ORNL/M-6353

**OAK RIDGE
NATIONAL
LABORATORY**

LOCKHEED MARTIN

**Quarterly Progress Report for the
Chemical and Energy Research Section
of the Chemical Technology Division:
January–March 1997**

R. T. Jubin

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Chemical Technology Division

QUARTERLY PROGRESS REPORT FOR THE
CHEMICAL AND ENERGY RESEARCH SECTION OF
THE CHEMICAL TECHNOLOGY DIVISION:
JANUARY-MARCH 1997

R. T. Jubin

Date Published- January 1998

Prepared by the
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managed by
LOCKHEED MARTIN ENERGY RESEARCH CORP.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-96OR22464

CONTENTS

ACRONYMS	vii
EXECUTIVE SUMMARY	ix
1. HOT CELL OPERATIONS	1
1.1 COMPREHENSIVE SUPERNATANT TREATMENT	1
1.1.1 Purpose and Scope	1
1.1.2 Progress	1
1.2 PARTITIONING OF SLUDGE COMPONENTS BY CAUSTIC LEACHING	2
1.2.1 Purpose and Scope	3
1.2.2 Progress	3
1.3 HOT DEMONSTRATION OF PROPOSED COMMERCIAL NUCLIDE REMOVAL TECHNOLOGY	4
1.3.1 Purpose and Scope	4
1.3.2 Progress	5
1.3.3 Presentations	7
1.4 DEVELOPMENT AND TESTING OF INORGANIC SORBENTS	7
1.4.1 Purpose and Scope	8
1.4.2 Progress	8
1.5 DEVELOPMENT AND TESTING OF GLASS AND GROUT WASTE FORMS	10
1.5.1 Purpose and Scope	10
1.5.2 Progress	10
1.6 SEARCH FOR TECHNETIUM IN NATURAL METALLURGICAL RESIDUES	11
1.6.1 Purpose and Scope	12
1.6.2 Progress	12
2. PROCESS CHEMISTRY AND THERMODYNAMICS	13
2.1 SLUDGE TREATMENT STUDIES	13
2.1.1 Purpose and Scope	13
2.1.2 Progress	13
2.1.2.1 Enhanced Sludge Washing	13
2.1.2.2 Acid Treatment	14
2.2 TECHNICAL ASSISTANCE IN REVIEW OF ADVANCED REACTORS	14
2.2.1 Purpose and Scope	15
2.2.2 Progress	15
2.3 THERMODYNAMICS AND KINETICS OF ENERGY-RELATED MATERIALS	15
2.3.1 Purpose and Scope	16
2.3.2 Progress	16

2.3.2.1	Solidification of the Y-Ba-Cu-O System	16
2.3.2.2	Oxidation State of Copper in Y123	16
3.	MSRE REMEDIATION STUDIES	18
3.1	URANIUM CONVERSION	18
3.1.1	Purpose and Scope	18
3.1.2	Progress	18
3.2	URANIUM DEPOSIT REMOVAL, DENATURING OF FLUORINATED CHARCOAL	19
3.2.1	Purpose and Scope	19
3.2.2	Progress	20
3.3	SALT DISPOSITION	20
3.3.1	Purpose and Scope	21
3.3.2	Progress	21
3.4	PUBLICATIONS	22
4.	CHEMISTRY RESEARCH	22
4.1	ARTIFICIAL ANTIBODY STRATEGY FOR URANYL SEPARATION	22
4.1.1	Purpose and Scope	22
4.1.2	Progress	23
4.2	FUNDAMENTAL CHEMISTRY OF ACTINIDES AND FISSION PRODUCTS IN MOLTEN SALTS	24
4.2.1	Purpose and Scope	24
4.2.2	Progress	24
4.3	IN-LINE SPECTROSCOPIC SENSOR FOR ALUMINUM INDUSTRIES	24
4.3.1	Purpose and Scope	25
4.3.2	Progress	25
4.4	SOLUBILITIES OF UO_3 IN CARBONATE BUFFER SOLUTIONS AT HIGH TEMPERATURE ($>100^\circ C$)	25
4.4.1	Purpose and Scope	25
4.4.2	Progress	25
4.5	PUBLICATIONS	26
5.	SEPARATIONS AND MATERIALS SYNTHESIS	27
5.1	CHEMICAL AND PHYSICAL PRINCIPLES IN MULTIPHASE SEPARATIONS	27
5.1.1	Purpose and Scope	27
5.1.2	Progress	27
5.1.2.1	Interface Deformation and Breakup	27
5.1.2.2	Interactions and Coalescence of Drops	28
5.1.2.3	Enhancement of Transport Processes Through Electrohydrodynamic Flows	28

5.2	NUCLEATION, GROWTH, AND TRANSPORT PHENOMENA	28
5.2.1	Purpose and Scope	29
5.2.2	Progress	29
5.2.2.1	Forced Hydrolysis	29
5.2.2.2	Sol-Gel Processing in Alkoxide Systems	30
5.2.2.3	Supercritical Fluids Processing of Particles and Inorganic Membranes	30
5.2.2.4	Ultrafine Particle Synthesis by Inverse Electrostatic Spraying ..	31
5.3	PHASE EQUILIBRIA MODIFICATION BY ELECTRIC FIELDS	31
5.3.1	Purpose and Scope	31
5.3.2	Progress	31
5.4	MAGNETIC-SEEDING FILTRATION	32
5.4.1	Purpose and Scope	32
5.4.2	Progress	33
5.5	ELECTROSTATIC OZONATION	33
5.5.1	Purpose and Scope	34
5.5.2	Progress	34
5.6	PUBLICATIONS	34
6.	SOLUTION THERMODYNAMICS	35
6.1	INTERACTIONS OF SOLUTES, SOLVENTS, AND SURFACES	35
6.1.1	Objective	35
6.1.2	Progress	35
6.2	ELECTRODISPERSION OF H ₂ O IN SUPERCRITICAL CO ₂	36
6.2.1	Objective	36
6.2.2	Progress	36
6.3	MOLECULAR-BASED STUDY OF REVERSE MICELLES IN SUPERCritical CO ₂	36
6.3.1	Objective	36
6.3.2	Progress	37
6.4	PUBLICATIONS	37
7.	BIOTECHNOLOGY RESEARCH	38
7.1	KINETICS OF ENZYME-CATALYZED REACTIONS	38
7.1.1	Purpose and Scope	38
7.1.2	Progress	38
7.2	BIOMOLECULAR ELECTRONICS	39
7.2.1	Purpose and Scope	39
7.2.2	Progress	40

7.3	ENZYMES FROM EXTREMOPHILES IN BIOPROCESSING AND BIOREMEDIATION	40
7.3.1	Purpose and Scope	40
7.3.2	Progress	40
7.4	ENZYMATIC CONVERSION OF BIOMASS TO HYDROGEN	41
7.4.1	Purpose and Scope	41
7.4.2	Progress	41
7.5	REMOVAL OF METALS FROM AQUEOUS WASTE STREAMS	42
7.5.1	Purpose and Scope	42
7.5.2	Progress	42
7.6	BIOREMEDIATION OF PCBs AT ELECTRIC POWER SUBSTATIONS	43
7.6.1	Purpose and Scope	43
7.6.2	Progress	43
7.7	BIOMIMETICS/BIOMATERIALS LEADERSHIP FOR OAK RIDGE	43
7.7.1	Purpose and Scope	44
7.7.2	Progress	44
7.8	PUBLICATIONS AND PRESENTATIONS	44
7.8.1	Published	44
7.8.2	Submitted Manuscripts	44
7.8.3	Presentations	44
7.8.4	Patent Actions	45

ACRONYMS

ACB	activated charcoal bed
AMP	ammonium molybdophosphate
CASD	Chemical and Analytical Sciences Division (ORNL)
CSRD	Cesium Removal Demonstration
CST	crystalline silicotitanate
CV	column volumes
DLS	dynamic light scattering
DMPIC	1,2-dimethyl-3-propylimidazolium chloride
DOE	U.S. Department of Energy
DTA	differential thermal analysis
ED/IX	electrodialysis-ion exchange
EHD	electrohydrodynamic
ESP	Efficient Separations and Processing Crosscutting Program
FTIR	Fourier transform infrared
HFIR	High Flux Isotope Reactor
HGMF	high-gradient magnetic filtration
HLW	high-level waste
HMTA	hexamethylenetetramine
IES	inverse electrostatic spraying
IR	infrared
IRWST	In-Reactor Water Storage Tank
MSRE	Molten Salt Reactor Experiment
MVST	Melton Valley Storage Tank
NIER	National Institute for Environmental Renewal
ORNL	Oak Ridge National Laboratory
PCBs	polychlorinated biphenyls
PSI	Photosystem I
PSII	Photosystem II
RCRA	Resource Conservation and Recovery Act
SAXS	small-angle X-ray scattering
SPM	scanning probe microscope
STS	scanning tunnel spectroscopy
TCLP	Toxicity Characteristic Leaching Procedure
TFA	Tank Focus Area
TVA	Tennessee Valley Authority
UT	The University of Tennessee, Knoxville
XRD	X-ray diffraction

EXECUTIVE SUMMARY

This report summarizes the major activities conducted in the Chemical and Energy Research Section of the Chemical Technology Division (CTD) at Oak Ridge National Laboratory (ORNL) during the period January–March 1997. Created in March 1997 when the CTD Chemical Development and Energy Research sections were combined, the Chemical and Energy Research Section conducts basic and applied research and development in chemical engineering, applied chemistry, and bioprocessing, with an emphasis on energy-driven technologies and advanced chemical separations for nuclear and waste applications.

The report describes the various tasks performed within seven major areas of research: Hot Cell Operations, Process Chemistry and Thermodynamics, Molten Salt Reactor Experiment (MSRE) Remediation Studies, Chemistry Research, Separations and Materials Synthesis, Solution Thermodynamics, and Biotechnology Research. The name of a technical contact is included with each task described in the report, and readers are encouraged to contact these individuals if they need additional information.

Activities conducted within the area of *Hot Cell Operations* included column testing of Amberlite IRC-718 resin to remove strontium from ORNL Melton Valley Storage Tank (MVST) supernatant, analyses of leachates and residues from leaching tests on samples of sludge from Hanford tanks, hot cell testing of candidate sorbents and ion exchangers under continuous flow conditions using MVST supernatant, and development and batch testing of spherical sorbents containing sodium titanate to remove strontium. Other tasks in this area involved immobilization of sludge in a cement-based grout and collaborative efforts to remove technetium isotopes from metallurgical mining residues.

Within the area of *Process Chemistry and Thermodynamics*, testing of Hanford sludge confirmed the need for hydrofluoric acid treatment to prevent silica deposition. Other initiatives included the use of the "TRENDS" code to model the distribution of iodine during a design basis accident and collaborative efforts with Russian scientists to determine the solidification conditions of yttrium, barium, and copper oxides from their melts.

MSRE Remediation Studies involved recovery and stabilization of ^{233}U ; investigation of the chemistry of activated charcoal, uranium hexafluoride, and fluorine at different temperatures; and identification of the mechanism of formation for the uranium hexafluoride found in the MSRE piping system.

Included in the area of *Chemistry Research* were investigations of the properties of sol-gel glasses templated with uranyl ions and the effect of hydrogen bonding on uv-vis spectra of uranyl chloride complex species in room-temperature molten salts. Other tasks within this area involved collaborative efforts with colleagues in the Chemical and Analytical Sciences Division to design and test a noncontact fiberoptic Raman sensor for high-temperature aluminum electrolyte processes and to establish a protocol for accurately measuring solubilities of UO_3 in carbonate solutions at high temperature.

In the area of *Separations and Materials Synthesis*, fundamental studies that were in progress explored the use of electromagnetic fields to enhance transport processes in multiphase separations;

investigated the mechanisms, kinetics, and thermodynamics of nucleation and particle growth in systems for the synthesis of ultrafine inorganic particles; and examined the use of electric fields to modify phase equilibria in multiphase separations processes. Other efforts involved the application of magnetic-seeding filtration to remove solids from waste streams and the enhancement of oxidation of organic pollutants in aqueous solutions by using electric fields to form microbubbles containing ozone.

Solution Thermodynamics included molecular-based studies of solutions in supercritical fluids, attempts to demonstrate the feasibility of producing stable microdispersions of water in supercritical carbon dioxide using high-intensity electrical fields, and a multi-institutional initiative to develop a molecular understanding of reverse miscelles in supercritical carbon dioxide through small-angle scattering experiments and molecular simulation calculations.

