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Quarterly Progress Report for the Chemical and Energy Research Section of the Chemical Technology Division: July–September 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: JULY–SEPTEMBER 1997

R. T. Jubin

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CONTENTS

ACRONYMS

ACB	auxiliary charcoal bed
ACC	Applied CarboChemicals, Inc.
AFP	Alternative Feedstocks Program
ANL	Argonne National Laboratory
BDSA	biologically derived succinic acid
BES	Basic Energy Sciences (DOE)
CNF	Central Neutralization Facility
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
EIX	electrochemical ion exchange
EMSP	Environmental Management Science Program (DOE)
ESP	Efficient Separations and Processing Crosscutting Program (DOE)
ESW	Enhanced Sludge Washing
FDP	fructose 1,6-diphosphate
FDPase	fructose 1,6-diphosphatase
FTIR	Fourier transform infrared
G6P	glucose-6-phosphate
G6PDH	glucose-6-phosphate dehydrogenase
6PGDH	6-phosphogluconic dehydrogenase
HFIR	High Flux Isotope Reactor
HGMF	high-gradient magnetic filtration
HLW	high-level waste
HMTA	hexamethylenetetramine
IES	inverse electrostatic spraying
MSRE	Molten Salt Reactor Experiment
MVST	Melton Valley Storage Tank
NREL	National Renewable Energy Laboratory
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
PNPC	*p*-nitrophenyl D-(+)-cellobioside
PNP	*p*-nitrophenol
PPP	pentose phosphate pathway
PSI	Photosystem I
PSII	Photosystem II
R&D	research and development
RBI	Recombinant BioCatalysis, Inc.
R-F	resorcinol-formaldehyde
SALS	small-angle light scattering
SANS	small-angle neutron scattering

SAXS	small-angle X-ray scattering
SPME	solid-phase microextraction
SRTC	Savannah River Technology Center
TFA	Tank Focus Area
TGA	thermogravimetric analysis
TRUEX	transuranium extraction
TSP	trisodium phosphate
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 at Oak Ridge National Laboratory (ORNL) during the period July–September 1997. The 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 nine major areas of research: Hot Cell Operations, Process Chemistry and Thermodynamics, Molten Salt Reactor Experiment (MSRE) Remediation Studies, Chemistry Research, Biotechnology, Separations and Materials Synthesis, Fluid Structure and Properties, Biotechnology Research, and Molecular Studies. The name of a technical contact is included with each task described, and readers are encouraged to contact these individuals if they need additional information.

Activities conducted within the area of *Hot Cell Operations* included completion of testing of sorbent materials to remove radionuclides from ORNL Melton Valley Storage Tank (MVST) supernatant; analyses of leachates, residues, and rinse solutions from tests on samples of sludge from Hanford tanks; hot cell testing of an experimental unit for radionuclide removal by electrochemical ion exchange; and development and batch testing of spherical sorbents containing sodium titanate to remove fission products. Another task involved immobilization matrices for use with MVST sludge.

Within the area of *Process Chemistry and Thermodynamics*, the problem of solids formation in Enhanced Sludge Washing was addressed. Other initiatives included support to the U.S. Nuclear Regulatory Commission in the area of advanced reactor design and collaborative efforts with Russian scientists to determine the solidification conditions of yttrium, barium, and copper oxides from their melts.

MSRE Remediation Studies focused on recovery of ^{233}U and its transformation into a stable oxide, passivation of fluorinated charcoal in the auxiliary charcoal bed, and identification of the mechanism of UF_6 formation in the MSRE gas piping system. Technical support to this project is also described.

Within the area of *Chemistry Research*, activities included studies relative to molecular imprinting for use in several areas of separations technology and investigation of the chemistry of actinides and fission products in molten salts.

Biotechnology initiatives included the production of commercially valuable chemicals from a renewable feedstock (biologically derived succinic acid), as well as efforts to enhance the production of ethanol through development of advanced bioreactor systems.

In the area of *Separations and Materials Synthesis*, fundamental studies explored the use of electromagnetic fields to enhance transport processes in multiphase separations, investigated 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. New initiatives within this area involved the use of electric fields to improve distillation efficiency, bench-scale testing of electrocoagulation as a wastewater treatment technology, investigation of particle interactions in reactive systems, and chemical leaching of mercury-contaminated soils. In addition, areas of possible industrial interaction were investigated.

Fluid Structure and Properties included molecular-based studies of solutions in supercritical fluids, attempts to produce stable microdispersions of water in supercritical carbon dioxide using high-intensity electrical fields, a multi-institutional initiative to develop a molecular understanding of reverse miscelles in supercritical carbon dioxide through experimentation and molecular simulation calculations, and molecular-based prediction of the structure and properties of long-chain molecules undergoing shear flow.

Within the area of *Biotechnology Research*, experiments continued to characterize Photosystem II photosynthesis and to investigate the process of hydrogen production by photosynthetic water splitting. Associated research focused on the development of molecular optoelectronic devices. In enzyme-related work, the kinetic characteristics of thermophilic and mesophilic cellulases were studied, efforts were made to maximize the efficiency of the enzymatic production of hydrogen from glucose, and preparations were under way to cultivate test fungi under a microcycle regime. Also within this area, funding was received for establishment of the Oak Ridge Complex as the recognized center for biomimetics and biomaterials.

In the final area—*Molecular Studies*—as part of an initiative to enhance our microscopic-level understanding of aqueous electrolyte solution, development of a new intermolecular potential model for water continued. Related tasks included the investigation of simulation algorithms for nonequilibrium systems and a study of mixed-solvent electrolytes by integral equation methods. Also in progress were refinement of an efficient code for modeling in situ bioremediation processes and extension of a molecular formalism to reaction kinetics in supercritical fluid solvents.

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: This task was completed at the end of the reporting period. A final report entitled *Removal of Cesium, Technetium, and Strontium from Tank Waste Supernatant* (ORNL/TM-13612) was completed and sent out for technical review. The report summarizes the experimental results and compares them with results from other studies at different U.S. Department of Energy (DOE) sites. All the milestones for the program were achieved.

1.1.1 Purpose and Scope

This task involved testing sorbent materials for removing cesium, strontium, and technetium from DOE storage tank supernatant at Oak Ridge and other sites. Batch tests were used to evaluate and select promising materials for supernatant treatment to reduce the amount of waste for final disposal. Small-column tests were made on selected sorbents to verify the batch data and to obtain additional data for process design. Methods were also evaluated for recovering the radionuclides from the sorbents. Supernatants used in the various tests were retrieved from Melton Valley Storage Tanks (MVSTs) W-25, W-27, and W-29. These supernatants are very similar to those in the tanks at the other DOE sites.

1.1.2 Progress

This task was completed at the end of the reporting period, and all the milestones were met. A final report entitled *Removal of Cesium, Technetium, and Strontium from Tank Waste Supernatant* (ORNL/TM-13612) was completed and sent out for technical review. The report summarizes the experimental results and compares them with results from other studies at different DOE sites.

1.2 PARTITIONING OF SLUDGE COMPONENTS BY CAUSTIC LEACHING

(R. D. Hunt, B. Z. Egan, B. B. Spencer, J. L. Collins, D. D. Ensor,* and C. W. Chase)

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Summary: Analyses have been completed on samples of leachates, residues, and rinse solutions resulting from all of the caustic leach tests on sludge samples from Hanford tanks S-104, SX-113, C-105, C-107, C-104, and S-101. The leach times ranged from 21 to 126 h. Leach temperatures ranged from 50 to 93°C. The NaOH concentration ranged from 3.99 to 6.33 *M*. Preparation of a report that evaluates these alternative processing conditions is under way.

1.2.1 Purpose and Scope

Many underground storage tanks contain high concentrations of nonradioactive components such as aluminum, chromium, and phosphates. These materials can significantly increase the volume of the high-level waste (HLW), which requires vitrification and disposal. Therefore, processes that can effectively partition the radioactive and nonradioactive components can lead to considerable cost savings. The Enhanced Sludge Washing (ESW) process, which uses inhibited water washes and caustic leaches to separate the radioactive materials from the nonradioactive components, is the current baseline procedure for the treatment of the HLW sludges at Hanford. The objective of this task is to measure the caustic dissolution behavior of sludge components from selected Hanford sludge samples. The effects of process variables such as NaOH concentration, temperature, and leaching time on the efficacy of the caustic leaching process are also evaluated.

