. The slope change was detected both on the in-line detector and in the fractions that were analyzed later.

The column was rinsed and then eluted as in the previous loadings. Before the elution was started, a 3-CV rinse with deionized water was concluded. An extra amount (11 CV) of acid was used to try to remove most of the cesium from the column. The curve was very similar to the third elution with the peak at about 3 CV and a concentration of 13 C/C₀ in the effluent. During the elution, the bed decreased to a volume of 8.4 cm³ and stayed at that volume during a rinse with deionized water. The column was then drained and removed from the system and stored for later reuse or additional analysis. A count of the column showed that 5.2 μ Ci of ¹³⁷Cs (equivalent to about 0.5 mL of supernatant) was left on the column. In addition, ⁶⁰Co and ¹⁰⁶Ru were concentrated on the resin, with the cobalt equivalent to almost 500 mL of supernatant remaining and 0.11 μ Ci of ruthenium present. The amount of ruthenium in the feed supernatant was below the detection limits.

1.5.2.2 RF Resin at 1 N Hydroxide and 3.5 CV/h

An experiment was completed using RF resin obtained from the Radiochemical Engineering Development Center (REDC) at ORNL (Bibler resin from W. Bond, currently in use at the REDC) of -60+80 mesh size, in which the feed rate through the bed was 3.5 CV/h. Three previous experiments were completed with resin obtained from Bibler and supernatant at 0.1 N hydroxide concentration. For this run, 6.029 g of resin (tapped volume, 8.3 cm³) was treated with 10 CV of 0.5 M HNO₃, followed by 7 CV of deionized water. During this treatment, the bed volume decreased to 7.3 cm³. The bed was then treated with 2 M NaOH for 10 CV at the expanded volume of resin and rinsed with deionized water for 3 CV. The resin expanded to 13.86 cm³ during caustic treatment. Approximately 10.7 cm³ of the resin was placed in the 1.5-cm-ID test column and had a bed height of 6.5 cm. The weighted bed follower described previously was also used during this run. The column was filled with a surrogate salt solution of 5 N NaNO₃ and 1 N NaOH in preparation for loading.

The column was installed as previously described. Supernatant feed was started through the bed at 3.5 CV/h. This supernatant was also used for the first SuperLig loading in the multiple-loading run (1×10^{-5} M cesium). Once feed was started through the bed, the effluent became brown and remained that color for 2 to 3 CV; the dark color could be seen as the effluent passed through the tubing and filter. During the first 4 CV of feed through the bed, the bed volume increased to about 11.1 cm³ and remained at that level for the rest of the loading. During the run, there was difficulty maintaining a constant flow

rate due to bubbles arising in the lines and migrating to the column pump. The loading was continued to a 70% breakthrough of the cesium. The initial breakthrough did not occur until 7 CV, and the curve was then very steep to 50% at about 20 CV. The column was rinsed with several column volumes of deionized water following the loading in preparation for the elution.

The RF resin was eluted using 0.5 N HNO₃ in downflow at about 3.5 CV/h. The bed started at a volume of 12.9 cm³ after the previous loading and water rinse and ended at a volume of 9.1 cm³ after elution and rinse. A peak of about 3.4 C/C₀ occurred at about 6 CV of eluent. The curve is very broad and does not return to the baseline after 12 CV. After the elution and rinse were complete, the column was drained and removed from the system to storage.

1.5.2.3 Batch Tests of the UOP IONSIV IE-911 CST

The following describes the results for batch tests of the UOP IONSIV IE-911 CST material (lot no. 999096810001) to be used in the CsRD. The tests are designed to help select the supernatant to be used in the CsRD. The supernatant selected would then be transferred to the feed tank (W-29) for the operation of the demonstration. Tank W-29 contained a heel of liquid and a layer of solids from the previous operations using the tank. Tank W-29 is the same feed tank used during the solidification campaigns.

Tank W-29 has been estimated to contain approximately 11,000 gal of liquid above a sludge layer. The present cesium concentration in W-27 is 3.3×10^5 Bq/mL. By calculation, the mixture of W-27/W-29 should produce a cesium concentration of 5.1×10^5 Bq/mL, and the mixture of W-31/W-29 should produce a concentration of 6.1×10^5 Bq/mL based on the available analyses of the contents of the W-29 and W-31.