In the final area—*Biotechnology Research*—Photosystem II photosynthesis was demonstrated by simultaneous photoevolution of H_2 and O_2 using several newly acquired Photosystem I-deficient mutants of *Chlamydomonas*, and a technique was established to control the orientation of Photosystem I reaction centers on gold surfaces. In enzyme-related work, the kinetic characteristics of thermophilic cellulases and a beta-glucosidase from recombinant biocatalysis were studied, and efforts were made to maximize the efficiency of the enzymatic production of hydrogen from glucose. Other biotechnology initiatives included the demonstration of a pilot-scale ion-exchange system and an advanced technology based on ligands of biochemical origin for the removal of toxic metals from waste streams at industrial or environmental sites, a collaborative endeavor to investigate anaerobic microbial dechlorination of polychlorinated biphenyls at electric power substations, and a programmatic development effort to establish the Oak Ridge Complex as the recognized center for the newly emerging area of biomimetics and biomaterials.

1. HOT CELL OPERATIONS

B. Z. Egan

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

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Summary: A column test using Amberlite IRC-718 to remove strontium from Oak Ridge National Laboratory (ORNL) Melton Valley Storage Tank (MVST) W-27 supernatant was completed. Over 700 column volumes (CV) of feed was processed before the strontium reached 25% breakthrough. Nitric acid is being tested for stripping the strontium from the column. A 1 M nitric acid solution recovered about 55% of the strontium from the column after about 3 CV. Batch tests indicate that 3 M nitric acid could be used to elute most of the strontium.

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

Supernatant from MVST W-27, which had been previously treated to remove most of the cesium and strontium, was used in a column test to measure strontium removal. The strontium content of the supernatant was adjusted to about 1.5 mg/L by adding strontium nitrate, and ^{85}Sr tracer was added for analytical purposes. Based on previous batch tests, Amberlite IRC-718 was chosen as the sorbent for the column test. The sorbent was packed into a 1-cm-diam column to give a bed height of 4 cm. In the column, the sorbent was washed with a solution containing 0.16 M sodium hydroxide and 4.5 M sodium nitrate, then with 0.1 M nitric acid, and again with the alkaline salt solution. The feed supernatant was then fed to the column at a flow rate of about 8 CV/h. Fractions of effluent were

collected and analyzed by gamma spectroscopy. Over 200 CV was obtained before the strontium breakthrough reached 1%. The run was terminated after 719 CV (2.3 L), by which time the strontium breakthrough had reached about 25%. It was estimated that 2.85 mg of strontium was loaded onto the column.

The ability to remove the strontium from the resin is also important. Efforts are under way to elute the strontium from the column. First, any residual feed solution was washed from the column with a solution containing 4.5 *M* sodium nitrate and 0.16 *M* sodium hydroxide. This reduced the strontium activity in the eluate to near background. The column was then washed with 6 CV of 0.1 *M* nitric acid. Finally, 1 *M* nitric acid was added at a flow rate of 2.3 CV/h, and a total of 11 CV of eluant was collected. The strontium concentration reached a maximum after about 1.3 CV, and about 55% of the strontium was removed after about 3 CV.

Several batch tests were conducted using sieved sorbent that was loaded with strontium. For these tests, 50 mg of the sorbent was added to preweighed centrifuge tubes. Strontium was added onto the sorbent samples by adding 5 mL of MVST supernatant and mixing on a wrist-action shaker for 24 h. The solutions were then removed and analyzed using an LKB Wallac Compugamma Gamma Counter to measure the strontium loading on the sorbent.

To the separate loaded sorbent samples, 5-mL volumes of 1, 2, 3, and 6 *M* nitric acid were added and mixed for several hours. The solutions were then removed and analyzed for strontium. The results indicated that most of the strontium (95%) could be removed from the sorbent using 3 *M* nitric acid. Additional tests are planned.

"Comprehensive Supernatant Treatment" was presented at the Efficient Separations and Processing Crosscutting Program, 1997 Technical Exchange Meeting, January 29, 1997, in Gaithersburg, Maryland.

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

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Summary: Analyses of leachates and residues from leaching tests on samples of sludges from Hanford tanks S-104 and SX-113 have been completed, and the data have been evaluated. Leaching conditions were determined for increasing the dissolution of aluminum, chromium, and phosphorus. A caustic leach test on Hanford tank C-104 sludge was completed, and samples of the

*Tennessee Technological University, Cookeville, Tennessee.

original sludge, sludge residue, leachate, and wash solution are being analyzed. Preparations were completed for a second leach test on the C-104 sludge at 50°C to measure the effect of temperature on the caustic dissolution behavior.

1.2.1 Purpose and Scope

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

1.2.2 Progress

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

Because of a malfunction in the mixer apparatus, it was necessary to remove the equipment from the hot cell and repair it. Modifications were also made to the mixing system to improve the operation. Entry into the hot cell also provided the opportunity for some cleanup and waste disposal.

Analyses of leachates and residues from leaching tests on samples of sludges from Hanford tanks S-104 and SX-113 have been completed, and the data have been evaluated. Compared with previous tests, the leaching time, temperature, and the ratio of leachant to sludge were increased to try to increase the caustic dissolution of the desired components from the sludges. For the S-104 sludge, increasing the leaching time to 126 h, the temperature to 80°C, the sodium hydroxide concentration to 6.33 M, and the ratio of the volume of leach solution to sludge mass near 30 increased the aluminum dissolution to 96%, the chromium removal to 99%, and the phosphorus removal to 96%. For SX-113 sludge under similar conditions, improvements were also noted in the dissolution of aluminum (79%) and chromium (66%). Caustic leaching conditions were also determined for removing 97% of the aluminum, 71% of the chromium, and 94% of the phosphorus from C-105

sludge and 82% of the aluminum, 70% of the chromium, and 94% of the phosphorus from C-107 sludge. All results are based on comparing the sludge residue analyses with the original sludge analyses.

A caustic leach test on Hanford tank C-104 sludge was completed. The sludge sample (2.2 g) was leached with 25 mL of 4 M NaOH at 80°C for 65 h. The residue was washed three times with "inhibited" water. Samples of the original sludge, sludge residue, leachate, and wash solution have been sent for analysis.

In preparation for a second test on the C-104 sludge, the leaching apparatus used in the hot cell was rebuilt. Because of previous mechanical failures, a more powerful mixing motor and a larger gearbox, along with an improved transmission link, were installed in the new apparatus. Other preparations were completed for the next leaching test at 50°C to determine the effect of temperature on the caustic dissolution behavior of the C-104 sludge. Information was assembled and summarized for the Tank Focus Area (TFA) Midyear Review in Richland, Washington. The principal investigator participated in the program review.

A sample of sludge from Hanford tank S-101 was received. This sample will be available for future caustic dissolution tests.

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

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Summary: This task covers work in the continuous removal and concentration of radioactive components of supernatant at the various DOE sites. The primary objective is to test candidate sorbents 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 all of them can be compared on the same basis. During the last quarter, three column loadings were conducted in support of the Cesium Removal Demonstration (CsRD) Project using the MVST W-29 feed and UOP's IE-911 crystalline silicotitanate (CST).

1.3.1 Purpose and Scope

This task covers the operation of an experimental test unit that is located in a Building 4501 hot cell. This equipment is designed to test radionuclide removal technologies under continuous operation on actual ORNL MVST supernatant, Savannah River HLW supernatant, and Hanford supernatant. The latter two may be simulated by adding the appropriate chemicals and/or nuclides to the MVST supernatant. The technologies tested are housed in modules or placed in columns that can

be attached to the experimental system inside the hot cell and continuously fed the test supernatant until the nuclide of interest exhausts the capacity of the module. Initial candidate sorbents for cesium removal are the resorcinol/formaldehyde resin, CSTs, Superlig® 644 resin, and granular potassium cobalt hexacyanoferrate. Sodium and potassium are competitors for cesium removal. The results of these tests will be compared with batch results and small-column test results obtained in the Comprehensive Supernate Treatment task. The results will be used to supply the CsRD Project with the information to determine the design parameters for that project. The rate of removal, resin required, and regeneration requirements are important design parameters, and the loading capacity of each sorbent will help to determine the size of the column required and help define the final volume of solid waste to be disposed of.

This task works in close cooperation with the Efficient Separations and Crosscutting Program (ESP) and the TFA in order to ultimately transfer the technologies being developed to the end user. As part of this work, TFA requested through ESP that we test the electrodialysis-ion-exchange (ED/IX) system from AEA Technology because ORNL was the only site with sufficient available supernatant for testing this multiple-cycle system.

1.3.2 Progress

The hot demonstration tests were designed to test the CST commercial sorbent on a small scale using the MVST supernatant that would be used in the CsRD 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 objectives of the CsRD support program were as follows:

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

The experimental plan included sampling the MVST W-29 tank, preparing the CST, and determining the primary operating parameters of the bench-scale system, along with procedures for

collecting the effluent samples and submitting the samples to Analytical Services Organization for radiological and chemical analyses. The plan also included verifying the procedure for preparing the loaded column for Toxicity Characteristic Leaching Procedure (TCLP) testing.

The planned operating conditions included flow rates of 3 and 6 CV of supernatant per hour through the bed using a CST volume of approximately 10–13 mL in the 1.45-cm-ID glass columns. One column loading would proceed until at least 90% breakthrough of the cesium occurred, and the loaded column would be submitted for TCLP analysis. One loading would use two columns of CST in series, with the second column loaded to greater than 50% breakthrough.

The first test treated 12.6 L of W-29 supernatant over a period of 217 h. The test was conducted at a flow rate of 6 CV/h using a column containing 10.1 mL of the CST. The column was loaded to 90% cesium breakthrough. The breakthrough curve followed the same line as a previous experiment. The cesium-loaded column was removed from the cell and was sent to ORNL Chemical and Analytical Sciences Division (CASD) for TCLP testing. No problems were encountered during the operation of the column, and the results were consistent with previous results obtained using CST. During the test, at about 700 CV, the feed bottle was changed, and a second bottle was installed. The cesium content of the two feed solutions was different. The difference in the cesium concentrations of the two bottles caused problems in interpreting the data after the bottles were changed.

The next experiment in support of the CsRD was conducted concurrently with a run of the CsRD under similar conditions. The flow rate was 3 CV/h for 550 CV; the 50% cesium breakthrough occurred at 475 CV. The 50% cesium breakthrough for the CsRD column was within 1% of the small-column breakthrough. The cell column was loaded to about 60% breakthrough at 550 CV and contained about 65 mCi of ^{137}Cs after loading. The slope of the cell column loading curve was steeper than the CsRD loading curve, as expected, based on the geometries of the two columns. Sample counting results for the ^{137}Cs loading gave similar results to the curve generated by the cell on-line detector. At the lowest cesium breakthroughs, the samples (counted for 12–18 h) indicated breakthroughs of less than 0.05% through more than 80 CV, while the cell on-line detector gave 0.1% breakthroughs for the same period. Once cesium breakthrough passed about 0.5%, the curves were identical. A column loaded with cesium was provided to the CASD for TCLP testing to qualify the CsRD run for the Nevada Test Site.

The final test was conducted with two columns in series, similar to one of the CsRD runs. The flow rate was 6 CV/h. More than 12 L of W-29 supernatant was treated over a 190-h period. The first column was loaded to >80% cesium breakthrough, and the second column was loaded to beyond the 50% breakthrough level. The cell system attained 50% cesium breakthrough on the first column

(containing 11.6 mL of CST) at about 440 CV and 50% breakthrough on the second column at 492 CV (assuming both columns were operated as one long column of 23.2 mL at 3 CV/h flow rate). The breakthrough curves for the two columns followed the same line as the previous test. Preliminary indications are that the 50% cesium breakthrough from the second CsRD column was about 520 CV, although the CsRD analytical results were somewhat scattered. The loading of the cell columns was about 58 mCi of ^{137}Cs in the first column and about 46 mCi of ^{137}Cs in the second column. The cesium-loaded columns were removed from the cell and sent to CASD for TCLP testing. No problems were encountered during the operation of the columns during either test, and the results were again consistent with all previous results obtained using CST preparations. Feed samples from both tests have been sent for analysis.

The results of the cell experiments with the CSTs were presented at the CST Gate Review at Hanford, Washington, in January 1997. Results of cell experimental work in the cell ion-exchange experimental test program from the previous year were presented at the annual ESP Technical Exchange Meeting in Gaithersburg, Maryland.

1.3.3 Presentations

D. D. Lee and J. F. Walker, Jr., "Hot Demonstration of Proposed Commercial Cesium Removal Technology," presented at WATTEC, February 1997, Knoxville, Tenn.