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 HLW sludge that must undergo 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, and leaching times.

Analyses have been completed on samples of leachates, residues, and rinse solutions resulting from all of the leach tests on sludge samples from Hanford tanks S-104, SX-113, C-105, C-107, C-104, and S-101. The leach times ranged from 21 to 126 h. Leach temperatures ranged from 50 to 93°C. The NaOH concentration ranged from 3.99 to 6.33 *M*.

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*Tennessee Technological University, Cookeville, Tennessee.

The maximum aluminum removal was 96% from S-104, 79% from SX-113, 97% from C-105, 82% from C-107, 90% from C-104, and 98% from S-101. The maximum chromium removal was 99% from S-104, 66% from SX-113, 71% from C-105, 70% from C-107, 74% from C-104, and 86% from S-101. Significant amounts of radioactive cesium were also removed by the caustic leaches. The cesium removal ranged from 47% from C-104 to 99% from S-104 under the different leaching conditions. Preparation of a report that evaluates these alternative processing conditions is under way.

These findings, as well as earlier dissolution and transuranium extraction (TRUEX) results for Oak Ridge sludges, will be discussed in two presentations at the Tenth Symposium on Separation Science and Technology for Energy Applications, to be held in Gatlinburg, Tennessee, on October 21–24. A poster entitled "Dissolution of ORNL HLW Sludge and Partitioning of Actinides Using the TRUEX Process" and a talk entitled "Issues on High-Level Tank Waste Sludge Leaching" will be presented at the symposium.

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

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Summary: The continuous-flow-cell system was operated with AEA Technology's electrochemical–ion-exchange (EIX) test rig from England with batch BSC-187 of resorcinol-formaldehyde (R-F) resin. Elution of the cesium was accomplished with the electrochemical elution technology.

The chemical and radiological analyses of the previous test using the commercial crystalline silicotitanate (CST) IONSIV 911 and W-29 MVST feed that were used in the Cesium Removal Demonstration (CsRD) run were completed. Based on these analyses, the results reported previously for ^{137}Cs did not change. Additional breakthrough curves were obtained for lead, barium, ^{90}Sr, uranium, ^{134}Cs, and total cesium.

1.3.1 Purpose and Scope

This task involves the operation of an experimental unit designed and constructed to test radionuclide removal technologies during continuous operation on Oak Ridge National Laboratory (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 experimental unit is located in an ORNL hot cell. This unit provides a test bed for investigating new technologies that become available during this program and complements the comprehensive supernatant task by using larger engineering-scale, continuous equipment to verify and expand the batch studies. It also complements the Tank Focus Areas (TFA) CsRD at Oak Ridge by providing sorbent selection information, evaluation and testing of proposed sorbents, and operational experience and characteristics using the sorbent and supernatant to be used in the demonstration.

There is close cooperation with the Efficient Separations and Processing Crosscutting Program (ESP) and the TFA in order ultimately to transfer the technologies being developed to the end user. TFA requested through ESP that we test AEA Technology's EIX system as part of this ESP program because ORNL was the only site with sufficient available supernatant for testing the multiple-cycle EIX system.

Initial candidate sorbents for cesium removal were the R-F resin, CSTs, SuperLig 644C resin, 3M WWL 644 WEB material with SuperLig 644 Embedded, Rohm & Haas CS-100 resin, and granular potassium cobalt hexacyanoferrate. The results of these tests were compared with batch results and small-column tests results obtained in the Comprehensive Supernatant Treatment Task. The results were used to supply the CsRD with information to determine the design parameters and sorbent for that project. The rate of removal, resin required, and regeneration requirements are important design parameters, and the loading capacity of each sorbent will help to determine the size of the column required and help define the final volume of solid waste to be disposed of.

1.3.2 Progress

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

The continuous cesium removal system in Cell C was operated to test the sorbent (UOP CST IONSIV 911) and supernatant that will be used in the CsRD. A sample of MVST W-29 supernatant was withdrawn from the tank and transferred to Cell C for use in the test. The analyses for the sample (W29080896-2) were completed by the Chemical and Analytical Sciences Division; results are shown in Table 1.

The test was run for 560 column volumes (CV) at a flow rate of 6 CV/h and achieved 50% breakthrough of the ^{137}Cs at about 505 CV. The analytical results did not change the preliminary results reported last month. Breakthrough curves for ^{137}Cs, ^{134}Cs, and total cesium were almost identical. Breakthrough curves were also obtained for ^{90}Sr, uranium, total beta, total alpha, barium, zinc, and lead, based on the analyzed periodic samples obtained during the loading.

Table 1. Major components in MVST W-29 supernatant (pH 12.7)

Component	Concentration
Cations	
Sodium	4.15 *M*
Potassium	0.376 *M*
Aluminum	4.17 mg/L
Calcium	1.42 mg/L
Rubidium	1.28 mg/L
Silicon	44 mg/L
Zinc	1.35 mg/L
Copper	0.07 mg/L
Total cesium	0.58 mg/L
Total strontium	1.65 mg/L
Barium	0.865 mg/L
Cadmium	0.24 mg/L
Chromium	3.44 mg/L
Mercury	0.258 mg/L
Nickel	1.04 mg/L
Lead	2.89 mg/L
Arsenic	<0.25 mg/L
Uranium	13.3 mg/L
Anions	
Nitrate	4.03 *M*
Nitrite	0.44 *M*
Chloride	3050 mg/L
Sulfate	0.16 *M*
Radionuclides	
^{137}Cs	0.46 *M*Bq/mL
^{60}Co	500 Bq/mL
^{99}Tc	342 Bq/mL
^{90}Sr	4.1 kBq/mL
Gross alpha	30 Bq/mL
Other	
Total carbon	1480 mg/L
Inorganic carbon	980 mg/L

1.3.2.2 Continuation of the AEA Technology EIX Testing

The AEA Technology EIX system built in England was received at ORNL and installed in the hot cell in place of the standard column and connected to the rest of the cell-flow system. The EIX system consists of the EIX cells, tanks, valves, and power supply necessary to test the concept with MVST supernatant. The tests were conducted with R-F resin from batch BSC-187, which was stored at AEA Technology. This particular small batch has recently shown good cesium uptake results in cold tests at AEA and in preliminary column tests using MVST W-27 supernatant in the hot cell at ORNL (~2% breakthrough at 70 CV). A series of loadings and elutions with the EIX cells was completed using MVST W-27 supernatant at a flow rate of 6.6 CV/h.

The results of the loading tests showed very good agreement with both the cold testing of simulants at AEA Technology in the United Kingdom and with the previous column tests here at ORNL using W-27 feed. The cells were not loaded to 50% cesium breakthrough due to the length of time that would have been required, but projections indicated that 50% breakthrough would have been greater than 150–200 CV, with 1% breakthrough occurring at 70–90 CV.

The EIX elutions using the electrochemical elution of cesium were conducted on both cells used in the tests. The elutions were performed according to protocols developed at AEA Technology, using the simulant for W-27 feed with about 60 ppm total cesium. The actual W-27 feed contains about 1 ppm total cesium. Initial results showed very little cesium removed electrochemically during the 5-h elution. Further testing at AEA and here at ORNL revealed that divalent cations present in the actual W-27 feed prevented the efficient elution of the cesium in the normal time frame. When the elution was continued past the normal 5 h, the cesium began to elute and resulted in >90% elution by electrochemical means on both cells tested when the elution was carried out to 10 h. The W-27 feed contained much greater amounts of calcium than normal MVST liquids (30–40 ppm vs 1–3 ppm) because it had been stored at pH 7.4 and then raised to pH 13.2 in the laboratory before use in the experiment.

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

Contact: J. L. Collins
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Summary: Two chemical conversion methods were developed for making pure sodium titanate microspheres; both required the use of hydrous titanium oxide gel spheres made by the

hexamethylenetetramine (HMTA) internal gelation process. One method involved the hydrothermal conversion of hydrous titanium oxide gel spheres with sodium hydroxide and sodium salts. The other method utilized an alkoxide conversion process for converting hydrous titanium oxide gel spheres to a pure sodium titanate. As part of the optimization process, the prepared sorbents were tested in batch experiments for the removal of strontium from simulated MVST W-29 supernatant. For comparison, commercial sodium titanate sorbents and other strontium-selective sorbents were also tested. The microspherical sorbents worked as well as or better than the commercial engineered forms of sodium titanate in removing the strontium. A Notice of Allowance for the patent application entitled "Method of Preparing Hydrous Titanium Oxide Spherules and Other Gel-Forms Thereof" was received in January 1998. Eichrom Industries, Inc., obtained the license for this patent technology in June 1997.