Based on that analysis, the estimate of the amount of supernatant that would be pumped into the W-29 tank for use in the CsRD is ~22,000 gal, producing a level of about 90% of the total available volume in the 50,000-gal tank. The CsRD will use up to 25,000 gal of the W-29 supernatant for the test. Based on these estimates, a 2:1 ratio of W-27/W-29 and a 2:1 ratio of W-31/W-29 were selected to produce feed material for the batch tests with CST. The two tanks that can be used in the CsRD are W-27 and W-31. Tank W-27 supernatant has been used in the characterization and sorbent-selection tests conducted to date. It is fairly low in ¹³⁷Cs, low in most RCRA metals, and well characterized. Tank W-31 is supposed to contain higher levels of ¹³⁷Cs, has ~10 ppm chrome (5 ppm is the RCRA limit), and is at a pH of ~11.9, compared with W-27 at a pH of ~7.4. Tank W-27 also contains more cold cesium

than the fission product yield alone would predict, and the values of total cesium in W-29 and W-31 are not known accurately at this time.

The supernatant from MVST tank W-29 used for the batch test series was obtained from the Building 2026 Analytical Services samples that had been sent for analysis by David Van Essen for the Out-of-Tank Evaporator Test completed in March and April of 1996. A total of six bottles of the evaporator feed were sampled (7–8 mL per bottle), resulting in a composite of approximately 45 mL. This sample was transferred to Building 4501 for use in the batch contact tests.

The pH of the W-29 composite was confirmed by titration to the phenothalein endpoint to be about 13.44 (1 mL of W-29 required 2.80 mL of 0.1 *N* HCl for neutralization). To make the feed mixtures for the batch tests, 20 mL of W-29 sample was mixed with 40 mL of W-27 sample, and 20 mL of W-29 was mixed with 40 mL of the W-31 sample. The W-27 and W-31 samples were archived samples obtained in December of 1994 and stored in Building 4501 since that time. For comparison, a 60-mL sample of W-27 was also submitted to the same set of batch tests.

The batch feeds were checked for pH after mixing (the W-27-only feed was adjusted first by adding 1.431 g of NaOH pellets and mixing), with the pH of the W-31/W-29 mixture titrating to 13.08, the W-29/W-27 mixture at 11.20, and the W-27-only feed at 12.95. The W-29/W-27 mix was adjusted by adding 0.204 g of NaOH and the pH checked again, resulting in a pH of 12.30. An additional 0.191 g of NaOH was added, resulting in a final pH of 12.76 for the mix.

When the W-29 and W-31 were mixed, no precipitation occurred either initially or after standing overnight. When W-29 and W-27 were mixed, an immediate precipitation occurred consisting of a whitish-fluffy, slow-settling material occurred. When NaOH was added to the W-27 sample, immediate precipitation also occurred, with considerably more volume and slower settling than the W-27/W-29 mix. After overnight settling, the W-27/W-29 mix had a total liquid height of 25 mm and a sludge layer height of 5 mm. The W-27-only sample had a total height of 26 mm and a sludge layer of 9 mm. After adding the extra 0.4 g of NaOH for pH adjustment to the W-27/W-29 mix, the solids were still fluffy but settled rather quickly (5–10 min produced a clear layer more than half of the total depth).

The two feeds with solids were filtered to produce a clear liquid for the batch tests using 0.45- μ m syringe filters giving a total of ~45 mL of each. To determine the ^{137}Cs activity in the feed samples, a 0.5-mL sample was removed from each feed bottle for analysis by gamma spectroscopy. The results are shown in Table 1.

Table 1. Comparison of potential MVST feed mixtures for the Cs Removal Demonstration

Supernatant	Hydroxide, <i>M</i>	pH	¹³⁷ Cs, μCi/mL	¹³⁴ Cs, μCi/mL	Ratio, 137/134	Density, g/cm ³
W-27 (adj.)	0.089	12.95	10.07	0.0435	132	1.268
W-27/W-29	0.057	12.76	15.53	0.376	41.3	1.240
W-31/W-29	0.121	13.08	18.046	0.536	33.7	1.238

These results are consistent with estimates based on the mixing of the supernatants using the analyses for the December 1994 samples for pH, ¹³⁷Cs, ¹³⁴Cs, and density (with the W-29 analyses based on the W-24 supernatant that was later transferred to W-29).