D. D. Lee, J. F. Walker, Jr., P. A. Taylor, and D. W. Hendrickson, "Cesium Removal Flow Studies Using Ion Exchange," presented at 1997 AIChE Spring National Meeting in Houston, March 9-13, 1997.

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

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Summary: Several composite spherical sorbents containing sodium titanate have been prepared and analyzed in batch tests to measure strontium removal. The results compared favorably with commercial ion exchangers. Efforts are under way to prepare pure sodium titanate microspheres using an alkoxide conversion methodology. Methods of preparing composite microspheres containing ammonium molybdophosphate (AMP) for removing cesium from acidic solutions are being evaluated.

Two batches of hydrous titanium oxide microspheres were prepared by the hexamethylene-tetramine (HMTA) internal gelation process for use in converting the titanium oxide to sodium titanate. In the conversion process, the hydrous titanium oxide microspheres were washed with water, then reacted with sodium ethoxide, and finally hydrolyzed with water. After further treatment, the microspheres will be evaluated in batch tests for removing strontium from simulated supernatant solution.

1.4.1 Purpose and Scope

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

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

1.4.2 Progress

An apparatus for the alkoxide conversion of hydrous titanium oxide microspheres to pure sodium titanate microspheres is being assembled, and the necessary chemicals have been obtained. The alkoxide conversion methodology was used earlier to prepare microspheres that were about 70% tetrasodium nonatitanate and had good strength with a low tendency for surface erosion. The average slow-pour density (1.09 g/mL) was the same as commercially available granular sodium titanate. The average crush strength was about 2000 g. In 24-h batch tests, the sodium titanate microspheres removed up to 98% of the strontium from MVST W-29 supernatant.

Two batches of hydrous titanium oxide microspheres were prepared by the HMTA internal gelation process for use in converting the hydrous titanium oxide microspheres to sodium titanate microspheres. The conversion process involved several steps. First, about 325 mL of the hydrous titanium oxide microspheres was soaked in absolute ethanol to displace the free water in the microspheres. The microspheres were then heated at about 70°C for 7 h in a solution of sodium ethoxide and absolute ethanol to convert the microspheres to titanium ethoxide. About half of the reaction solution was then replaced with deionized water, and the mixture was heated to 65–70°C for 7 h. The purpose of this step was to convert the titanium ethoxide to sodium titanate. Finally, the solution was drained from the microspheres, and the microspheres were washed thoroughly with deionized water.

After further treatment, the microspheres will be evaluated in batch tests with MVST supernatant simulant to determine their effectiveness for removing strontium. Samples of air-dried microspheres will also be analyzed to determine how effective the conversion process was in making the tetrasodium nonatitanate. These results will be compared with sodium titanate microspheres that were made in an earlier preparation.

Attempts are being made to replace the silicone oil used in the HMTA internal gelation process. This would eliminate a secondary organic washing step to remove the silicone oil. The HMTA internal gelation apparatus was cleaned, and the lines were replaced. The reservoir will be filled with a binary mixture containing 60% isoamyl alcohol and 40% perchloroethylene to replace the silicone oil. A preparation of hydrous titanium oxide microspheres will be made to see if there are any operational problems.

There is a need at the Idaho National Engineering Laboratory for effective engineered sorbents for removing radionuclides and RCRA metals from acidic wastes. Ammonium molybdophosphate (AMP) has been shown to have good capacity for removing cesium from nitric acid solutions over the full range of acidity with no loss in capacity, even in solutions containing up to 4 M sodium nitrate. However, AMP is commercially available only as a fine powder and unstable granular forms that are not suitable for column operations. The HMTA internal gelation process provides a potential method for making AMP microspheres that can be used in columns. Therefore, this process is being evaluated for preparing composite microspheres containing AMP embedded in zirconium monohydrogen phosphate or titanium monohydrogen phosphate. Both these matrices are also good sorbents for a number of cations in solutions, such as groundwater. Hydrous titanium oxide and titanium phosphate have also been used to remove uranium from seawater. Batch tests were conducted using commercial AMP powder to establish baseline data for removing cesium from MVST W-27 supernatant that had been acidified. The AMP powder removed 77 to 87% of the cesium. Microspheres will be prepared, and their behavior will be compared with the AMP powder.

A paper entitled "Development and Testing of Spheroidal Inorganic Sorbents" was presented at the ESP Technical Exchange Meeting, January 28, 1997, in Gaithersburg, Maryland. Information was compiled, and a presentation was prepared for the ESP Midyear Review at Gaithersburg, Maryland.

Preparation of microspheres using the HMTA internal gelation process was demonstrated for a representative of Eichrom Industries, and transfer of the technology to Eichrom Industries was discussed.

1.5 DEVELOPMENT AND TESTING OF GLASS AND GROUT WASTE FORMS (A. J. Mattus and R. D. Spence*)

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Summary: The equipment for preparing glass and cement-based grout containing MVST sludge was installed and tested. Samples of a surrogate sludge, as well as actual sludge from MVST W-25, were immobilized in a cement-based grout. The grouts were tested for bleed-water formation and penetration resistance.

1.5.1 Purpose and Scope

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

1.5.2 Progress

Modifications to the hot-cell facility were completed, and all of the equipment necessary to prepare cement-based grouts and glass from actual MVST transuranic, mixed sludge was installed and tested. The cell has now become a dedicated hot cell for preparing grout and various types of glasses from ORNL wastes in preparation for regulatory testing. Most equipment was redesigned to be able to utilize the manipulators in the confines of the cell to prepare waste forms from very radioactive sludges and liquids. A number of special tools were designed for use in the hot cell.

*ORNL Chemical Technology Division, Engineering Development Section.

Actual transuranic sludge from MVST tank W-25 was immobilized in a cement-based grout. In addition, a reference surrogate sludge, formulated to represent an average of all the sludges in the tanks, was immobilized in the same cement-based grout. The grout products were tested for bleed-water formation. A small amount of bleed-water was produced above the surrogate-based grout but was reabsorbed overnight. Bleed-water formation is undesirable because the more soluble radioelements, such as ^{137}Cs , will concentrate on the top of the sludge, and after water reabsorption and drying, a radioactive dusting problem could result. The grout produced from the actual waste sludge contained no bleed water at all and also appeared to thicken faster during mixing.

Both the actual waste-based grout and the surrogate grouts were cast in polyvinylchloride vessels for use in testing penetration resistance. This testing was performed daily over 1 week to establish the relative rate of set, as reflected by the resistance measured when a 1/40-in.-diam plunger was forced into the grout surface. Results showed that the grout containing actual sludge from the waste tanks hardened much faster than the surrogate waste-based material, with the rate of set appearing to be nearly twice as fast using the actual waste. This observation is consistent with the fact that the bleed water, which chemically reacts with the cement phases, was more reactive. Therefore, the observed set rate was faster as a result of this enhanced cement-water reactivity. After 28 d of curing, samples of grout have been submitted for the EPA's TCLP. Preparations are now under way to begin tests with soda-lime-based glasses on these same sludges.

1.6 SEARCH FOR TECHNETIUM IN NATURAL METALLURGICAL RESIDUES (A. J. Mattus, G. W. Parker,* G. D. Del Cul, Y. Kamyshev,† Y. Efremenko‡)

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Summary: A collaborative effort with the Kidd Creek Mine in Dennison, Ontario, Canada, will determine the cost of reinstalling a flotation circuit at their site to recover tin. An experimental setup has been put in place for removing technetium isotopes from a tin metal target.

*Visiting guest scientist.

†ORNL Physics Division, guest scientist.

‡ORNL Physics Division and The University of Tennessee at Knoxville Physics Department, guest scientist on dual assignment.

1.6.1 Purpose and Scope

This multidivisional and university Seed Money project is directed at establishing the feasibility of a joint DOE and mining industry project to prove the existence of $^{97,98,99}\text{Tc}$ in tin minerals at a great depth below the earth. Normally, such isotopes originate only from above-ground nuclear tests reactors or fission of some uranium isotopes in the earth by solar radiation. This work is a supplement to well-funded, ongoing international efforts in the physics community to prove nucleon instability by experimental observation of baryon instability and remains among the most essential problems of modern-day physics. It is theorized and shown by calculation that cosmic energy as muons or neutrinos may cause natural isotopes of tin to form a distribution of technetium isotopes in sufficiently deep mines where the energy is properly attenuated. Ideally, at 2000 m below the earth in tin mines, multitonne quantities of tin ore (cassiterite) would be recovered and carefully concentrated, roasted, and smelted, avoiding surface contamination that produces an ash residue. It is thought that the technetium, as well as any rhenium present, will deposit in the resulting ash. The ash, once washed with water, would be concentrated and the technetium present analyzed by laser photo ionization spectrometers from the concentrated aqueous solution. A lower analytical detection limit of 10^6 atoms of technetium will be necessary to establish the presence of technetium isotopes.

1.6.2 Progress

During this quarter, it was found that the Kidd Creek Mine in Dennison, Ontario, Canada, will aid us in costing an effort to reinstall a flotation circuit at their site to again recover tin. In the past, the tin ore grade dropped significantly along with market prices, causing the recovery of tin to be uneconomical. Fortunately, drill core samples below 2500 m have shown that the tin ore grade is rising again, from the 0.1% tin range in the past to over 0.8% tin. This fact has caused the mine to become more interested in the reinstallation of a recovery process that was removed years ago. As part of our work this year, we will put together cost figures for such an activity that will be proposed to both DOE and mine management next fiscal year.

Recently, the mine geologist confirmed that concentrations of uranium in the ore were so low as to be below detection limits and also that molybdenum content was less than 0.002%. The presence of these elements could complicate our efforts in finding technetium produced from cosmic energy-induced transmutations in tin. Further discussions directed toward identifying all costs for reinstallation of tin recovery equipment and other tasks will be finalized during the last quarter of the fiscal year.

Additionally, an experimental setup has been put in place for removing technetium isotopes from a tin metal target. This tin sample will be melted in a tube furnace, and the melt will then be oxidized with oxygen to tin oxide. The temperature of the furnace will be raised to 950°C to volatilize technetium and capture it in a dilute hydrochloric acid solution. This solution will be used for electroplating technetium onto a platinum metal cathode at 3–4 V dc and approximately 100 mA/cm². It is expected that only 10¹⁰ to 10¹² atoms of technetium will be available to plate. The plated technetium will be analyzed for its isotopic distribution, utilizing a laser ionization mass spectrometer capable of measuring such distributions and total mass on 10⁶ atoms of technetium. As a result of the energy of the beam employed with the tin target, it is expected that the distribution will be skewed toward a distribution expected 1 mile below the earth in tin mines.

2. PROCESS CHEMISTRY AND THERMODYNAMICS

E. C. Beahm

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

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Summary: A test with sludge from Hanford underground storage tank SX-113 and a test on quartz used for verification showed that acid treatment containing hydrofluoric acid must be carried out so that an excess of fluoride is maintained. This is necessary to prevent the vapor-assisted transport of a silicon species and the deposition of silica in cooler regions.

2.1.1 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.

2.1.2 Progress

2.1.2.1 Enhanced Sludge Washing

Controlled precipitation of sodium phosphate fluoride is being evaluated in bench-scale tests with flocculants and surfactants. The flocculants were not effective in preventing the formation of

sticky crystals. A cationic surfactant aided in producing crystals that settled, but it also produced a foam. Tests of other materials are being run.

2.1.2.2 Acid Treatment

When sludge from Hanford tank SX-113 was treated with a combination of 3 *M* nitric acid plus 3 *M* hydrofluoric acid at 75°C, a porous crystalline material formed in the airspace above the liquid. This sludge contains a relatively large fraction of silica in the form of diatomaceous earth. Hydrofluoric acid is used to convert silica to the SiF_6^{-2} , which is soluble. In this way, the formation of silica gel, which can prevent pumping, coat surfaces, and retard separations, can be avoided.

However, the test results from treatment of SX-113 show that reducing the fluoride concentration in solution by reaction with excess silica or perhaps with other materials that form stable fluorides can result in transport of a silicon-containing species out of solution and ultimately in the deposition of silica in cooler, wet regions. This was verified by a bench-scale test in which silica in the form of quartz was treated using the same conditions as the test with sludge from Hanford tank SX-113. In the bench-scale test, the same deposition in the cooler gas space was observed.

It is likely that this vapor-assisted deposition of silica occurs when the fluoride in solution is consumed by reaction with silica. This would result in the conversion of some of the SiF_6^{-2} to silicon tetrafluoride, which is a gas. Silicon tetrafluoride would decompose in a cooler, wet region to form silica and hydrofluoric acid.