1.4.1 Purpose and Scope

The general objectives of this task are to develop, prepare, and test new and unique inorganic ion exchangers *made as microspheres* by the internal gelation process to remove fission products, actinides, and other metals [such as the Resource Conservation and Recovery Act (RCRA) metals] from waste streams occurring at the various DOE sites. The initial microspheres will be made of materials that have already been shown to be highly effective as cesium and strontium sorbents. The initial effort is to make a more column-usable inorganic ion exchanger for removing strontium from waste tank supernatants. Sodium titanate has been determined as possibly the best sorbent for removing strontium from alkaline supernatants with high salt concentrations.

Composite microspheres containing varying amounts of sodium titanate homogeneously embedded in microspheres of hydrous titanium oxide have been prepared utilizing the internal gelation process. These materials were also characterized by batch tests and compared with the best commercially available strontium-selective sorbents.

Two chemical conversion methods were also developed for making pure sodium titanate microspheres; both required the use of hydrous titanium oxide gel spheres made by the HMTA internal gelation process. One method involved the hydrothermal conversion of hydrous titanium oxide gel spheres with sodium hydroxide and sodium salts. The other method utilized an alkoxide conversion process for converting hydrous titanium oxide gel spheres to a pure sodium titanate. As part of the optimization process, the prepared sorbents were tested in batch experiments for the removal of strontium from simulated MVST W-29 supernatant. For comparison, commercial sodium titanate sorbents and other strontium-selective sorbents were also tested. The microspherical sorbents worked as well as or better than the commercial engineered forms of sodium titanate in removing the strontium.

1.4.2 Progress

Batch-test results comparing the effectiveness of the microspherical sorbents that were developed with commercial sorbents for removing strontium from simulated MVST W-29 supernatant are given in Table 2. The composition of the supernatant was as follows: 3.9 *M* $NaNO_3$, 1.0 *M* NaOH, 0.14 *M* Na_2CO_3, 0.1 *M* NaCl, 0.25 *M* KNO_3, 1.0×10^{-4} *M* $CaCO_3$, and 1.1×10^{-5} *M* Sr (1 ppm). Strontium was added as strontium nitrate, which was traced with the gamma emitter ^{85}Sr ($t_{1/2}$ = 64.8 d). Each test was conducted by mixing about 0.025 g of exchanger with ~5 mL of simulated supernatant for 24 h. Masses of undried microspheres used were equivalent to 0.025 g of air-dried microspheres. The best of the air-dried microspheres that were prepared by hydrothermal conversion and the composite hydrous titanium oxide microspheres that were embedded with about 23% sodium titanate powder and dried at 110°C removed 98.5 to 98.8% of the strontium, which was similar to the 98.3% strontium removal by granular sodium titanate, obtained from AlliedSignal. The distribution ratios ranged from 12,600 to 17,300 mL/g. Undried hydrous titanium oxide microspheres that were embedded with about 23% sodium titanate powder worked the best in removing the strontium, about 99.9%. The $D_{24\,h}$ was 101,000 mL/g. Pure hydrous titanium oxide microspheres and granular hydrous titanium oxide obtained from DuNord worked equally well in removing about 95.5% ($D_{24\,h}$ = 4,300 mL/g) of the strontium, which was better than the 92.2% ($D_{24\,h}$ = 2,400 mL/g) removed by granular IONSIV® IE-911 obtained from UOP. The sodium titanate microspheres prepared by an alkoxide conversion method worked only a little better than the hydrous titanium oxide microspheres.

Batch tests with microspheres prepared by the hydrothermal conversion method were also conducted with a 0.1 *M* $NaNO_3$ solution with a strontium concentration of 100 ppm. The pH of the solution was adjusted to 12 with sodium hydroxide. The D_{24h} values for the microspheres ranged from 150,000 to 700,000 mL/g. The $D_{24\,h}$ obtained for AlliedSignal's granular sodium titanate was ~200,000 mL/g. The percentages of strontium that were removed by the microspheres ranged from 99.8 to 99.9%.

Table 2. Removal of strontium from simulated MVST W-29 supernatant by sorbents

Sorbent[a]	D^b (mL/g)	R (%)
IONSIV® IE-911 (gr), UOP	2,400	92.2
HTiO (gr), DuNord	4,300	95.5
NaTi (gr), Allied-Signal	12,600	98.3
HTiO ϕ^c	4,300	95.5
NaTi $\phi^{c,d}$	5,600	96.4
NaTi $\phi^{c,e}$	14,000	98.5
(23% NaTi/HTiO) ϕ^f	17,300	98.8
(23% NaTi/HTiO) ϕ^g	101,000	99.9

[a] ϕ = microspheres; (gr) = granular or engineered form.
[b] Mixing time = 24 h; supernatant/sorbent ratio = ~200.
[c] Air dried.
[d] Prepared by alkoxide conversion method.
[e] Prepared by hydrothermal conversion method.
[f] Dried at 110°C.
[g] Not dried.

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

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Summary: Work on this project has not yet begun, and plans are being made to start receiving sludge samples from the various tanks in October 1997.

1.5.1 Purpose and Scope

Sludges from three different tanks—Old Hydrofracture Facility W-4, and W-23—are being used in a hot cell dedicated to producing glasses and cement-based grouts for the purpose of comparative testing of both types of immobilization matrices. The data produced will allow prospective vendors to judge the suitability of these types of waste forms for immobilization of sludges in the MVSTs. Following chemical analysis of the sludges, Savannah River Technology Center (SRTC) will use the data to formulate soda-lime–based glasses. The SRTC formula will be tested using a surrogate, and, if a satisfactory glass is produced, the actual sludge will be used in the ORNL hot cell.

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*ORNL Chemical Technology Division, Engineering Development Section.

Glass loadings on an oxide basis are expected to be in the 45% range. Additionally, analytical data will be used along with a surrogate to produce a satisfactory cement-based grout with a maximum waste loading. Similarly, grout will be produced in the hot cell by utilizing the formula. The testing of the glass and grout include the Product Consistency Test for the glass, the Toxicity Characteristic Leaching Procedure along with bleed water, and penetration resistance for the grout.

1.5.2 Progress

A safety summary has been put in place for the project, and the sampling of the tank sludges is expected over the next few months.

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 model of the sodium phosphate–sodium fluoride–sodium hydroxide–water system was developed to provide direction on how to avoid the formation of phosphate solids in ESW. The concentration of sodium hydroxide in solution is the main driving force for solid formation.

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 Experimental

Unwanted formation of solids in sludge pretreatment can be controlled by process temperatures, by excess caustic, or by the use of additives. Lime (calcium oxide or calcium hydroxide) can react with phosphate to produce a calcium phosphate, which can react with fluoride to produce calcium fluoride. This is a potential way to reduce the concentration of phosphate and fluoride in solution and aid in preventing the formation of sodium phosphate and sodium phosphate fluoride. Two samples of Hanford T-104 sludge were treated simultaneously to evaluate the effectiveness of lime (calcium hydroxide) in preventing the formation of sodium phosphate fluoride. Both samples were leached at 75 °C for 24 h with 3.9 g of 3.8 *M* sodium hydroxide per gram of sludge. These conditions were selected because of earlier test results from T-104 sludge. After leaching and settling, the samples were filtered at 75 °C through 0.45-μm syringe filters. At this point in the test sequence, one of the filtered leachates was treated with 0.2 g of calcium hydroxide per gram of initial sludge. The other leachate had no additional chemicals. Both samples were mixed for 30 min and allowed to cool to ambient. The sludge residues after leaching were washed at 75 °C three times for 30 min. After each wash, the solutions were filtered at 75 °C, and 0.05 g of calcium hydroxide per gram of initial sludge was added to one of the two wash solutions. The leachates and wash solutions were examined periodically for several weeks. Sticky solids formed in both the calcium hydroxide–treated and the untreated leachates within an hour after they were removed from heat and allowed to approach ambient temperature. No solids formed in any of the treated or untreated wash solutions. These test results show that calcium hydroxide did not prevent the formation of solids in caustic leaching of T-104 sludge.