The batch tests were designed to give an estimate of the performance of the UOP IONSIV IE-911 CST material with each of the two tank mixes and a comparison with the W-27 used in the resin-selection tests. Four liquid-to-solid ratios (10:1, 100:1, 500:1, and 1000:1) were used to cover a range of supernatant-to-CST ratios. The tests were set up as ~18-h batch shake tests with no intermediate sampling. The results are based on the amount of ¹³⁷Cs removed from the 5-mL solution during that time. The resin was also rinsed three times with water after the supernatant was removed, dried in air, and then counted to try to determine the specific activity of the ¹³⁷Cs loaded at the various liquid-to-solid ratios.

After the supernatant additions to the cones were completed, the cones with supernatant and CST were placed on a rocking contactor for the prescribed contact time. Two of the liquids were placed in cones without CST to check for supernatant/tube interaction. When contacting was complete, the tubes were removed and the liquid in each tube was withdrawn and placed into new cones. A sample of the liquid in each cone was then filtered and placed in a new cone. Finally, a sample of the filtered liquid was taken to determine by gamma spectroscopy the ¹³⁷Cs remaining in the solution. Two samples of each feed liquid were taken as well, for the initial concentration baseline. Samples of the unfiltered liquid from three of the cones containing the CST were also taken to determine if any of the CST had broken down and dissolved in the liquid during the sampling process. The solid CSTs left in the tubes were washed three times with water and then allowed to air dry before weighing and counting.

The results for the determination of the density of the feed materials are the average of five samples of 5 mL each. The densities are as follows: W-31/W-29—1.2380, W-27/W-29—1.2401, and W-27—1.2681. This agrees well with the predicted densities based on the December 1994 analyses on samples taken by Vic Fowler using W-24 analytical results for W-29.

The counting results for the samples of liquid removed from each of the tubes containing CSTs were used as the basis for recommending that tank W-27 be used for the CsRD after it had been adjusted to pH >12.5 using sodium hydroxide.

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: Test results from two Enhanced Sludge Washing sequences run on sludge from Hanford underground storage tank T-104 provided direct evidence that phosphate reprecipitated into the sludge residue-leachate mixture when the temperature was decreased from 75°C to ambient. This results in the formation of a gelatinous material that sticks to the walls of the container. The results show that phosphate solids will form if the correct leaching temperature is not maintained throughout the process.

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

There are three ways to control Enhanced Sludge Washing so that it is effective in removing aluminum while avoiding the formation of gels or reprecipitation of solids in leachates or wash solutions: (1) precipitation control, (2) excess caustic, and/or (3) temperature control. Precipitation control requires specialized facilities and process operations such as seeding and filtration. Excess caustic involves the cost and handling of amounts of sodium hydroxide greater than that necessary to convert aluminum oxide hydroxide to the aluminate ion. While use of excess caustic will probably be required, temperature control will be a key factor in a successful Enhanced Sludge Washing process.

Two test sequences were carried out on sludge from Hanford underground storage tank T-104. In one test sequence, the temperature was 75°C throughout the process. In the other test sequence, the 75°C temperature was maintained only during leaching, and the process was then carried out at room temperature. The two tests were conducted in parallel to ensure that temperature was the only variable.

There was a marked difference in the behavior of phosphate in the two tests. In the test in which the leachate was maintained at 75°C during settling and filtration, the amount of phosphate was approximately 10 times greater than in the leachate from the sequence in which the settling and filtration were performed at room temperature. This is direct evidence that the phosphate reprecipitated into the sludge residue-leachate mixture when the temperature was reduced to ambient, resulting in more phosphate in the sludge residue after leaching. This resulted in higher concentrations in the wash solutions at ambient temperature than in those at 75°C. In the test sequence maintained at 75°C, most of the phosphate remained in the leachate and was not present in the sludge residue at the time of washing.

There are several implications from these results. First, the temperature of the leachate enhanced the solubility of the phosphate. Second, leaching at an elevated temperature and then conducting the rest of the process at ambient temperature could possibly increase the rate of dissolution of phosphate, but reprecipitation would return the concentration to that consistent with room temperature. The reprecipitated phosphate is rather gelatinous and sticks to container walls. Third, if the correct leaching temperature is not maintained throughout the process, phosphate solids will form whenever it is lowered.