Material that formed above the liquid when sludge from Hanford tank SX-113 was treated with 3 *M* nitric acid plus 3 *M* hydrofluoric acid was identified as amorphous silica that contained some fluoride. This result supports a mechanism that was proposed to account for the transport of silica from sludge treatment with nitric acid and hydrofluoric acid. The formation amorphous silica by this mechanism must be controlled in acidic treatment of sludge to prevent deposition in unwanted places such as tank domes, ventilation systems, and sample lines.

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

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Summary: The distribution of iodine in containment during an AP600 design-basis accident was evaluated using models in the "TRENDS" code. A design-basis accident was formulated in which significant bypass of the pH control system occurs.

2.2.1 Purpose and Scope

The objective of this project is to provide assistance to the U.S. Nuclear Regulatory Commission staff in reviewing the four advanced reactor designs submitted under 10 CFR Part 52. This work specifically addresses the following issues: (1) the distribution of iodine species in containment following a loss-of-coolant accident, (2) the generation of 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.

2.2.2 Progress

A design-basis accident for the AP-600 reactor was formulated in which significant bypassing of the pH control system occurs. This accident sequence was conceived to present the maximum possible bypassing of the pH control system. Containment flooding would leave a small amount of water in the In-Reactor Water Storage Tank (IRWST). Under normal conditions, containment drainage gutters direct all water from condensation (including radiolytically produced acids) into the IRWST, further lowering the pH.

Some iodine released from the reactor coolant system is retained in the IRWST and never encounters pH control chemicals. Some volatilization of this iodine occurs and is transported into the principal containment airspace.

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

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Summary: Work on the collaboration with Dr. Gennady Voronin of Moscow State University continued. The goal of this joint effort is to determine the solidification conditions of yttrium, barium, and copper oxides from their melts. These conditions include temperature, pressure, oxygen partial pressure, the chemical composition of the melt, and the phase and chemical composition of the growing solids. Differential thermal analysis (DTA)/thermogravimetric analysis and hydrogen reduction have been used to determine the oxygen content of melts from phase-pure $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Y123) at partial oxygen pressures ranging from 0.1 to 0.000006 MPa. The technique is currently being applied to Y134 (Y123 + BaCuO_2). With the discovery of Y123, several attempts to determine the oxidation state of copper in Y123 have been made. Y123 can be expressed in terms of the formula $\text{YBa}_2\text{Cu}^{\text{II}}_{2+2x}\text{Cu}^{\text{III}}_{1-2x}\text{O}_{7-x}$ ($0 \leq x \leq 0.5$). However, it is possible that all of the copper in Y123 is Cu^{2+} or a combination of Cu^{1+} and Cu^{2+} and that some oxygen is present in the form of peroxide. We are currently seeking simple chemical evidence for the presence of peroxide, O_2^{2-} . The Lovibond peroxide test kit and potassium permanganate (KMnO_4) have been used with acidic solutions that contained dissolved Y123. The results were not consistent. The Lovibond test indicated a high peroxide content, while the KMnO_4 test indicated that no peroxide was present.

2.3.1 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 being placed on the phase fields that include the superconducting compounds.

2.3.2 Progress

2.3.2.1 Solidification of the Y-Ba-Cu-O System

Experimental work on the two-year collaboration with Dr. Gennady Voronin of Moscow State University continued. The goal of this joint effort is to determine the solidification conditions of yttrium, barium, and copper oxides from their melts. These conditions include temperature, pressure, oxygen partial pressure, the chemical composition of the melt, and the phase and chemical composition of the growing solids. The liquidus and solidus surfaces in the four-component Y-Ba-Cu-O (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.

The experimental phase on the Y123 melts was completed. The Y123 melts were prepared at different temperatures under partial oxygen pressures of 0.1, 0.02, 0.01, 0.001, 0.0001, and 0.00006 MPa. After the melts were allowed to equilibrate, they were reduced with hydrogen in order to determine the melt's oxygen content. These results from the Y123 experiments are being used by Dr. Voronin to develop a formal description of Y123 melt, as well as a thermodynamic simulation of the equilibria and prediction of the composition and thermodynamic functions of the liquid. It is interesting to note that the 0.02 MPa results at 1014 and 1053°C indicate the presence of two immiscible liquids. The results at the other partial oxygen pressures showed no sign of an immiscible liquid. This experimental technique is currently being applied to YBa_3Cu_4 (Y123 + BaCuO_2). The preliminary results are shown in Table 1.

2.3.2.2 Oxidation State of Copper in Y123

With the discovery of Y123, several attempts to determine the oxidation state of copper in Y123 have been made. Y123 can be expressed in terms of the formula $\text{YBa}_2\text{Cu}_{2+2x}^{\text{II}}\text{Cu}_{1-2x}^{\text{III}}\text{O}_{7-x}$ ($0 \leq x \leq 0.5$). However, it is possible that all the copper in Y123 is Cu^{II} or a combination of Cu^{I} and Cu^{II} and that some oxygen is present in the form of peroxide. Iodometric titrations and hydrogen reductions cannot distinguish between the possibilities. Attempts to determine the correct Y123 formula with a variety of techniques such as X-ray photoelectron and X-ray absorption spectroscopies

have proven to be inconclusive. We are currently seeking simple chemical evidence for the presence of peroxide, O_2^{2-} . Samples of $YBa_2Cu_3O_{6.9}$ were dissolved in HCl or HNO_3 , and a peroxide test kit from Lovibond was used to determine the peroxide concentration in these acidic solutions. This qualitative test indicated the presence of a considerable amount of peroxide. In addition, when $YBa_2Cu_3O_{6.4}$, which should contain no peroxide if the $YBa_2Cu^{II}_3(O^{2-})_{6+x}(O_2^{2-})_{0.5-x}$ formula is correct, was dissolved, the Lovibond test indicated a comparable amount of O_2^{2-} . Therefore, the Lovibond test is not suitable for the Y-Ba-Cu-O system due to an interference, or the current Y123 formulas are incorrect. Two other commercial test kits will be used with Y123.

Peroxide is a well-known oxidizing agent. However, O_2^{2-} will behave as a reducing agent if a very strong oxidant such as MnO_4^- is present.

After a 100- to 150-mg sample of $YBa_2Cu_3O_{6.9}$ was dissolved, a $KMnO_4$ solution was slowly titrated, and no peroxide was observed. This result confirmed an earlier study, which used 6-mg samples of Y123 and monitored the production of Mn^{2+} with electron spin resonance spectroscopy. Possible interferences are being investigated.

Table 1. Oxygen content of Y134 ($Y123 + BaCuO_2$) melts at various temperatures and oxygen partial pressures

Oxygen partial pressure (MPa)	Temperature ($^{\circ}C$)	Oxygen content
0.1	1052	7.60
0.1	1118	7.82
0.1	1252	7.48
0.01	1049	7.27
0.01	1152	7.39
0.01	1215	7.15
0.01	1249	7.02
0.001	1027	7.22
0.001	1092	7.32
0.001	1152	7.07
0.001	1226	6.94

3. MSRE REMEDIATION STUDIES

L. M. Toth

3.1 URANIUM CONVERSION (G. D. Del Cul, J. C. Rudolph, D. W. Simmons, J. Caja, E. Hickman, and L. M. Toth)

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Summary: Fissile ^{233}U is being recovered, trapped and removed as an essential part of the remediation and decommissioning activities presently under way at the Molten Salt Reactor Experiment (MSRE). Uranium hexafluoride (UF_6), trapped in NaF along with uranium-laden activated charcoal, represents the bulk of the inventory. For permanent storage, all of the ^{233}U needs to be recovered and transformed into a stable oxide. The experimental work to develop and test the simpler, most cost effective-process is already under way. The selection process for the actual processing facility is being completed.

3.1.1 Purpose and Scope

The MSRE at ORNL has been shut down since 1969, when the fuel salt was drained from the core into two drain tanks at the reactor site. In January 1994, analytical measurements of gas samples taken from the gas piping circuitry connected with the drain tanks indicated the presence of fluorine, 350 mm Hg, and uranium hexafluoride, 70 mm Hg. Although radiolysis was known to generate F_2 , the formation of UF_6 and its transport from the fuel salt were unexpected. These samples proved that these gaseous products had moved through the piping to a charcoal bed since the reactor was shut down. After this finding, a multiyear project was launched to remediate the potentially hazardous conditions generated by the movement of fissile material and reactive gases.

The extensive remediation and clean-up activities related to the MSRE involve (1) the trapping of the gaseous products; (2) deactivation, removal, and recovery from the activated charcoal bed; (3) stabilization and reconditioning of the fuel salt; (4) recovery of ^{233}U ; and (5) conversion of ^{233}U compounds into a stable oxide for final safe storage and disposition.

One of the essential tasks is the recovery and conversion of all of the ^{233}U materials into a stable oxide for permanent storage.

3.1.2 Progress

A simplified, closed-loop conversion system has been proven at 1/10 scale in the laboratory. This test was performed using approximately 100 g of depleted uranium. The uranium was converted to an oxide using steam hydrolysis at elevated temperatures and moderate pressures. The HF gas that

was released was trapped in a sodium hydroxide scrubber. All of the gases involved can be condensed in the scrubber; therefore, this is a fully closed system. The potential of using ammonia to reduce operating temperatures and corrosion still requires further examination. The product from this test was a black uranium oxide, which contained only 290 ppm of residual fluoride.

A sketch of the prototype reaction vessel has been sent out for estimates from several manufacturers. The selection process to determine the processing facility for the actual conversion operation is being completed. An examination of what the fluoride limit will be for final storage of the uranium oxide has been initiated. Because no packaging standard exists for ^{233}U , some testing may be required to provide information on an acceptable fluoride limit.

3.2 URANIUM DEPOSIT REMOVAL, DENATURING OF FLUORINATED CHARCOAL (G. D. Del Cul, D. W. Simmons, and L. M. Toth)

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Summary: The chemistry of activated charcoal, uranium hexafluoride, and fluorine at different temperatures is being investigated. Differential thermal calorimetry, X-ray photoelectron spectroscopy, γ -irradiation, Fourier transform infrared (FTIR), Raman, and nuclear magnetic resonance techniques are being used to determine the nature of the bonding, thermal and chemical stability, reactivity, conversion toward gaseous carbon-fluorine products, radiolytic decomposition, and other related properties. These R&D activities are in support of the MSRE remediation program.

3.2.1 Purpose and Scope

The MSRE activated charcoal bed (ACB) contains a volume of approximately 506 L of activated charcoal (6–16 mesh). The top 12 in. of the ACB is known to have about 2.3 kg of intercalated ^{233}U fluorides and oxyfluorides. According to the laboratory tests, a few feet of fluorinated charcoal is believed to extend beyond the uranium front. The rest of the ACB, about 90 ft of 6-in. pipe, should consist of unreacted charcoal.

When subjected to rapid heating, fluorinated charcoal can decompose, generating gaseous products (CF_4 , C_2F_6 , etc.). Under confined conditions, the sudden exothermic decomposition can produce high temperatures and pressures of near-explosive characteristics.

To proceed with the planned remediation and uranium recovery activities at the MSRE, it will be necessary to tap into the ACB to allow the installation of piping and instrumentation. The drilling-tapping operations can result in local heating in excess of the 100°C . Fluorinated charcoal starts to thermally decompose at temperatures above 100°C . As a consequence, it is necessary to chemically

transform the reactive fluorinated charcoal into a more stable material to safely conduct the remediation and recovery activities.

3.2.2 Progress

Preliminary calculations to determine the heat of reaction of possible "reactive" gases and fluorinated charcoal were performed with an enhanced version of SOLGAS. The results indicated that NH_3 , HI , NO , NO_2 , CO , $\text{CH}_2=\text{CH}_2$, $\text{CH}\equiv\text{CH}$, H_2O , H_2 , CS_2 , SO_2 , B_2H_6 , BCl_3 , and SiH_4 were likely candidates.

All of the possible candidates were experimentally tested using small batches of C_xF (about 1 g of material) contacted for at least 10 days with each reagent. At the end of each soaking period, the reagent was evacuated and the treated samples heated rapidly using a torch.

Of all the reagent tested, only ammonia gas was able to transform the potentially reactive fluorinated charcoal into a stable material that can be safely heated.

Ammonia can be administered to the ACB as a volatile denaturing agent that results in the conversion of the C_xF to carbon and ammonium fluoride, NH_4F . The charcoal laden with NH_4F can be heated without risking any sudden decomposition. The only consequence of heating the treated material will be the volatilization of NH_4F as a mixture of NH_3 and HF that would recombine primarily as NH_4F on surfaces below 200°C . Of course, the remaining charcoal would ignite in air or oxygen at higher temperatures.