2.1.2.2 Modeling

A model of the sodium phosphate–sodium fluoride–sodium hydroxide–water system has been developed to provide direction concerning how ESW should be carried out to avoid the formation of solids containing phosphate. The concentration of sodium hydroxide in solutions containing phosphate and fluoride is the main driving force to solid formation. It will be more difficult to control solids at higher sodium hydroxide concentrations. At 25 °C, the maximum concentration of phosphate in solution with 3 *M* sodium hydroxide is 0.04 mol/kg of water. At higher phosphate concentrations, solid trisodium phosphate (TSP) would form. A phosphate concentration of 0.15 mol/kg of water could be tolerated in a 1 *M* sodium hydroxide concentration at this temperature.

The model also shows that the presence of even a small concentration of fluoride can bring about a large reduction in the phosphate concentration that can remain in solution. Fluoride and phosphate combine to form sodium phosphate fluoride hydrate. The solubility of a sodium phosphate solution can be cut in half by the addition of as little as 0.05 mol of fluoride per kilogram of water.

Bench-top tests at chemical compositions close to those at which the model predicted solid formation are being run to validate its capabilities.

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

Two accident sequences were formulated to bypass the pH control system in a containment. Most iodine is eventually transported to the flooded containment, where TSP raises the pH high enough to prevent volatilization. However, a substantial fraction of the iodine remains in a containment water tank that never fully drains. This water does not access the TSP but instead is the repository for acids produced by radiolysis in containment. The continual lowering of pH in this volume does lead to some production of I_2, which is vented to the containment airspace, and a small amount is vented to the atmosphere.

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

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Summary: Experimental work on the collaboration with Dr. Gennady Voronin of Moscow State University has been completed as directed by DOE. The goal was to determine the solidification conditions of yttrium, barium, and copper oxides from their melts. These conditions include temperature, partial oxygen pressure, chemical composition of the melt, and chemical composition of the growing solids. Differential thermal analysis (DTA)/thermogravimetric analysis (TGA) and

hydrogen reduction have been used to determine the oxygen contents of melts from $YBa_2Cu_3O_{7-x}$ (Y123), Y123 + $BaCuO_2$ (1:1), and Y123 + CuO (1:4.3) at partial oxygen pressures ranging from 0.1 to 0.000006 MPa. A manuscript, which describes phase transitions and oxygen content in the melts of Y123 and Y123 + $BaCuO_2$ (1:1), has been prepared and is under review.

Several attempts to determine the oxidation state of copper in superconducting Y123 have been made. However, a comprehensive evaluation of all potential oxidation states at different oxygen stoichiometries has not been made. While Y123 is usually expressed in terms of the formula $YBa_2Cu^{+2}_{2+2x}Cu^{+3}_{1-2x}O_{7-x}$ ($0 \leq x \leq 0.5$), 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. Our current study uses both oxidizers and reductants to determine the proper representation of Y123 at its different oxygen stoichiometries. Samples of $YBa_2Cu_3O_6$, $YBa_2Cu_3O_{6.36}$, $YBa_2Cu_3O_{6.64}$, and $YBa_2Cu_3O_{6.9}$ have been dissolved in hydrochloric acid solutions with potassium permanganate (strong oxidizer) or sodium thiosulfate (strong reductant). The solutions were then neutralized. Since each oxygen stoichiometry can be represented in three distinct ways, key components from each possible formulation with the exception of the formulas with Cu^{+3} were treated in the same manner as the Y123 samples. An analysis indicates that the best representations for $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_{6.36}$ are $YBa_2Cu_2^{(+2)}Cu^{(+1)}O_6^{(-2)}$ and $YBa_2Cu_{2.72}^{(+2)}Cu_{0.28}^{(+1)}O_{6.36}^{(-2)}$, respectively. The results with $YBa_2Cu_3O_{6.64}$, and $YBa_2Cu_3O_{6.9}$ imply the presence of Cu^{+3}. A manuscript on these findings will be prepared shortly, and this evaluation of the oxidation states of copper will be concluded as soon as the paper has been accepted for publication.

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 collaboration with Dr. Gennady Voronin of Moscow State University has been completed as directed by DOE. Three of the seven proposed compositions were evaluated. The goal of this joint effort was to determine the solidification conditions of yttrium, barium, and copper oxides from their melts. These conditions include temperature, partial oxygen pressure, chemical composition of the melt, and phase and chemical composition of the growing solids. The liquidus and solidus surfaces in the yttrium-barium-copper-oxygen (YBCO) system will be determined in terms of temperature, composition, and oxygen chemical potential.

The phase transitions and oxygen content in the melts of Y123 and Y123 + $BaCuO_2$ (1:1) at partial oxygen pressures of 0.1, 0.01, 0.001, 0.0001, and 0.000006 MPa have been determined experimentally. A manuscript, which describes these results, has been prepared and is under review.

The oxygen contents in Y123 + CuO (1:4.3) melts have been determined, and the results are shown in Table 3. As soon as all of the phase-transition temperatures have been determined, the data set will be sent to Dr. Voronin, who is developing a formal description of YBCO melts as well as a thermodynamic simulation of the equilibria and prediction of the composition and thermodynamic functions of the liquid. As soon as his analysis is complete, another manuscript, which describes the models for Y123, Y123 + $BaCuO_2$ (1:1), and Y123 + CuO (1:4.3) melts, will be prepared. It is interesting to note that the results for Y123, Y123 + $BaCuO_2$ (1:1), and Y123 + CuO (1:4.3) have been different.

2.3.2.2 Oxidation States of Copper and Oxygen in Y123

With the discovery of Y123, several attempts to determine the oxidation state of copper in superconducting Y123 have been made. However, a comprehensive evaluation of all potential oxidation states at different oxygen stoichiometries has not been made. While Y123 is usually expressed by the formula $YBa_2Cu^{+2}_{2-2x}Cu^{+3}_{1-2x}O_{7-x}$ $(0 \le x \le 0.5)$, 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. Our current study uses both oxidizers and reductants to determine the proper representation of Y123 at its different oxygen stoichiometries. Examples of possible representations are provided below.

1. $YBa_2Cu_3O_6$ (insulator, lowest oxygen)
   - A. $Y^{(+3)}Ba_2^{(+2)}Cu_2^{(+2)}Cu^{(+1)}O_6^{(-2)}$
   - B. $Y^{(+3)}Ba_2^{(+2)}Cu^{(+3)}Cu_2^{(+1)}O_6^{(-2)}$
   - C. $Y^{(+3)}Ba_2^{(+2)}Cu_3^{(+1)}O_2^{(-1)}O_4^{(-2)}$
2. $YBa_2Cu_3O_{6.36}$ (metal, onset of superconductivity)
   - A. $Y^{(+3)}Ba_2^{(+2)}Cu_{2.72}^{(+2)}Cu_{0.28}^{(+1)}O_{6.36}^{(-2)}$
   - B. $Y^{(+3)}Ba_2^{(+2)}Cu_{1.36}^{(+3)}Cu_{1.64}^{(+1)}O_{6.36}^{(-2)}$
   - C. $Y^{(+3)}Ba_2^{(+2)}Cu_3^{(+1)}O_{2.72}^{(-1)}O_{3.64}^{(-2)}$
3. $YBa_2Cu_3O_{6.64}$ (plateau in technetium vs oxygen content)
   - A. $Y^{(+3)}Ba_2^{(+2)}Cu_{0.28}^{(+3)}Cu_{2.72}^{(+2)}O_{6.64}^{(-2)}$
   - B. $Y^{(+3)}Ba_2^{(+2)}Cu_{1.64}^{(+3)}Cu_{1.36}^{(+1)}O_{6.64}^{(-2)}$
   - C. $Y^{(+3)}Ba_2^{(+2)}Cu_3^{(+1)}O_{3.28}^{(-1)}O_{3.36}^{(-2)}$
4. $YBa_2Cu_3O_{6.9}$ (maximum technetium)
   - A. $Y^{(+3)}Ba_2^{(+2)}Cu_{0.8}^{(+3)}Cu_{2.2}^{(+2)}O_{6.9}^{(-2)}$
   - B. $Y^{(+3)}Ba_2^{(+2)}Cu_{1.9}^{(+3)}Cu_{1.1}^{(+1)}O_{6.9}^{(-2)}$