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

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Summary: Several batches of hydrous titanium oxide microspheres have been prepared. Equipment modifications for converting hydrous titanium oxide microspheres to sodium titanate at elevated temperatures were completed. Three batches of hydrous titanium oxide microspheres embedded with fine particles of sodium titanate have been prepared using the internal gelation process.

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 sodium hydroxide 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

A Series 4532 Floor Stand Reactor made by the Parr Instrument Company was modified for use in the elevated-temperature conversions. A stainless steel mesh basket was built to hold the hydrous titanium oxide microspheres in the pressure vessel. The head of the reactor vessel was modified, and several special safety features were added. The thermowell and stirring assembly were adapted to allow the impellers to be positioned above the basket of microspheres to provide constant flow of the sodium hydroxide solution through the microspheres during the conversion process. Conversion tests will begin after the apparatus and procedures are approved.

Several batches of hydrous titanium oxide microspheres were prepared. Some of these materials will be used to evaluate two different schemes for conversion to sodium titanate and preparation of sodium titanate microspheres. Sodium titanate powders are being procured from several commercial sources. Materials will be selected for use in making hydrous titanium oxide/sodium titanate composite microspheres.

Sodium titanate was obtained as a slurry from Boulder Scientific Company. A portion of the sodium titanate slurry was placed in a blender equipped with stainless steel blades and blended at the highest speed for 30 min. The blended material was then sieved through a 200 mesh (75- μm sieve openings) stainless steel sieve. The slurry of sodium titanate particles that passed through the sieve was centrifuged, and the liquid was removed by decantation. The wet, centrifuged sodium titanate particles had the consistency and appearance of toothpaste. Some samples were air dried to constant weight, and other samples were dried at 110°C for 24 h. The ratios of the weights of the wet, centrifuged sodium titanate to the air-dried and oven-dried materials were 3.78 and 4.91, respectively. A sample of the air-dried sodium titanate was examined with a scanning electron microscope to determine the range of particle sizes. The diameter of the particles ranged from 0.9 to about 60 μm , with about 90% of the particles being in the 0.9- to 10- μm range. About 60% of the particles had diameters of about 1 μm .

Conditions are being optimized to prepare composite microspheres containing the maximum amount of sodium titanate. Three batches of composite microspheres containing the sodium titanate

powder embedded in hydrous titanium oxide were prepared using the internal gelation process. Broth mixtures were used that yielded microspheres having weight ratios of hydrous titanium oxide to sodium titanate (based on air-dried weights) of 9.9, 6.6, and 4.9. The corresponding microspheres were calculated to contain about 9, 13, and 17% sodium titanate, respectively. Selected materials will be tested for removing strontium from aqueous waste solutions.

The principal investigator participated in the Efficient Separations Processes Crosscutting Program Midyear Review in Gaithersburg, Maryland, April 16-18, 1996.

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 is on hold, awaiting finalization of the revised proposal and 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 hydrochloric acid and nitric acid 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, and a revised proposal has been prepared. 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 finalization of the revised proposal and 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: A differential thermal analysis (DTA)/thermogravimetric analysis (TGA) was used to study the phase transitions of phase-pure $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ (123) at partial oxygen pressures ranging from 1 to $10^{-4.3}$ atm. Each sample of sintered 123 was allowed to equilibrate for 2 h at a temperature slightly below the first phase transition. The temperature of the 123 sample was increased at a rate of $1^\circ\text{C}/\text{min}$ until a temperature of 1295°C was reached. The temperatures of the two phase transitions (based on the DTA results)—(1) $123 \rightarrow \text{Y}_2\text{BaCuO}_5$ (211) + liquid and (2) $211 + \text{liquid} \rightarrow \text{liquid}$ —were determined. Our current results for the $123 \rightarrow 211 + \text{liquid}$ transition are in excellent agreement with K. W. Lay's earlier study with a DTA/TGA system. Unfortunately, our results do not agree with those obtained by T. B. Lindemer in an earlier study. Efforts are under way to account for these discrepancies.