Since the passivation using NH_3 gas appears to fulfill the requirements, column experiments are under way.

3.3 SALT DISPOSITION (D. F. Williams, S. L. Loghry, and L. M. Toth)

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Summary: Uranium hexafluoride, UF_6 , has never been generated in laboratory tests on simulated fuel salt exposed to the high gamma flux from a spent High Flux Isotope Reactor fuel element. Nevertheless, considerable amounts of fluorine are generated. However, we have found that on heating the radiolyzed salt with its fluorine (generated by radiolysis) cover gas to 205°C (the temperature at which the MSRE fuel salt was annually annealed) for a period of 1–2 weeks, a considerable amount of UF_6 appeared in the cover gas due to the simple oxidation of the UF_4 in the solid salt solution. These findings support the discontinuance of the annual MSRE annealing operation that was recommended in the late 1980s until a clear understanding of the phenomena taking place could be developed.

3.3.1 Purpose and Scope

This R&D effort is focused on identifying the mechanism of formation of the UF_6 found in the MSRE gas piping system and the associated effects of long-term radiolysis on the fuel salt itself. As a result of these studies, it is anticipated that the reasons for the unexpected appearance of UF_6 during the annealing cycles could be found and an efficient and safe means of salt removal from the MSRE drain tanks will result.

3.3.2 Progress

Efforts again were concentrated on experiments related to MSRE remediation: (1) irradiation of simulant salt in an oxygen atmosphere, (2) annealing treatment of irradiated simulant salt, and (3) ClF_3 trapping tests.

The third and fourth cycle of irradiations of the simulant salt designated MSR-3 were completed, and the measured fluorine generation rate and plateau damage limit agree with previous work. Infrared (IR) spectroscopic analysis of the cover gas after each cycle of irradiation showed that no UF_6 was present. This irradiated salt was then subjected to a treatment that mimics the annual fuel-salt annealing operation conducted between 1971 and 1989. One atmosphere of fluorine was charged to the irradiation specimen, and the sample was rapidly heated to 205°C and held at this temperature for 2 weeks. During this treatment the cover gas pressure decreased steadily and was periodically restored to 1 atm by addition of fluorine. The fluorine consumed during this operation corresponds to recombination with about 40% of the metal sites produced by radiolysis.

Strong UF_6 absorption bands were detected in the cover gas after this treatment. Based upon the strength of the IR bands, it is estimated that about 30% of the uranium was removed as UF_6 . This result indicates that heating of the salt is required to either generate or liberate UF_6 . To answer the question of whether UF_6 is generated by the heat treatment or merely liberated by heating, an annealing treatment of unirradiated salt (with a fluorine cover gas) will be compared with an annealing treatment of irradiated salt (with a helium cover gas).

A brief study of the trapping of ClF_3 by fixed beds of alumina and molecular sieve was carried out in order to address some unresolved questions about the safety and performance of the Reactive Gas Removal System at MSRE. The performance (i.e., loadings and flow limits) of these materials with ClF_3 is roughly equivalent to that found during earlier work with F_2 trapping. The levels of halogen oxides generated were very low, and the ClO_2 concentration was far below the lower explosion limit. This work has been documented in a draft report (ORNL/TM-13403) that will be issued in April 1997.

In summary, UF_6 was found in the cover gas from a frozen MSRE simulant salt for the first time. It appears that heating of the salt for a prolonged period is required to remove uranium from the salt.

3.4 PUBLICATIONS

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4. CHEMISTRY RESEARCH

L. M. Toth

4.1 ARTIFICIAL ANTIBODY STRATEGY FOR URANYL SEPARATION (S. Dai, Y. Shin, M. Burleigh, and L. M. Toth)

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Summary: The properties of sol-gel glasses templated with uranyl ions have been investigated. Techniques have been developed to remove the template uranyl ions from silica matrices to create uranyl-imprinted sol-gel silica glasses. A significant increase in affinity *and* selectivity of the imprinted sol-gel sorbents over control blanks has been observed, while the surface areas of both remain equal. The enhanced capacity and selectivity are tentatively attributed to the change of the binding constant and the modification of the microporous structure of the sol-gel glasses induced by the imprinting technique. We have been invited to contribute a paper to a special issue of *Chemical Materials* dedicated to advanced applications of sol-gel technology.

4.1.1 Purpose and Scope

Recently, the approach of imprinting organic polymers with neutral molecule and ion templates has shown promise in several areas of separations technology. The idea behind imprinted materials is to combine the binding ability of specifically chosen functional groups or ligands for target substrates with shape- and size-selective cavities "imprinted" in a rigid polymer matrix to produce materials that will selectively bind target substrates with high affinity. The imprint is produced by a template present during the formation of the solid matrix. After the templating species is removed from the polymer, a predetermined arrangement of ligands and a tailored binding pocket are left. Such imprinted polymers have been used to resolve racemates and separate mixtures of metal cations. Other recent applications of templating include the preparation of lamellar silica, templated molecular sieves, and biominerals.

There is, to our knowledge, no molecular-template approach to imprinted sol-gel materials for radionuclide recognition. In this task, we are conducting research, the goal of which is to elucidate the scientific basis for developing imprinted sol-gel materials that will exhibit enhanced recognition and selective binding of radionuclide ions. The fundamental principles that are developed through this research should be directly applicable to the ultimate design and synthesis of novel imprinted sol-gel materials that will be more selective and efficient than the current extraction technologies in mixed waste characterization, treatment, and disposal.

4.1.2 Progress

It is known that the uptake of uranyl ion by silica sorbent materials is strongly pH dependent due to the equilibria of surface-functional groups. The lower the pH of the solution, the lower is the adsorption capacity of the sorbent. In fact, the adsorption capability of silica-based sorbents toward UO_2^{2+} is negligible below a pH of 2. This characteristic in the uranyl binding to silicates prompted us to adopt acid washing as a method to efficiently remove the uranyl template ions from our sol-gel glasses. Uranyl-free imprinted glasses were obtained by soaking the UO_2^{2+} -doped glasses with nitric acid overnight. The pH dependence of adsorption capacities for imprinted and blank sol-gel sorbents has been determined experimentally. The adsorption capacities of the imprinted glass are greater than those of the control blank at all pH values investigated. The chemical equilibrium analysis leads to the conclusion that the surface complexation of uranyl ion with the imprinted sample is stronger than that of the control blank sample. Adsorption isotherms for the sorbent samples were obtained by immersion in HOAc/NaOAc (0.26 M/0.54 M) buffer solutions (pH = 5.06) containing various concentrations of uranyl ion (10^{-3} to 10^{-2} M) for 24 h. The use of this buffer solution was essential to keep the solution pH constant while the uranyl concentration was varied. Uranyl uptake from the solution was measured by the decrease of the total uranyl concentration in the solution. The use of buffered solutions ensures the same pH value for all samples, thereby resulting in the same surface charge of the sorbents. Accordingly, any adsorption differences can only be attributed to the uranyl adsorption equilibrium constants, rather than to changes in the surface charge. The imprinted sample rebinds uranyl ion more strongly than the blank sample. The adsorption isotherms of both glasses cannot be described by Langmuir adsorption model (type I). The general shapes are close to that of type V.

4.2 FUNDAMENTAL CHEMISTRY OF ACTINIDES AND FISSION PRODUCTS IN MOLTEN SALTS (S. Dai, Y. Shin, M. Burleigh, and L. M. Toth)

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Summary: The effect of hydrogen bonding on uv-vis spectra of uranyl chloride complex species was investigated in room-temperature molten salts. The variation of the hydrogen-bonding capability can be used to rationalize the solubility difference of UO_3 in the melt systems investigated. A paper has been submitted to *Inorganic Chemistry* for publication.

4.2.1 Purpose and Scope

The overall objective of this research is to explore fundamental chemistry involving actinides and fission products in high-temperature and room-temperature molten salts. The subject investigated during this quarter is a continuation of the research aimed to probe fundamental interactions involved in dissolution of actinide oxides in molten salts. The knowledge gained through this investigation will help to rationally design pyrochemical or ambient chemical processing involving ionic liquids.

4.2.2 Progress

More materials of 1,2-dimethyl-3-propylimidazolium chloride (DMPIC) were synthesized for preparation of basic melts composed of DMPIC/ AlCl_3 mixtures. The optical spectrum of the uranyl chloride complex was reinvestigated using melts obtained by the dissolution of UO_2Cl_2 instead of UO_3 . The same optical spectra were obtained for both systems, thereby indicating no effect of oxide impurities on the optical spectrum of the uranyl chloride complex. Similarly, we have experimentally shown that there were no differences between the spectrum measured using the melt with phosgene pretreatment and that without this pretreatment. These results further substantiated our previous assertion that the change in the vibronic intensity ratios in the optical spectra of the uranyl complex in room-temperature melts can be attributed to the hydrogen bonding.

4.3 IN-LINE SPECTROSCOPIC SENSOR FOR ALUMINUM INDUSTRIES (S. Dai)

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Summary: Along with our colleagues in the CASD, we have successfully designed and tested a noncontact fiberoptic Raman sensor for high-temperature aluminum electrolytic processes involving melts formed from NaF , AlF_3 and Al_2O_3 at 1000°C . Speciation of such fluoride melts has been conducted.

4.3.1 Purpose and Scope

This is the second year of the small-scale research funded by a cooperative research and development agreement (CRADA) program with CASD. The objective is to develop in-line fiberoptic sensors for three U.S. aluminum companies (Kaiser Aluminum, Alumax, and Reynolds). The success of the program will lead to a significant reduction of energy consumption for this industry.

4.3.2 Progress

Several NaF-AlF₃ melts with different molar ratios were prepared for Raman spectral studies. The AlF₃ was obtained from ROC/RIC (Belleville, NJ) and purified by sublimation in a closed graphite container at 920–940°C. The cryolite (Na₃AlF₆) used was Greenland handpicked natural cryolite. Raman spectra for the prepared samples were obtained using a noncontact fiberoptic Raman setup from room temperature to high temperature. The equilibrium between AlF₄⁻ and AlF₆³⁻ in molten Greenland salts has been established via Raman spectroscopy.

4.4 SOLUBILITIES OF UO₃ IN CARBONATE BUFFER SOLUTIONS AT HIGH TEMPERATURE (>100°C) (S. Dai)

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Summary: Along with our colleagues in CASD, a protocol for accurately measuring solubilities of UO₃ in carbonate solutions at high temperature was established. The setup has been used to determine solubilities of UO₃ at three temperatures.

4.4.1 Purpose and Scope

This project was funded by a research program in CASD. The objective of this research is to provide experimental solubility data of radionuclides in high-temperature aqueous solutions, which are important in understanding the hydrothermal oxidation processing of DOE hazardous and mixed wastes.

4.4.2 Progress

Microspectrophotometric protocol for determining concentrations of uranyl carbonate complexes in high-temperature aqueous solutions was established. The protocol involves heating capillaries of saturated uranyl carbonate solutions in a constant aluminum block for 1 week, followed by microfiltration. The filtrates are then used in the microspectroscopic measurement. The method was validated in a comparative study of determination of the UO₃ solubility at 150°C using two different

starting solutions. One solution consists of UO_3 in contact with aqueous carbonate solutions, while the other is a supersaturated uranyl carbonate solution. After being heated in a furnace at 150°C for 3 weeks, the determination of uranyl concentrations in the solutions resulted in the same value (in the range of experimental errors). This indicated that the dissolution equilibrium has been reached and the solubility thus determined was reliable. We have also conducted a series of the dissolution kinetic investigations. These experiments showed that the rate of approaching the above dissolution equilibrium from the supersaturated samples is much slower than that of the undersaturated samples.

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5. SEPARATIONS AND MATERIALS SYNTHESIS

D. W. DePaoli

5.1 CHEMICAL AND PHYSICAL PRINCIPLES IN MULTIPHASE SEPARATIONS (D. W. DePaoli, C. Tsouris, X. Zhang, and M. A. Spurrier)

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Summary: Fundamental studies that explore the use of electromagnetic fields to enhance transport processes in multiphase separations are continuing. Progress was made in several areas, including (1) modeling of the breakup of a stretching liquid bridge with an applied electric field, (2) drop deformation and breakup from a capillary tube in liquid-air and liquid-liquid systems, (3) interactions between droplets in multiple jets during electrospraying of liquids in air, (4) quantification of the characteristic regimes of inverse electrostatic spraying, and (5) development of experimental techniques for quantification of mixing in electrohydrodynamic flows.