C. $Y^{(+3)}Ba_2^{(+2)}Cu_3^{(+1)}O_{3.8}^{(-1)}O_{3.1}^{(-2)}$

As reported earlier, samples of $YBa_2Cu_3O_6$, $YBa_2Cu_3O_{6.36}$, $YBa_2Cu_3O_{6.64}$, and $YBa_2Cu_3O_{6.9}$ have been dissolved in solutions of hydrochloric acid and potassium permanganate, a strong oxidizer. The solutions were then reduced with sodium thiosulfate. Recently, similar experiments were performed with the various forms of $YBa_2Cu_3O_x$, which were dissolved in solutions of hydrochloric acid and sodium thiosulfate, a strong reductant. The solutions were then oxidized with potassium permanganate. Key components from each possible formulation, with the exception of the formulas with Cu^{+3}, were treated in the same manner as the Y123 samples. The recent results confirmed the earlier ones, and they indicated that the best representations for $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_{6.36}$ are $YBa_2Cu_2^{(+2)}Cu^{(+1)}O_6^{(-2)}$ and $YBa_2Cu_{2.72}^{(+2)}Cu_{0.28}^{(+1)}O_{6.36}^{(-2)}$, respectively. The results with $YBa_2Cu_3O_{6.64}$ and $YBa_2Cu_3O_{6.9}$ imply the presence of Cu^{3+}. A manuscript on these findings will be prepared shortly, and this evaluation of the oxidation states of copper will be concluded as soon as the paper has been accepted for publication. However, if this task were to continue in its present direction, future experiments would involve different oxidizers and reductants as well as different superconductors with copper.

2.3.2.3 Collaborations

This project has continued its collaborative efforts with two other Basic Energy Sciences (BES) projects at ORNL. This project has manipulated the oxygen content in five large Y123 crystals for the BES project that is led by Herbert Mook, Pengcheng Dai, and Mohana Yethiraj. After the crystals have reached the desired oxygen content, magnetic dynamics experiments, which permit direct observation of the superconducting band, are performed on the underdoped Y123 crystals. Preparation of a manuscript, which describes our recent magnetic dynamic results, is under way. The second collaboration involves the BES project that is led by Mariappan Paranthaman and Amit Singhal. After the Y123 has been prepared through the sol-gel technique, the sample is analyzed with our DTA/TGA apparatus. Since our task has performed the same experiments on Y123 samples that were prepared by conventional means, a direct comparison of the different sample preparations can be made.

Table 3. The oxygen content of Y123 + CuO (1:4.3) melts at various temperatures and partial oxygen pressures

Partial oxygen pressure (MPa)	Temperature (°C)	Oxygen content (mol)
0.1	981.9	11.07
0.1	1011.3	10.27
0.1	1111.2	8.95
0.1	1193.6	8.75
0.1	1277.2	8.70
0.01	938.1	10.48
0.01	972.4	9.24
0.01	1028.2	8.29
0.01	1113.1	8.09
0.01	1196.6	8.02
0.01	1275.5	7.89
0.001	941.7	8.04
0.001	1027.6	8.07
0.001	1109.6	7.96
0.001	1197.2	7.87
0.001	1277.5	7.79
0.0001	1116.3	7.91
0.0001	1186.6	7.79
0.0001	1276.5	7.65
0.000006	1111.1	7.69
0.000006	1196.6	7.57
0.000006	1277.7	7.50

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 presently 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 Oak Ridge has been shut down since 1969, when the fuel salt was drained from the core into two 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, as well as its transport from the fuel salt, was unexpected. The 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) trapping 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.

3.1.2 Progress

A conversion process was selected and fully tested at one-fifth scale. Noteworthy characteristics of this process that distinguish it from others that have been developed are the following:

- simplicity and adaptability to small-scale hot cell operation;
- absence of moving parts and very compact size;
- absence of stirring, filtering, or transfer between vessels;
- minimization of secondary wastes and uranium losses; and
- ability to process NaF traps and uranium-laden activated charcoal.

Fabrication of the full-scale prototype system for the conversion process is under way. A reevaluation of available facilities for conversion continues. A cost estimate for documentation necessary to upgrade Building 4501 to receive and process fissionable materials was received from the Safety Analysis Group in Engineering in June. This review indicated that no physical upgrades to Building 4501 appeared to be necessary. Estimates for similar documentation for Buildings 3019 and 3525 were also prepared and are being reviewed by facility personnel. The reevaluation is being performed because of operational inflexibility and concerns that the size of the hot cell containment will not be adequate in Building 3019. An overall analysis of the different facilities for performing conversion will be completed and a decision milestone set for December 1.

3.2 URANIUM DEPOSIT REMOVAL AND PASSIVATION OF FLUORINATED CHARCOAL (G. D. Del Cul, D. W. Simmons, L. D. Trowbridge, 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, gamma 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 research and development (R&D) activities are in support of the MSRE remediation program.

3.2.1 Purpose and Scope

The MSRE auxillary 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. In addition, 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, is believed to consist of unreacted charcoal.

Fluorinated charcoal, when subjected to rapid heating, can decompose to generate gaseous products (CF_4, C_2F_6, etc.). Under confined conditions, the abrupt, exothermic decomposition (deflagration) 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 for the installation of piping and instrumentation. The drilling-tapping operations can result in local heating in excess of 100°C. Because the fluorinated charcoal starts to thermally decompose at these temperatures, it is necessary to chemically transform this reactive fluorinated charcoal into a more stable material prior to the removal of the uranium in the ACB.

3.2.2 Progress

Preliminary operating parameters for the passivation process have been established based on the results from our R&D program. Laboratory testing of a 6-in.-diam charcoal bed section established the centerline and surface temperature for combinations of ammonia concentrations and flow rates. Additional testing is planned with small quantities of fluorinated charcoal loaded in the 6-in.-diam test section. This test specimen will be treated with the sequence of increasing ammonia concentrations and flows similar to that planned for the actual ACB passivation operation.

3.3 SALT DISPOSITION STUDIES (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 (HFIR) 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, the associated effects of long-term radiolysis on the fuel salt itself, and those physical-chemical reactions that might occur during remelting of the fuel salt. 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 that an efficient and safe means of salt removal from the MSRE drain tanks will result. Based on these studies, testing of specialized salt-removal techniques will also be performed.

3.3.2 Progress

Primary attention was focused on assessing the reduction chemistry and phase segregation associated with melting highly irradiated, fluorine-deficient MSRE simulant salt. Backscattered electron imaging and the associated X-ray dispersive spectra on a metallographic preparation of the inner capsule wall in contact with the melt revealed a ~5-μm-thick zirconium-rich outer metal layer. A small proportion of uranium (~0.7 wt %) also appears to be uniformly distributed in this layer. In addition to this uniform surface layer, submicron particles of almost pure uranium are apparent above the zirconium layer at a few locations. It is certain that this material originated in the sample (i.e., it is not a contaminant), but it is not yet clear whether the metallographic preparation is responsible for its present distribution. A more complete picture of the melt chemistry will emerge from the ongoing elemental analysis of the various distinct features of the experimental capsule.

The MSR-4 plug irradiation specimen inserted into the HFIR cooling pool last quarter has seen extensive irradiation (~ 45 Wh/g) and yet has generated very little radiolytic gas. This sample was removed from the HFIR cooling pool and analyzed extensively. No anomalies or clear explanations for the virtual absence of radiolysis in this sample were evident after analysis and inspection. Because of the very slow quench rate during the original solidification of MSR-4, it was decided to remelt the sample and quench it quickly before returning the sample for reirradiation.

For the ultimate safe remelting of the fuel salt in the drain tanks, we are developing a pool-melt method for creating a small pool in the center of the frozen salt and adjusting that chemistry with an HF/H_2 sparge. More heat would then be applied, and the chemistry of the larger molten pool further adjusted. The process would be repeated until the entire drain tank contents were totally molten. Work with a calcium nitrate–potassium nitrate "pool-melt" simulant salt has shown that such molten pools are reasonably controlled by a central cal-rod type of heater. Methods of monitoring the pool dimensions are currently being considered.