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

A sintered sample of phase-pure 123 was used in a series of experiments with a DTA/TGA. The phase transitions of 123 were examined at partial oxygen pressures ranging from 1 to $10^{-4.3}$ atm. Before each experiment, 0.30 g of the sintered 123 was ground into a powder. The sample was then transferred into an alumina sample holder and placed into the DTA/TGA. A constant gas flow rate was used regardless of the partial oxygen pressure. The oxygen content was determined with an oxygen analyzer. The temperature of the sample was quickly raised to 860°C , which is below the first phase transition (based on several different analytical techniques). The sample remained at this temperature for 2 h. At the end of the equilibration, the temperature of the 123 sample was increased at a rate of $1^\circ\text{C}/\text{min}$ until a temperature of 1295°C was achieved. The temperatures (based on DTA results) of the two phase transitions— $123 \rightarrow \text{Y}_2\text{BaCuO}_5$ (211) + liquid and $211 + \text{liquid} \rightarrow \text{liquid}$ —are provided in Table 2. The TGA results indicate slightly higher phase-transition temperature.

Our current results for the $123 \rightarrow 211 + \text{liquid}$ transition are in excellent agreement with K. W. Lay's earlier work with a DTA/TGA system. Unfortunately, our results do not agree with those obtained by T. B. Lindemer in an earlier study. Lindemer's paper (*Physica C* 178, 93-104 [1991]) stated that the difference was probably due to the heating rate. However, our current heating procedure should have eliminated this possibility. In addition, Lindemer reported that 211, $\text{YBa}_3\text{Cu}_2\text{O}_{6+x}$ (132), and BaCuO_x were formed from the first phase transition of 123 at an oxygen pressure below 94 Pa while only 211 and BaCu_2O_2 were formed from the same transition at an oxygen pressure above 94 Pa. Samples of the first phase transition of 123 at 1000 Pa and 10 Pa of oxygen were prepared for X-ray diffraction analysis. With the exception of the 132, the same products were observed. Efforts are under way to account for these discrepancies.

Table 2. Temperatures of the two phase transitions

$\log p\text{O}_2$ (MPa)	$123 \rightarrow 211 + \text{L}$ ($^{\circ}\text{C}$)	$211 + \text{L} \rightarrow \text{L}$ ($^{\circ}\text{C}$)
-0.994	1038.1	1240
-1.994	1010.1	1200.1
-2.494	991.9	1185.9
-2.994	981.4	1160.7
-3.494	968	1137
-3.994	956.3	1128.3
-4.494	951.4	1128
-4.994	950.7	1114.5
-5.294	951	1112.4

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. Construction of the systems was completed the first week of June, with equipment checkout and programming completed near the end of June. All instrumentation functioned properly, and modem communication with the machine was tested and confirmed. The demonstration trailer was shipped to the Tobyhanna Army Depot on June 26, 1996.

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.

Construction of the systems was completed the first week of June, and leak checking, instrumentation checkout, and programming were completed near the end of June. All instrumentation functioned properly, and modem communication with the machine was tested and confirmed. The demonstration trailer was shipped to the Tobyhanna Army Depot on June 26, 1996.

Staff from ORNL will be at the site in the beginning of July to initiate the demonstration. As part of the equipment startup, samples of the inlet stream will be obtained for analysis.

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

Contact: 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 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. The Cell Unit Facility (CUF) unit was received from Savannah River and tested with surrogate sludge outside the hot cell. Following a number of modifications to the unit, it was placed inside the hot cell; a final operational check is in progress. Operational tests with Gunite sludge composites are expected to be completed next quarter.

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

The assembled CUF unit was received from Savannah River and tested with surrogate sludge outside the hot cell. A number of modifications were made to the CUF, including a larger reservoir and cooling coils, electric solenoid valves, and a piston-type back-pulse activator. The modified unit will operate with up to 1 L of sludge feed at a back-pressure of 20 psi and a tangential velocity of 8 ft/s across

the sintered tube. The flow rate and temperature are constantly monitored outside the cell electronically, while pressures are read from standard gauges on the unit. The CUF unit was placed inside the hot cell, and a final operational check is in progress. Operational tests with Gunitite sludge composites are expected to be completed next quarter.

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 convert nitrate directly to nitrogen gas utilizing aluminum metal with amalgamated surfaces is in preparation. The experimental equipment for processing 200 mL of 4 M nitrate-based solution has been set up and a safety review completed. Tests of the principle involved are expected to be conducted next quarter.

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

The experimental equipment for processing 200 mL of 4 M nitrate-based solution has been set up and a safety review completed. A thermal conductivity detector will measure nitrogen produced in a helium cover gas. Tests of the principle involved are expected to start soon.

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