5.1.1 Purpose and Scope

This program is comprised of several fundamental studies that explore the use of electromagnetic fields to enhance the efficiency of multiphase separations processes. Experimental, theoretical, and computational methods are employed to investigate the effect of electromagnetic fields on transport processes in liquid-liquid, gas-liquid, and solid-liquid systems. This work will provide the information necessary to devise novel means to dramatically improve transport rates in these systems, thus providing widespread benefit for separations processes such as solvent extraction and distillation as well as applications in environmental and biotechnology areas. The areas of current focus are (1) interface deformation and breakup, including electrostatic spraying (both "normal" and "inverse"), drop formation, drop oscillations, stretching liquid bridges, and drop impact; (2) interactions and coalescence of drops; and (3) enhancement of transport processes through electrohydrodynamic flows.

5.1.2 Progress

5.1.2.1 Interface Deformation and Breakup

Numerical simulations of effects of an electric field on stretching liquid surfaces using a one-dimensional model have been completed in collaboration with Professor Basaran at Purdue University. A manuscript describing the computational and experimental methods and results is being prepared for publication in the *Journal of Electrostatics*. The model has been extended to two-dimensional calculations in order to more accurately simulate the effects of electric field on surface stability and breakup. A model based on the "volume of fluid" method has been modified to simulate

drop deformation and breakup from a capillary tube in liquid-air and liquid-liquid systems. Extensive computations have been carried out for liquid-air systems at different physical conditions. This study is particularly important in exploring the velocity field of drop liquid, which is essential for predicting mass transfer during drop formation.

Research work conducted in collaboration with the Georgia Institute of Technology on electrostatic spraying of air in water through electrified capillaries focused on the spraying modes with respect to two dimensionless quantities, Reynolds number and a Weber number modified to include electrical forces. It was found that a dripping mode occurs at low Weber numbers and high Reynolds numbers, while a spraying mode occurs at high Weber numbers and low Reynolds numbers. At moderate Weber and Reynolds numbers, an intermediate dripping-spraying mode is observed. These results can be explained based on the charge relaxation times of air and water and are important in selecting optimum conditions for energy-efficient and effective electrostatic spraying.

5.1.2.2 Interactions and Coalescence of Drops

Work has been initiated to analyze the poorly understood electrohydrodynamic interactions between droplets in multiple jets during electrospraying of liquids in air. The interactions are studied experimentally using a phase-Doppler anemometer, measuring the distribution of droplet size and axial velocity in terms of the distance between two nozzles.

5.1.2.3 Enhancement of Transport Processes Through Electrohydrodynamic Flows

Recent research on inverse electrostatic spraying has indicated that the electrohydrodynamic flows generated may be exploited for mixing in single-phase and multiphase systems. Experiments employing high-speed imaging and phase-Doppler velocimetry are being developed to quantify the flows and level of mixing under various conditions. Preliminary results show promise for these methods.

5.2 NUCLEATION, GROWTH, AND TRANSPORT PHENOMENA (M. Z. Hu, C. H. Byers, and J. T. Zielke)

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Summary: This project involves fundamental studies of the mechanisms, kinetics, and thermodynamics of nucleation and particle growth in systems for the synthesis of ultrafine inorganic particles. Dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS) studies of the thermal hydrolysis of aqueous solutions of zirconyl salts were completed. In addition, it was shown that under thermal hydrolysis conditions, the aqueous-alcohol solutions of inorganic salts can be kinetically efficient alternatives to alkoxide systems for sol-gel processing. Studies of the hydrolysis and condensation of zirconium butoxide under base-catalyzed conditions were completed, while the

growth kinetics and structure of polymers under acid-catalyzed conditions were studied extensively by SAXS. The data indicate that growth of zirconium polymers occurs by a diffusion-limited, cluster-cluster aggregation process. Preliminary studies for two new approaches for ultrafine particle synthesis have also been conducted. Three publications presenting the results of these studies were prepared.

5.2.1 Purpose and Scope

This materials sciences research program involves fundamental studies of chemically reactive systems for synthesis of ultrafine (particularly nanosized), monodispersed particles (i.e., metal-oxide ceramic precursor powders). A primary goal is the understanding of the mechanisms, kinetics, and thermodynamics of nucleation and particle growth under controlled sol-gel and chemical processing conditions.

Our current emphasis lies with the chemistry, reaction engineering, colloidal/interfacial sciences, and materials sciences in two major reaction systems: (1) alkoxide precipitation (via acid- or base-catalyzed hydrolysis and condensation) from water-alcoholic solvent; and (2) forced hydrolysis via hydrothermal processing of inorganic salt solutions. Experiments utilize several specially developed techniques, including low-power DLS, rapid-mixing flow cell coupled with FTIR and SAXS, as well as X-Ray diffraction (XRD), electron microscopy, Raman spectroscopy, and electrostatic spraying.

It is anticipated that the results of this work will have significant impacts upon development of advanced materials such as nanophase ceramics that have properties that are dramatically improved over those of traditional ceramics. These advanced ceramics are potential candidates for structural ceramics, electroceramics, catalysts, nanocrystalline thin films, coatings, and nanostructured inorganic membranes. Nanosized particles represent the major precursors for the fabrication of nanophase materials.

5.2.2 Progress

Progress was made in four distinct areas of materials synthesis: (1) synthesis and characterization of nanosized, monodispersed ceramic precursor particles by forced hydrolysis, (2) sol-gel processing for advanced materials synthesis in alkoxide systems, (3) supercritical fluids processing in preparation of ultrafine particles and inorganic membranes, and (4) ultrafine particle synthesis by inverse electrostatic spraying (IES).

5.2.2.1 Forced Hydrolysis

We have completed DLS and SAXS studies of the thermal hydrolysis of aqueous solutions of zirconyl salts for synthesis of cubic-shaped, nanocrystalline zirconia particles. The nucleation and growth processes from a zirconium oligomer to a monoclinic zirconia particle were explored, with

particular emphasis on the kinetic characterizations. Two manuscripts were prepared during this reporting period. Moreover, we discovered that under thermal hydrolysis conditions, the aqueous-alcohol mixture solutions of inorganic salts can be kinetically efficient alternatives to alkoxide systems for sol-gel processing. Preliminary results showed that the addition of isopropanol to zirconyl salt aqueous solutions dramatically improved the kinetic performance by decreasing the induction period and increasing the particle growth rate. Addition of alcohol solvent can be used to control particle morphology. Instead of cubic-shaped particles, perfect spherical particles are produced from thermal hydrolysis in aqueous-alcohol solutions. In addition, the temperature to induce the homogeneous precipitation dropped significantly with increasing alcohol concentration, decreasing the thermal energy requirement for the process. This alternative powder synthesis route opens up great opportunity in efficient production of diversified ceramic precursor powders. Our study elucidated that this alcohol solvent effect may be partially attributed to a reduction of dielectric constant. FTIR experiments are under way to verify the potential reactive mechanism. We are also in the process of setting up a research collaboration with Dr. Camden Hubbard's group within the ORNL Metals and Ceramics Division in order to access the High Temperature Materials Laboratory (HTML) facilities (XRD, TGA/DTA, etc.) for powder materials characterization.

5.2.2.2 Sol-Gel Processing in Alkoxide Systems

In collaboration with Amit Singhal and J.-S. Lin, we have completed studies on the hydrolysis and condensation of zirconium butoxide under base-catalyzed conditions using a rapid-mixing flow-cell technique coupled with FTIR and SAXS. Jason T. Zielke, who worked with us in this area, successfully defended his Master's thesis. One manuscript is in preparation.

Under acid-catalyzed conditions, the growth kinetics and structure of polymers in zirconium butoxide solutions were studied extensively by using the SAXS instrument. Data for both early and later stages were collected. It was concluded that the growth of zirconium polymers occurs by a diffusion-limited cluster-cluster aggregation process. One manuscript has been prepared on this subject.

5.2.2.3 Supercritical Fluids Processing of Particles and Inorganic Membranes

A research collaboration was initiated with Professor N.-P. Xu at Nanking University of Chemical Technology. Two research studies are planned: (1) microsphere formation of aluminum isopropoxide from rapid expansion of supercritical fluid solution using a nozzle with novel configuration and (2) ultrafine particle recovery by a unique inorganic membrane technique. Experimental apparatuses were set up during this reporting period.

5.2.2.4 Ultrafine Particle Synthesis by Inverse Electrostatic Spraying

The goal of this study is to explore the possibility of applying IES (electrostatic spraying of relatively nonconductive fluids into more conductive fluids) for continuous production of ultrafine particles. Several preliminary experiments have been conducted in collaboration with D. W. DePaoli. It was found that the reactive liquids could be well dispersed by IES; however, the produced particles tended to aggregate into undesirable larger flocs. Future experiments will be designed to stabilize the colloidal particles generated by adjusting the process conditions.

5.3 PHASE EQUILIBRIA MODIFICATION BY ELECTRIC FIELDS (C. Tsouris, V. M. Shah, S. S. Laughlin, and K. D. Blankenship)

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Summary: Fundamental studies are being undertaken that explore the use of electric fields to modify phase equilibria in multiphase separations processes. Experimental systems have been assembled and are currently used to investigate the effect of electric fields on vapor-liquid and liquid-liquid systems. Batch-distillation, vapor-liquid equilibria, and liquid-liquid equilibria experiments are in progress, using various liquid mixtures of polar-nonpolar, polar-polar, and nonpolar-nonpolar components. The results obtained to date suggest that electric fields may cause modification of vapor-liquid equilibria in some systems, while more experiments are needed to investigate the effects of electric fields on liquid-liquid equilibria.

5.3.1 Purpose and Scope

The primary objective of this project is to enhance separations by applying an electric field across an interface in order to change phase equilibria or the distribution of a solute between two phases. Electric fields have been known to interact with charge carriers, such as ions and electrons, leading to higher mass and heat transfer rates, fluid atomization, mixing, and pumping, which are transport phenomena. In contrast, the effects of electric fields on the behavior of noncharged molecules and the macroscopic thermodynamic behavior of the system are examined in this project. The behavior of various types of molecules under the influence of electric fields and the macroscopic effects of electric fields on such properties as dielectric constant and phase equilibria are investigated.

5.3.2 Progress

Experimental systems have been assembled and are currently used for vapor-liquid and liquid-liquid studies. Batch-distillation, vapor-liquid equilibria, and liquid-liquid equilibria experiments are in progress. Various liquid mixtures of polar-nonpolar, polar-polar, and nonpolar-nonpolar components are being used in these experiments. Experiments with binary mixtures of

nonpolar-nonpolar systems, such as toluene-hexane, showed no effect of electric fields on either batch distillation or phase equilibria. Experiments with isopropyl alcohol and water, however, which is a polar-polar system, showed a significant effect of electric fields in both batch distillation and phase equilibria. A specially designed continuous-flow cell has been constructed from Teflon and used in FTIR spectroscopy studies with the objective of determining the effect of electric fields on hydrogen bonding in pure liquids and mixtures. After some preliminary experiments, it was concluded that further cell modifications are needed in order to obtain meaningful measurements. Liquid-liquid equilibria experiments showed that a strong electric field across an interface causes electrohydrodynamic (EHD) flow that is undesirable for isolating and quantifying any electric-field effects on equilibria. Thus, the limitation in this system comes from EHD effects, rather than electrical breakdown, and allows only a moderate electric field across the interface that may not be strong enough to cause thermodynamic changes.

The results obtained to date suggest that electric fields may cause modification of vapor-liquid-equilibria in some systems, while more experiments are needed to investigate the effects of electric fields on liquid-liquid equilibria.

5.4 MAGNETIC-SEEDING FILTRATION (D. W. DePaoli, C. Tsouris, M. R. Chaitin, and M. A. Spurrier)

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Summary: Laboratory studies conducted previously in this project with model systems and waste surrogates have shown that magnetic-seeding filtration may be applicable for the removal of solids from a wide range of waste streams. Current efforts are focused on initiating bench testing of two systems: (1) removal of iron-containing precipitates that have caused significant problems in treatment of contaminated groundwater by ion exchange and (2) removal of solids/gels that may be formed in solutions that result from caustic leaching of tank sludges. Modeling aimed at developing predictive design tools is in progress.

5.4.1 Purpose and Scope

This project is focused on the development of magnetic-seeding filtration for the enhanced removal of magnetic and nonmagnetic particulates from DOE waste liquids. The technology involves the addition of a small amount of magnetic seed particles (such as naturally occurring iron oxide) to a waste suspension, followed by magnetic filtration. This technology is applicable to a wide range of liquid wastes, including groundwater, process waters, and tank supernatants. At this point, the state of development of the technology is at the bench scale; laboratory studies and fundamental modeling are currently being employed in this project to determine the capabilities of the process.