3.4 TECHNICAL SUPPORT TO MSRE REMEDIATION ACTIVITIES
(L. D. Trowbridge)

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Summary: Various technical issues regarding the use of chlorine trifluoride for removing uranium fluoride and oxyfluoride deposits have been evaluated. These nonvolatile uranium deposits have plugged portions of the MSRE off-gas system, preventing removal of the reactive gases from the system.

3.4.1 Purpose and Scope

Direct technical support to the MSRE Remediation project is provided so that the most effective implementation of the procedures is utilized. This included guidance, development, and evaluation activities in both the documentation and actual execution of processes.

3.4.2 Progress

Various technical issues regarding the use of chlorine trifluoride for removing uranium fluoride and oxyfluoride deposits have been evaluated. These deposits have been found in the off-gas system as nonvolatile deposits that plug portions of the MSRE off-gas system and prevent removal of the reactive gases, primarily fluorine and uranium hexafluoride, in that system. This work will serve as a resource for technical information needed by internal and external reviewers of this aspect of MSRE remediation plans.

Planning and safety analysis activities relating to the denaturing of the MSRE charcoal bed include preparation of a process description and a provisional sequence of concentrations and flows to be used. In addition, analyses of specific technical issues that have arisen during the development of safety documentation for this project have been undertaken. Among these topics are (1) heat evolution rates for various chemical reactions involved in C_xF passivation, (b) correlation of temperature between the ACB wall and axis, and (3) provisional estimation of operational temperature limits.

3.5 PUBLICATIONS

D. F. Williams, L. M. Toth, and G. D. Del Cul, *Recent Experimental Results Regarding the Mechanism of* UF_6 *Generation in MSRE Fuel Salt*, ORNL/CF-97/DRAFT, July 28, 1997.

L. D. Trowbridge, *Technical Bases for the Use of* ClF_3 *in the MSRE Reactive Gas Removal Project*, ORNL/ER-402, June 1997.

4. CHEMISTRY RESEARCH

L. M. Toth

4.1 MOLECULAR IMPRINTING APPROACH TO SMART INORGANIC/ORGANIC HYBRID SORBENTS (S. Dai, Y. S. Shin, M. Burleigh, and L. M. Toth)

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Summary: We have developed Schiff-base inorganic/organic hybrid sorbents to selectively recognize UO_2^{2+} and Ni^{2+}. This work is an extension of our previous molecular imprinting on silica-based materials. The essence of this work is an innovative combination of small-molecule templating synthesis with molecular imprinting synthesis in solid-state materials. This combinational synthetic methodology can be viewed as double imprinting. The sorbent materials made using double imprinting are expected to contain functionalized rigid cavities. Characterization and evaluation of these new sorbents are in progress.

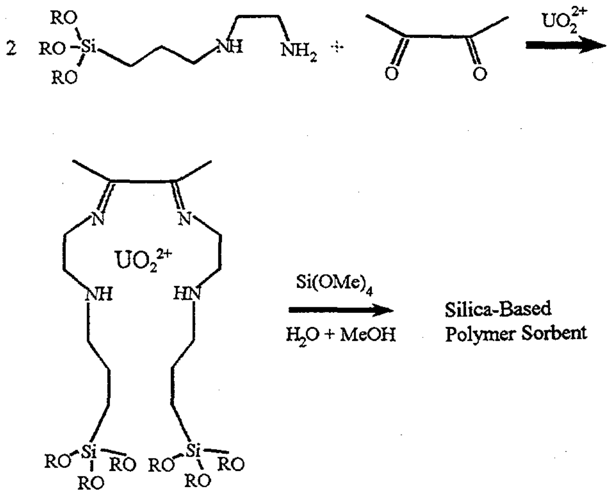
4.1.1 Purpose and Scope

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 is 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 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

Templating synthesis using metal ions is a well-known technique to assemble small molecules into macrocyclic ligands. These macrocyclic ligands are expected to have strong affinities for the templating metal ions. The functionalized silicon alkoxide monomers thus synthesized form hybrid polymers upon hydrolysis with tertamethyl orthosilicate. An example of this methodology is schematically shown in the figure. Hybrid silica sorbents templated by UO_2^{2+} and Ni^{2+} have been prepared. The color of these materials is red brown, as expected for Schiff-base complexes.



The protonation of the amine functional group in the macrocyclic structure was used to efficiently remove UO_2^{2+} and Ni^{2+} template ions from our sol-gel glasses. Nickel- and uranyl-free imprinted glasses were obtained by soaking the doped glasses with nitric acid overnight. This ORNL initial work played a key role in a joint DOE Environmental Management Science Program (EMSP) proposal that was awarded this year to The University of Tennessee and ORNL.

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 accepted for publication in *Inorganic Chemistry*.

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 designed 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 such 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 PUBLICATIONS

H.-M. Xiao, S. Dai, and J. P. Young, "A New Approach to Raman Spectroscopic Measurement of Corrosive Molten Salts," *Anal. Chem.*, submitted.

S. Dai, Y. Shin, C. E. Barnes, and L. M. Toth, "Enhancement of Uranyl Adsorption Capacity and Selectivity on Silica Sol-Gel Glasses via Molecular Imprinting," *Chem. Mater.*, a special issue dedicated to the advanced application of sol-gel process, in press.

Y.-H. Lee, S. Dai, and J. P. Young, "Surface Enhanced Raman Spectroscopy on Sol-gel Films Doped with Silver Particles," *J. Raman Spectr.* **28**, 635 (1997).

S. Dai, Y. Shin, L. M. Toth, and C. E. Barnes, "Comparative UV-Vis Studies of Uranyl Chloride Complex in Two Basic Ambient-Temperature Melt Systems: The Observation of Spectral and Thermodynamic Variations Induced via Hydrogen-Bonding," *Inorg. Chem.* **36**, 4900 (1997).

S. Dai, Y. Shin, C. E. Barnes, and L. M. Toth, "Spectroscopic Probing of Adsorption of Uranyl to Uranyl-Imprinted Silica Sol-Gel Glass via Steady-State and Time-Resolved Fluorescence Measurement," *J. Phys. Chem.* **101**, 5321 (1997).

N. A. Stump, R. G. Haire, and S. Dai, "Spectroscopic Investigations of Neptunium's and Plutonium's Oxidation States in Sol-Gel Glasses as a Function of Initial Valence and Thermal History," *Mat. Res. Soc. Symp.* Proc. **465**, 47 (1997).

S. Dai, L. M. Toth, G. R. Hayes, and J. R. Peterson, "Spectroscopic Investigation of Effect of Lewis Basicity on the Valent-State Stability of an Uranium(V) Chloride Complex in Ambient Temperature Melts," *Inorg. Chim. Acta* **256**, 143 (1997).

J. P. Young, S. Dai, Y. Lee, and H. Xiao, "Application of Raman Spectroscopy to High-Temperature Analytical Measurements," pp. 215–23 in *Sensor and Modeling in Materials Processing*, ed. S. Viswanathan, R. G. Reddy, and C. C. Malas, TMS, Warrendale, Pa., 1997.

5. BIOTECHNOLOGY

B. H. Davison

5.1 ALTERNATIVE FEEDSTOCKS PROGRAM FOR CHEMICALS AND PETROLEUM REFINING INDUSTRIES (B. H. Davison, N. P. Nghiem, and B. E. Suttle)

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Summary: "Production of Chemicals from Biologically Derived Succinic Acid (BDSA)" received one of the 1997 R&D 100 awards that were presented at the ceremony and banquet in Chicago on September 25, 1997. The entry was submitted jointly by ORNL, Argonne National Laboratory (ANL), National Renewable Energy Laboratory (NREL), Pacific Northwest National Laboratory (PNNL), and Applied CarboChemicals, Inc. (ACC). The study of fermentation process scaleup was completed this quarter. The reproducibility of results obtained in the 75- and 500-L fermenters has clearly demonstrated that the fermentation process can be easily scaled up. The completion of this series of experiments marked the accomplishment of another important milestone of the project.