5.4.2 Progress

Experimental work on flocculation and filtration of synthetic polystyrene microspheres, sodium titanate sorbent particles, ANL magnetic sorbent particles, MVST surrogate suspension, and Radiochemical Engineering Development Center surrogate low-level waste has been completed. The effects of solution properties, such as pH and ionic strength, and operating parameters, such as energy input in the flocculation tank, flow rate of particle suspension through the magnetic filter, particle concentration, particle size, filter packing density, and magnetic-field strength on the separation efficiency of the particles have been studied. Removal efficiencies of greater than 99% were obtained for all types of particles under various conditions. It was also found that particle breakthrough from the filter occurs faster as the strength of the magnetic field is decreased and the flow rate is increased. Efforts to model particle flocculation and filtration were continued. Turbulent-shear-flocculation modeling results showed that only less than 10% of particle collisions lead to flocculation. Modeling of high-gradient magnetic filtration (HGMF) led to the calculation of the filtration efficiency of particles as a function of particle magnetic susceptibility, particle size, magnetic-field strength, filter packing density and saturation magnetization, filter length, and flow rate of the suspension. In summary, the experimental data showed that magnetic-seeding filtration is an effective method to separate colloidal particles from wastewaters. Furthermore, the modeling results showed that magnetically seeded HGMF processes can be designed and optimized based on geometrical factors, physical properties, and operating conditions.

A plan for bench-scale testing of magnetic-seeding filtration was developed that focuses on two systems: (1) removal of iron-containing particulates that foul groundwater treatment processes and (2) removal of solids that form in tank sludge-washing solutions. A letter report describing the plan was submitted to ESP management in fulfillment of a project milestone.

5.5 ELECTROSTATIC OZONATION (C. Tsouris, D. W. DePaoli, W.-T. Shin, and S. Yiaccoumi)

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Summary: The enhancement of oxidation of organic pollutants in aqueous solutions by using electric fields to form microbubbles containing ozone is investigated in this task. Experimental work is in its initial stages, and at this point, no results are reported.

5.5.1 Purpose and Scope

The primary objective of this project is to enhance the efficiency of ozonation processes by IES. Ozone is a strong oxidant of organic molecules with fast reaction kinetics; thus, in most cases ozonation is a mass-transfer-limited process that can be improved by decreasing the size of ozone-containing gas bubbles. Introduction of ozone in the form of microbubbles will enhance efficiency both by increasing the surface area per unit volume between the gas and liquid phases and by increasing the gas volume fraction (since smaller bubbles travel more slowly than larger bubbles). This project is aimed at applying the knowledge gained in our fundamental studies of IES to develop an efficient means for production of ozone-containing microbubbles. The work may significantly impact a wide range of processes, including operations in the pulp and paper industry, ultrapure water production for the semiconductor industry, municipal potable water production, and wastewater treatment.

5.5.2 Progress

G. Duncan Hitchens, Vice President of Lynntech, Inc. visited ORNL on February 20, 1997, to discuss his company's developments in ozonation technologies. Dr. Hitchens emphasized that a major limitation that Lynntech has experienced is efficient contacting of ozone-containing gas with the water to be treated; he expressed interest in collaborating with us regarding microbubble production for efficient mass transfer. Lynntech has devised an electrochemical ozone generator that produces ozone levels five times higher than conventional corona discharge generators; a combination of higher-concentration gas and efficient mass transfer may lead to greatly enhanced performance. To further pursue these ideas, C. Tsouris visited Lynntech on March 17, 1997, and obtained an ozonator to be used in our experiments. Experimental systems have been set up at ORNL to study improved electrostatic spraying and at Georgia Institute of Technology to measure the impact of microbubble production on ozonation efficiency. The experimental work is in its initial stages, and at this point no results are reported.

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6. SOLUTION THERMODYNAMICS

H. D. Cochran

6.1 INTERACTIONS OF SOLUTES, SOLVENTS, AND SURFACES (H. D. Cochran)

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Summary: Molecular-based studies of solutions in supercritical fluids include X-ray and neutron scattering experiments, molecular simulations, and integral equation theory to pursue fundamental understanding of how supercritical solutions behave in practical separations processes.

6.1.1 Objective

This program focuses on our fundamental interest in understanding the practical behavior of separation processes in terms of the underlying molecular interactions. It addresses two areas where previously available theory has proven inadequate: (1) supercritical solutions are characterized by interactions between molecules that are extremely disparate in size and attractive energy, and (2) the dynamics of adsorption is dominated by the effect of extreme nonhomogeneity.

6.1.2 Progress

Two manuscripts were prepared for the 4th International Symposium on Supercritical Fluids and subsequently submitted for publication in the *Journal of Supercritical Fluids*—"Molecular Adsorption: Repulsive and Attractive Supercritical Fluid Mixtures" and "SAXS and SANS Studies of Surfactants and Reverse Micelles in Supercritical CO₂." On the poster promoting the upcoming Symposium in Japan, our contribution is indicated as a "highlight" of the meeting.

A proposal, "Extraction of High-Value Food Components from Aqueous Dispersions in Supercritical CO₂," has been submitted to the U.S. Department of Agriculture Fund for Rural America from The University of Tennessee (UT).

6.2 ELECTRODISPERSION OF H₂O IN SUPERCRITICAL CO₂ (K. D. Heath, V. M. Shah, C. H. Byers, and H. D. Cochran)

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Summary: This Seed Money project aims to demonstrate the feasibility of producing stable microdispersions of water in supercritical carbon dioxide using high-intensity electrical fields. Apparatus is being assembled and tested.

6.2.1 Objective

This Seed Money project aims to demonstrate the feasibility of producing stable microdispersions of water in supercritical carbon dioxide using high-intensity electrical fields.

6.2.2 Progress

The apparatus has been assembled, hydrostatically tested, and operated with supercritical CO₂ with an existing view cell (2000 psi) at UT. A new 5000-psi view cell has been ordered. A high-voltage electrical feedthrough and electrodes are being installed in the existing cell. High-voltage testing will take place at UT next quarter before moving the equipment to ORNL. The hood for installation of the apparatus in Lab 208 of Building 4501 at ORNL has been decontaminated and prepared for the equipment installation.

6.3 MOLECULAR-BASED STUDY OF REVERSE MICELLES IN SUPERCRITICAL CO₂ (P. T. Cummings, H. D. Cochran, G. D. Wignall, J. M. DeSimone, E. J. Beckman, J. D. Londono, S.-T. Cui, S. Salaniwal, and K. D. Heath)

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Summary: This multi-institutional project aims to develop a molecular understanding of reverse micelles in supercritical carbon dioxide through small-angle scattering experiments and molecular simulation calculations and, in particular, to determine what molecular characteristics lead to successful surfactants for this application.

6.3.1 Objective

The aim of this multi-institutional project is to develop a molecular understanding of reverse micelles in supercritical carbon dioxide through SAXS experiments and molecular simulation calculations and, in particular, to determine what molecular characteristics lead to successful surfactants for this application.

6.3.2 Progress

We have developed and tested a new potential model for normal perfluoroalkanes which accurately predicts vapor-liquid equilibrium and critical points for those systems that have been measured. An existing accurate model for CO₂ has been implemented in our molecular dynamics code, and we have simulated infinitely dilute normal alkanes and perfluoroalkanes in supercritical CO₂. Chemical potential calculation is being programmed. Our current aim is to develop and validate accurate interaction models for these elementary binary systems and then move to more complex systems.

Commercially available Krytox surfactants and appropriate solvents for cleaning the SAXS and small-angle neutron scattering (SANS) cells have been specified and will be purchased. A suit of developmental surfactant samples synthesized by Professor Eric Beckman's group at the University of Pittsburgh is being put together by his graduate student for our use. The SAXS cell with its new diamond windows has been made leak tight in preparation for experiments.

6.4 PUBLICATIONS

- S. T. Cui, P. T. Cummings, and H. D. Cochran, "The Calculation of Viscosity of Liquid *n*-Decane and *n*-Hexadecane by the Green-Kubo Method," *Mol. Phys.*, submitted (1997).
- J. D. Moore, S. T. Cui, H. D. Cochran, and P. T. Cummings, "Lubricant Characterization by Molecular Simulation," *AIChE J.*, submitted (1997).
- L. L. Lee and H. D. Cochran, "Molecular Adsorption: Repulsive and Attractive Supercritical Fluid Mixtures," *J. Supercrit. Fluids*, submitted (1997).
- J. D. Londono, R. S. Dharmapurikar, G. D. Wignall, and H. D. Cochran, "SAXS and SANS Studies of Surfactants and Reverse Micelles in Supercritical CO₂," *J. Supercrit. Fluids*, submitted (1997).
- M. J. Stevens, M. Mondello, G. S. Grest, S. T. Cui, H. D. Cochran, and P. T. Cummings, "Comparison of Shear Flow of Hexadecane in a Confined Flow and in Bulk," *J. Chem. Phys.* **106**, 7303-14 (1997).
- D. Chillura-Martino, R. Triolo, J. B. McClain, J. R. Combes, D. E. Betts, D. A. Canelas, J. D. Londono, H. D. Cochran, G. D. Wignall, and J. M. DeSimone, "Neutron Scattering Characterization of Homopolymers and Graft-Copolymer Micelles in Supercritical Carbon Dioxide," *J. Mol. Str.* **383**, 3-10 (1996).

7. BIOTECHNOLOGY RESEARCH

E. Greenbaum

7.1 KINETICS OF ENZYME-CATALYZED REACTIONS (E. Greenbaum, J. Woodward, J. W. Lee, C. V. Tevault, and S. L. Blankinship)

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Summary: During this report period, Photosystem II (PSII) photosynthesis was demonstrated by simultaneous photoevolution of H_2 and O_2 using several newly acquired Photosystem I (PSI)-deficient mutants of *Chlamydomonas*: CC-3362 (A-66-8), CC-3363 (ACC-238), B4-PsaA delta-2, and F8-PsaA delta-2. Among them, the most noteworthy are B4-PsaA delta-2 and F8-PsaA delta-2. Both of them were created by deletion of the second exon of the PsaA gene in the chloroplast genome. The significance of this result is that this is the first example of photoactivity in deletion mutants of *Chlamydomonas reinhardtii*.

7.1.1 Purpose and Scope

This task is focused on fundamental research in photosynthesis and enzymology. Basic research on the physical and chemical mechanisms of photosynthesis is being performed using an original experimental approach. Sustained simultaneous photoevolution of molecular hydrogen and oxygen production is measured, as well as absolute single-turnover saturating flash yields. Current research is centered around photosynthesis in mutants of the green alga *Chlamydomonas reinhardtii* that lack detectable levels of PSI and its implication for thermodynamic conversion efficiency of light energy into chemical energy. In addition, experiments on the fundamental mechanisms of cellulose hydrolysis and enzymatic production of hydrogen is being studied by a variety of biochemical and biophysical techniques, including scanning tunneling microscopy and atomic force microscopy.

7.1.2 Progress

During this report period, PSII photosynthesis was demonstrated by simultaneous photoevolution of H_2 and O_2 using several newly acquired PSI-deficient mutants of *Chlamydomonas*: CC-3362 (A-66-8), CC-3363 (ACC-238), B4-PsaA delta-2, and F8-PsaA delta-2. Among them, the most noteworthy are B4-PsaA delta-2 and F8-PsaA delta-2. Both were created by deletion of the second exon of the PsaA gene in the chloroplast genome. Recent assays have confirmed that these mutants contain no detectable PSI activity. The first demonstration of H_2 and O_2 production was achieved by steady-state measurements. In these experiments, 35 mL of B4-PsaA delta-2 cell suspension containing 10 μ g chls/mL was put in into our dual-reactor-flow-detection system using helium plus 700 ppm CO_2 as the carrier gas. Actinic illumination ($200 \mu E/m^2 \cdot s$) was provided by an

array of light-emitting diodes at 660 nm (Q-BEAM 2001, Quantum Devices, Inc., Wisconsin). The onset of actinic illumination resulted in simultaneous photoevolution of H_2 and O_2 and was sustained for hours. The photoevolution of H_2 and O_2 by B4-PsaA delta has also been demonstrated in pulsed flashing light experiments and is consistent with the results that have been obtained with steady-state illumination.

Experiments were carried out to determine the binding isotherms of the purified cellulases CBH I and EG II to Foxfibre naturally colored cottons and commercial cotton linters. Sodium hydroxide extraction was found to render the colored cottons susceptible to cellulase hydrolysis. Photographs of the colored cotton varieties at magnifications of 150 $\times$ were prepared that show the distribution of the brown pigments in the cotton fibers and the effect of sodium hydroxide extraction. Based on these and earlier experiments with the colored cottons, a manuscript entitled "The effect of cellulases on the biodegradation and morphology of naturally colored cotton fibers" was prepared for inclusion in the ACS Symposium volume, *Enzyme Applications in Fiber Processing*.

7.2 BIOMOLECULAR ELECTRONICS (E. Greenbaum, J. W. Lee, I. Lee, and R. Collins)

Contact: E. Greenbaum
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Summary: We have established a technique to control the orientation of PSI reaction centers on gold surfaces. The orientation of functional PSI reaction centers was identified by scanning tunneling spectroscopy (STS), a technique that measures voltage versus current curve characteristic of *individual* PSI reaction centers. During the current quarter, additional work has focused on upgrading our scanning probe microscope (SPM) in order to measure the voltage generated by a single PSI reaction center directly.

7.2.1 Purpose and Scope

This research project is focused on the development of molecular optoelectronic devices. It is motivated by knowledge of the intrinsic photophysical properties of the reaction centers of photosynthesis: nanometer dimensions, picosecond response times, and the ability to generate potential differences of about 1 V upon absorption of a photon. The research is based on original discoveries in molecular electronics made in the Chemical Technology Division, Oak Ridge National Laboratory. These include (1) first demonstration of direct electrical contact with the electron transport chain of photosynthesis; (2) photoflash deposition of metallic platinum at the site of electron emergence from the PSI reaction center of photosynthesis; (3) establishment of a novel platinization "welding" technique that allows construction of two-dimensional arrays of PSI reaction centers on a metal surface; and (4) first demonstration of a biomolecular diode in a single isolated photosynthetic

reaction center. Taken together, these results indicate that purified reaction centers of photosynthesis are very promising structures for the development of the next generation of optoelectronic devices.

7.2.2 Progress

We have established a technique to control the orientation of PSI reaction centers on gold surfaces. The orientation of functional PSI reaction centers was identified by STS, a technique that measures the curve of voltage versus current characteristic of *individual* PSI reaction centers. During the current quarter, additional work has focused on upgrading our SPM in order to measure the voltage generated by a single PSI reaction center directly. This enhancement will enable us to perform frequency modulation and phase detection, and this will improve our sensitivity and lower background noise. We are also working to obtain the ability to perform surface potential imaging. This will allow us to image the relatively weak but long-range electrostatic interactions between single PSI reaction centers and atomic force microscopy tip while minimizing the influence of molecular topography.

7.3 ENZYMES FROM EXTREMOPHILES IN BIOPROCESSING AND BIO-REMEDIATION (J. Woodward and B. R. Evans)

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Summary: The enzyme GLY00102 was shown to have high specific activity on cellobiose. The optimum pH for activity and stability was 4.5 and 7.0, respectively. The temperature optimum was 90–100°C.

7.3.1 Purpose and Scope

The kinetic characteristics of thermophilic cellulases and a beta-glucosidase from recombinant biocatalysis have been studied during this reporting period.

7.3.2 Progress

This enzyme (GLY001-02) was shown to have high specific activity on cellobiose (780 units/mg protein at 80°C). The pH for optimum activity and stability was 4.5 and 7.0, respectively. The temperature optimum was 90–100°C, and it was stable at 80°C for 100 h only, losing 10% of its activity over that time. The enzyme had comparative activity on cellotriose, cellotetraose, and cellopentaose, indicating its usefulness for the hydrolysis of oligosaccharides produced by the action of cellulase on cellulose.

7.4 ENZYMATIC CONVERSION OF BIOMASS TO HYDROGEN (J. Woodward and K. A. Cordray)

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Summary: The key to efficient hydrogen production is the rate at which the sugars specific for glucose dehydrogenase are formed. Rates of hydrogen evolution of 80 μmol hydrogen/h have now been achieved. Experimentation with another hydrogen production pathway using glucose-6-phosphate as the substrate has shown that from 1 mol of glucose-6-phosphate, 2 mol of hydrogen was generated out of a theoretical maximum of 12. This, in effect, doubles the efficiency of the enzymatic production of hydrogen from glucose. Finally, in a preliminary experiment, we have successfully platinized glucose dehydrogenase, which was capable of oxidizing glucose.

7.4.1 Purpose and Scope

We have investigated substrate specificity of the enzyme glucose dehydrogenase for the sugars glucose, galactose, mannose, xylose, and 2-deoxyglucose.

7.4.2 Progress

Results show that with the exception of mannose, all can be oxidized effectively by glucose dehydrogenase, producing hydrogen in the presence of hydrogenase. Sucrose and lactose are also effective substrates for hydrogen production as long as invertase and lactase are present in the reaction mixture. We have also used steam-exploded aspen wood and a mixture of birchwood xylan and crystalline cellulose as substrates for hydrogen production. The key to efficient hydrogen production is the rate at which the sugars specific for glucose dehydrogenase are formed. Rates of hydrogen evolution of 80 μmol hydrogen/h have now been achieved. Also, we have experimented with another hydrogen production pathway using glucose-6-phosphate as the substrate and enzymes of the pentose phosphate pathway. Glucose-6-phosphate is regenerated as a by-product. From 1 mol of glucose-6-phosphate, 2 mol of hydrogen was generated out of a theoretical maximum of 12. This, in effect, doubles the efficiency of the enzymatic production of hydrogen from glucose. In a preliminary experiment, in collaboration with J. Lee and E. Greenbaum, we have successfully platinized glucose dehydrogenase. The enzyme was capable of oxidizing glucose. Further experiments are planned to determine under what conditions of modification, if any, will the platinized glucose dehydrogenase produce hydrogen.

7.5 REMOVAL OF METALS FROM AQUEOUS WASTE STREAMS (M. E. Reeves, V. M. Shah, J. C. Rudolph, and S. S. Laughlin)

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Summary: This project is the demonstration of a pilot-scale ion-exchange system and an advanced technology based on ligands of biochemical origin for the removal of toxic metals from waste streams at industrial or environmental sites to be identified in eastern Pennsylvania. This project is run by the National Institute for Environmental Renewal (NIER). The ion-exchange system consists of a filter system to remove suspended solids, followed by two 4-in.-diam by 5-ft-long ion-exchange columns in series to remove the metal ion contaminants. The exiting water was periodically sampled and analyzed for breakthrough. The system is designed to flow up to 2.2 L/min of contaminated water and is also set up for regeneration and precipitation of the regenerant. The entire system was controlled by a programmable logic controller, which is operated by a modem and is located in a trailer. Following completion of the demonstration of the ion-exchange process at Tobyhanna Army Depot, the system was transported back to ORNL.

7.5.1 Purpose and Scope

The objective of this work is to conduct a field demonstration of advanced separations technology based on ligands of biochemical origin for the removal of toxic metals from waste streams at industrial or environmental sites to be identified in eastern Pennsylvania. This is a joint project involving the Chemical Technology Division of the Oak Ridge National Laboratory, the Army Corps of Engineers Waterways Experiment Station in Vicksburg, Mississippi, Lehigh University, and Hazelton Environmental (a private firm). The project is overseen by the NIER in Mayfield, Pennsylvania.

7.5.2 Progress

The trailer system was returned to ORNL and is now in mothballs while alternate uses or additional demonstrations of the systems are explored. A draft of a final report on the Tobyhanna phase of field testing has been prepared and sent to the NIER program manager, James H. Saling. We anticipate a decision on whether further field or laboratory testing will be conducted during the coming reporting period.

7.6 BIOREMEDIATION OF PCBs AT ELECTRIC POWER SUBSTATIONS (M. E. Reeves, J. W. Barton, and K. T. Klasson)

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Summary: The objective of this work is to perform basic studies on anaerobic microbial dechlorination of polychlorinated biphenyls (PCBs) in support of a Tennessee Valley Authority (TVA)/Electric Power Research Institute Tailored Collaborative Project. The second phase of the intermediate-scale demonstration at TVA-Muscle Shoals was begun in early January 1997.

7.6.1 Purpose and Scope

The objective of this work is to perform basic studies on anaerobic microbial dechlorination of PCBs in support of a TVA/Electric Power Research Institute Tailored Collaborative Project. The overall goal is to perform a field demonstration of bioremediation technology for remediation of PCBs in soils at a TVA power substation site in Chattanooga, Tennessee. Contributions to the design of this demonstration project are being made by ORNL, University of Tennessee's Center for Environmental Biotechnology, and TVA at Muscle Shoals, Alabama.

7.6.2 Progress

The second phase of the intermediate-scale demonstration at TVA-Muscle Shoals was begun in early January 1997. The inoculum was delivered to Muscle Shoals by Mark Reeves in November 1996. We anticipate soon participating in a data review based on the two intermediate-scale demo runs, which will lead to final plans for a field demonstration this spring and/or summer.

7.7 BIOMIMETICS/BIOMATERIALS LEADERSHIP FOR OAK RIDGE (M. E. Reeves, K. B. Jacobson, R. J. Lauf, D. B. Hunsaker, Jr., W. H. Gray, W. D. Brosey, J. L. Cook, and D. O. Hobson)

Contact: M. E. Reeves
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Summary: Funding to conduct a program development effort that will result in broadening of scientific efforts across the Oak Ridge Complex in the area of biomimetics and biomaterials and in the establishment of the Oak Ridge Complex as the recognized center for work in this emerging new area was received.

7.7.1 Purpose and Scope

The objective of this work is to conduct a program development effort that will result in broadening of scientific efforts across the Oak Ridge Complex in the area of biomimetics and biomaterials and in the establishment of the Oak Ridge Complex as the recognized center for work in this emerging new area.

7.7.2 Progress

Funding was received into the Chemical Technology Division financial plan about March 15. A kickoff meeting has been held to initiate efforts toward accomplishing the goals of this project. Specific task assignments for various members of the planning team, as well as schedules for conducting/completing tasks, are being developed.

7.8 PUBLICATIONS AND PRESENTATIONS

7.8.1 Published

- M. Z.-C. Hu and M. Reeves, "Biosorption of Uranium by *Pseudomonas aeruginosa* Strain CSU Immobilized in a Novel Matrix," *Biotechnol. Prog.* **13**, 60–70 (January–February 1997).
- I. Lee, B. R. Evans, L. M. Lane, and J. Woodward, "Substrate-Enzyme Interactions in Cellulase Systems," *Bioresource Technology* **58**, 163–69 (1996).
- J. W. Lee and E. Greenbaum, "A New Perspective on Hydrogen Production by Photosynthetic Water-Splitting," in *Fuels and Chemicals from Biomass*, ACS Symposium Series 666, in press (1997).
- B. Saha and J. Woodward, eds., *Fuels and Chemicals from Biomass*, ACS Symposium Series 666, in press (1997).

7.8.2 Submitted Manuscripts

- B. R. Evans, I. Lee, J. Woodward, and S. V. Fox, "The Effect of Cellulases on the Biodegradation and Morphology of Naturally Colored Cotton Fibers," ACS Symposium Series (submitted).

7.8.3 Presentations

- E. Greenbaum, "New Photosynthetic Pathways: Renewable Fuels Production and Biomolecular Electronics," research seminar presented at Brookhaven National Laboratory, February 26, 1997, Upton, N.Y.
- E. Greenbaum, J. W. Lee, S. L. Blankinship, C. V. Tevault, and T. G. Owens, "A Quantitative Test of the 'Leaky' Z-Scheme of Photosynthesis," presented at the 41st Annual Meeting of the Biophysical Society, March 2–6, 1997, New Orleans, La.

- E. Greenbaum and J. W. Lee, "Hydrogen Production from Water: Recent Advances in Photosynthesis Research," presented at the 8th Annual U.S. Hydrogen Meeting, March 11-13, 1997, Alexandria, Va.
- E. Greenbaum, J. W. Lee, S. L. Blankinship, and T. G. Owens, "Measurement of H₂ and O₂ Flash Yields in PSI-Deficient Mutants of *Chlamydomonas* and Comparison with Predictions of the Z-Scheme," presented at the 14th Annual Eastern Regional Photosynthesis Conference, March 21-23, 1997, Woods Hole, Mass.
- J. W. Lee, I. Lee, and E. Greenbaum, "From Physics and Chemistry of Photosynthesis to its Potential Application in Nanofabrication and Optoelectronics," presented at the 14th Annual Eastern Regional Photosynthesis Conference, March 21-23, 1997, Woods Hole, Mass.

7.8.4 Patent Actions

- M. Z.-C. Hu, M. Reeves, and B. D. Faison, "Biomass Immobilization Matrices for Metal/Radionuclide Biosorption," application filed with U.S. Patent Office, March 1997.

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