5.1.1 Objective

The goal of the Alternative Feedstocks Program (AFP) is to develop cost-effective and environmentally acceptable technologies for the production of chemicals and materials from renewable feedstocks for use in the industrial and commercial sectors of the United States. This is an interlaboratory program to plan and carry out a program for DOE. ORNL's effort will contribute to the program planning and assessment activities, as well as laboratory research and development on bioprocessing technologies that will lead to pilot-scale demonstration with industry.

5.1.2 Progress

5.1.2.1 Programmatic and Industrial Partnering

The 1997 R&D 100 was awarded at the ceremony and banquet in Chicago on September 25, 1997. The entry was submitted jointly by ORNL, ANL, NREL, PNNL, and ACC. The title of the entry is "Production of Chemicals from Biologically Derived Succinic Acid (BDSA)." The award was also recognized at the ORNL 1997 R&D 100 reception in Oak Ridge, Tennessee, where the attendees included Dr. Al Trivelpiece, ORNL Director, and Congressman Zach Wamp. Dr. Brian Davison was asked to represent all of the 1997 ORNL R&D 100 winners and speak at the reception.

The metrics for the BDSA project were revised and submitted.

A preproposal entitled "Production of Chemicals from Lignocellulosic Hydrolysates" was submitted to the Office of Industrial Technologies in response to the solicitation of the Chemical Industry Initiative. The objectives of the preproposal are to add the ability to metabolize xylose efficiently to AFP-111 and to test its new capability for the production of succinic acid from industrial lignocellulosic hydrolysates. The participants of the preproposal include ORNL; ANL; ACC; and Arkenol, Inc.

5.1.2.2 Biocatalyst and Fermentation Development

The study of fermentation process scaleup was completed this quarter. The medium used was 25% light steep water. One more experiment was performed in the 75-L fermenter. The results obtained in this experiment verified the reproducibility of results at this scale.

After reproducibility of results was demonstrated at the 75-L scale, the fermentation process was taken to the next scale of 500 L. The conditions employed were exactly the same as those used in the experiments at the 75-L scale. Three experiments were successfully performed. Reproducibility of results in all three experiments was observed.

The reproducibility of results obtained in the 75- and 500-L fermenters has clearly demonstrated that the fermentation process can be easily scaled up. The experience gained through these experiments will be very useful for the further scaleup of the process to the production scale. The completion of this series of experiments marked the accomplishment of another important milestone of the project.

Our next effort will focus on the improvement of productivity. Previous results showed that the rate of succinic acid production was proportional to the cell density in the fermenter. Several methods of cell concentration will be considered. The first will be the use of membrane filtration to recover the cells from the spent fermentation broth. The recovered cells then will be recycled to the fermenter for further use. This method was chosen because it is by far the most widely accepted method for large-scale application by the industry.

5.2 ADVANCED BIOREACTOR SYSTEMS FOR ALCOHOL FUEL PRODUCTION (N. P. Nghiem, B. H. Davison, M. Y. Sun, M. S. Krishnan, T. L. Metheney, and M. M. Blanco-Rivera)

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Summary: Preliminary experiments on the production of ethanol from lignocellulosic hydrolysate by the NREL's recombinant *Zymomonas mobilis* strain were initiated. In these experiments, switchgrass hydrolysate obtained by dilute acid hydrolysis was used. The results showed very efficient glucose utilization.

5.2.1 Objective

The objective of this project is to develop and demonstrate advanced fermentation and separation systems for enhanced ethanol fermentation that operate continuously and have high productivity, high yield, and good operability with reduced energy requirements.

5.2.2 Progress

5.2.2.1 ORNL

Twenty-five weight-volume percent solid hydrolyzed cornstarch was used to test the ethanol tolerance of the coimmobilized glucoamylase–*Zymomonas mobilis* biocatalyst. Maximum ethanol concentration of 85 g/L (10% by volume), which is in the range acceptable to the bioethanol industry, was obtained. Other batch experiments indicated that this hydrolyzed cornstarch feed did not require additional nutrients for good ethanol production. Both 25 and 15 w/v % solid cornstarch hydrolysates were tested in a 2-in. fluidized-bed reactor having a working volume of 0.9 L. The solids in the feeds caused plugging and nonuniform liquid distribution within the reactor. Because a significant portion of the biocatalyst bed was not fully utilized, conversion was low. After six retention times, only 20% of the 15 w/v % solid feed was obtained in a single-pass continuous operation. The option of solid removal by filtration prior to ethanol production in the fluidized-bed reactor has been discussed with Morris Ag-Energy and will be applied in the next set of experiments.

Preliminary experiments on the production of ethanol from lignocellulosic hydrolysate by NREL's recombinant *Zymomonas mobilis* strain were initiated. In these experiments, switchgrass hydrolysate obtained by dilute acid hydrolysis was used. The results showed very efficient glucose utilization. However, xylose conversion was incomplete, probably due to the presence of the salts formed during the neutralization of the feed solution following the acid hydrolysis. Simultaneous saccharification and fermentation also was tested with the acid-pretreated switchgrass using an industrial cellulase. Good yield of ethanol and no accumulation of glucose were observed. Xylose accumulation was below 2 g/L.

The calculations of the second part of the mathematical model were completed. Calculated concentration profiles of maltodextrin, glucose, and ethanol in a fluidized-bed reactor using the coimmobilized biocatalyst show good agreement with the experimental data.

5.2.2.2 Bioengineering Resources, Inc.

In the area of ethanol production from corn-processing waste, 23 biomass gasifier manufacturers were identified, and 4 were selected for further consideration. Design information on substrate availability in solid and starchy wastes was collected. An initial economic assessment was made. In this economic analysis, two plant sizes (500 and 1000 dry tons/day) and two levels of moisture content of the waste (15 and 43%) were considered.

6. SEPARATIONS AND MATERIALS SYNTHESIS

D. W. DePaoli

6.1 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 of multiphase systems, particularly those that explore the use of electromagnetic fields to enhance transport processes, are continuing. Progress has been made in several areas including (1) drop deformation and breakup from a capillary tube in liquid-air and liquid-liquid systems, (2) wetting and stability of drops on solid surfaces, (3) mass transfer in liquid films, and (4) investigation of mixing in electrohydrodynamic flows.

6.1.1 Purpose and Scope

This program is comprised of several fundamental studies that explore transport processes in multiphase separations, with particular emphasis placed on the application of electromagnetic fields for enhancement. 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 information necessary to devise novel means to dramatically improve transport rates in these systems and, thus, will have 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. In addition, support was given to the EMSP biofiltration project in the application of finite-element mass-transfer modeling.

6.1.2 Progress

6.1.2.1 Drop Deformation and Breakup

A numerical model has been modified for simulating the dynamics of drop deformation and breakup from a capillary tube using volume-of-fluid and continuous-surface-force methods. Extensive computations have been carried out to simulate drop formation in liquid-liquid systems at different physical conditions. This study is of particular importance in exploring the velocity field of drop liquid, which is essential for predicting mass transfer in distillation and extraction processes. Moreover, the model predicts the generation and fate of satellites, which are important in spray-coating and ink-jet technologies. Two noteworthy results of this work are that flow regimes that result in no satellite formation have been discovered and very good agreement with our experimental results was found. Two manuscripts reporting the results are being prepared for submission to *Journal of Fluid Mechanics*.

6.1.2.2 Wetting and Stability of Drops on Solid Surfaces

A fundamental study is conducted to understand and improve the wettability and stability of liquid drops on solid surfaces. This work is conducted in collaboration with Professor R. M. Counce of The University of Tennessee and his student, B. A. Starkweather. The capability of solutions containing different surfactants and having varied pH values to remove oil or organic contaminants from solid surfaces is investigated. The research is of significant importance in industrial and environmental cleaning and degreasing and in oil-recovery processes. A manuscript reporting the results is in preparation for submission to *Journal of Colloid and Interface Science*.

6.1.2.3 Mass Transfer in Liquid Films

In support of the EMSP biofiltration project, a numerical model using the finite-element method has been developed to simulate mass transfer within a trickle-bed bioreactor. The model determines the substrate concentration in a reactor both along the reactor column and within the biomass film. The fundamental understanding developed will allow optimization of reactor design and operation.

6.1.2.4 Mixing in Electrohydrodynamic Flows

Studies of the capability of inverse electrostatic spraying (IES) for electrohydrodynamic micromixing of fluids have continued. Experiments were conducted that involved injecting a liquid containing a fluorescent dye through an IES nozzle into a glass tube through which a second liquid is flowed. The breakup and/or mixing of the injected fluid under various conditions of flow rate and applied voltage is monitored by illuminating the tube by a laser-light sheet and observing the distribution of fluorescent dye with a video camera. Quantification of the effectiveness of mixing has been made by image analysis; the variance of signal intensity (and, thus, dye concentration) was shown to decrease by more than two orders of magnitude for all fluid systems studied through the application of a high-voltage dc field. Additionally, as described in Sect. 6.2.2.4, a novel and potentially patentable method for improved ultrafine particle production employing electrohydrodynamic micromixing has been developed and proven. Further studies of electrohydrodynamic mixing will be aimed at correlating the measured effectiveness of mixing to operating conditions and the physical properties of the fluids and at evaluating the effectiveness of application to other reaction systems.

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

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Summary: Progress has been made in several aspects of synthesis, characterization, application, and processing of ultrafine particles, as well as advanced ceramic materials, including (1) homogeneous precipitation in inorganic salt solutions of mixed solvent, (2) modeling synthesis of nanocrystalline zirconia particles by forced hydrolysis, (3) microsphere formation of aluminum isopropoxide by supercritical fluids processing, (4) electrically enhanced ultrafine particle synthesis, and (5) synthesis and characterization of nanostructured perovskite materials for catalysis.

6.2.1 Purpose and Scope

This materials sciences research program involves fundamental studies of chemically reactive systems for the synthesis of ultrafine (particularly nanosized), monodispersed particles (i.e., 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 three major wet-chemical systems (1) homogeneous precipitation in inorganic salt solutions of mixed solvent, (2) forced hydrolysis via hydrothermal processing of inorganic salt aqueous solutions, and (3) acid- or base-catalyzed hydrolysis and condensation of organometallic compounds (such as alkoxides) in water-alcohol solutions. Experiments utilize several specially developed techniques, including real-time dynamic light scattering (DLS), rapid-mixing flow cell coupled with FTIR and small-angle X-ray scattering (SAXS), as well as high-temperature 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 nanoscale and nanophase ceramics that have dramatically improved properties over traditional "coarse-grained" ceramics. These advanced ceramics are potential candidates as structural ceramics, electroceramics, catalysts, nanocrystalline thin films, coatings, and nanostructured inorganic membranes.

6.2.2 Progress

6.2.2.1 Homogeneous Precipitation in Inorganic Salt Solutions of Mixed Solvent

Extensive experiments were carried out on the effect of processing parameters on the particle growth characteristics in mixed-solvent synthesis systems. A real-time DLS technique was used for automatic growth data collection. For the first time, we discovered two major types of characteristic growth curves: S growth and S-J growth, corresponding to the formation of colloidally stable sol particles and gel materials, respectively. Both SAXS and FTIR experiments were proposed to study mechanisms of fundamental interactions between macromolecules and zirconium hydrous polymers as well as solvent molecules.

The zirconia sol-gel materials produced from the mixed-solvent system under systematically designed conditions were studied by high-temperature XRD. Phase-transformation XRD spectra were collected. The relationship of phase-transformation patterns to the synthesis conditions were determined.

6.2.2.2 Modeling Synthesis of Nanocrystalline Zirconia Particles by Forced Hydrolysis

A refined population model was further developed to better predict the early-stage polymeric cluster growth. In addition to the particle-particle interactions between relatively large colloids (>10 nm), the real emphasis of this model is the interactions between relatively small size clusters through an aggregative mechanism, which were included to describe the nucleation process. This is a collaborative research effort with Professor M. T. Harris at the University of Maryland.

6.2.2.3 Microsphere Formation by Supercritical Fluids Processing

We have successfully completed data collection on solubility of aluminum alkoxide in supercritical propane. Further, a RESS [rapid expansion of supercritical (fluid) solution] nozzle was redesigned to produce monodispersed powders. Current work is focused on the development of thermodynamic models to predict the solubility of organometallic compounds in supercritical fluids. This is a collaborative work with Professor N. Xu at the Nanking University of Chemical Technology.

6.2.2.4 Ultrafine Particle Synthesis by Inverse Electrostatic Spraying (IES)

A technique that employs electrohydrodynamic micromixing for ultrafine particle synthesis was developed and proven. Scanning electron microscopy studies of the ultrafine particle samples indicated that monodispersed, submicron-sized, sphere-like powder materials were successfully produced by appropriately controlling the reaction and spraying conditions. A correlation between the particle size and the spraying voltage was observed. The developed IES reactive system offers the following advantages relative to the classical chemical synthesis in batch solutions: (1) faster particle formation rate, (2) continuous production, (3) higher solid fraction, (4) stability of the ultrafine particle sol, and (5) controllable size and monodispersity. Currently, a patent filing is in process. Based on these very promising results, we will pursue more detailed applied studies if funding can be secured to support this effort.

6.2.2.5 Synthesis and Characterization of Nanostructured Perovskite Materials for Catalysis

The current research is focused on developing perovskite-type materials with improved stability and low thermal-expansion coefficients by optimization of composite powder preparation and material compositions. Various powders of $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$-based perovskites with different compositions have been prepared by solid reactions and citric acid routes. The powder size and size distribution can be controlled using the proper method. The powders have been calcined at high temperatures to form different samples to be tested. Extensive high-temperature XRD experiments were conducted during Professor N. Xu's visit to ORNL, and the data are currently under analysis.

6.3 PHASE EQUILIBRIA MODIFICATION BY ELECTRIC FIELDS (C. Tsouris, V. M. Shah, M. A. Spurrier, 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, liquid-liquid equilibria, and vapor pressure experiments are in progress, using various liquid mixtures of polar-nonpolar, polar-polar, and nonpolar-nonpolar components. The results obtained to date show that electric fields have an effect on the vapor concentration of the vapor-liquid equilibria of some systems.

6.3.1 Purpose and Scope

The primary objective of this project is to enhance separations of mixtures by applying an electric field across an interface between two phases. Enhancement in separation may be produced either by increasing transport rates through the interface or by changing the phase equilibria. 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.

6.3.2 Progress

Experimental systems have been assembled and are currently used for vapor-liquid and liquid-liquid studies under strong electric fields. Batch-distillation, vapor-liquid equilibria, liquid-liquid equilibria, and vapor pressure 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, and isopropyl alcohol and toluene, which is a polar-nonpolar system, showed a significant effect of electric fields in both batch distillation and phase equilibria. It has been observed that, when a change in the vapor concentration occurs, the vapor temperature drops by approximately 0.5 °C. A specially designed cell has been constructed from

Teflon, glass, and stainless steel for vapor pressure and temperature measurements of pure liquids and mixtures under the influence of electric fields. These experiments are currently in progress.

Electrohydrodynamic experiments were also conducted in which bubble formation of air in various solvents, including water, methanol, ethanol, propanol, isopropanol, and butanol, under the influence of an electric field, has been investigated. Air bubbles were introduced through an electrified metal capillary, which was insulated by a glass tube. The tip of the capillary had a conical shape. The effect of an electric field, formed between the electrified capillary and an electrical ground immersed in the liquid at a distance of 10 cm above the capillary tip, on the bubble diameter and velocity was determined by using an optical technique for size measurements and a phase-Doppler velocimeter for velocity measurements. The bubble size decreased, and the bubble velocity increased with increased applied voltage. A dripping mode of bubble formation was observed at low voltages, which changed to a spraying mode as the applied voltage was increased. The average bubble size at spraying conditions was approximately 50 μm. Bubble velocities up to 2 m/s were measured by the phase-Doppler velocimeter at high values of applied voltage. A threshold value of the applied voltage on the metal capillary was found, above which air was pumped by the electric field into the liquid column. This voltage was different for the various solvents that have been used in these experiments.

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

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Summary: Laboratory studies with model systems and waste surrogates showed that magnetic-seeding filtration may be applicable for the removal of solids from a wide range of waste streams. Bench testing was conducted on the removal of iron-containing precipitates that have caused significant problems in treatment of contaminated groundwater by ion exchange; the results were successful, but it is unlikely that the technology will be immediately implemented. Significant progress was made in development of predictive design tools.

6.4.1 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.

6.4.2 Progress

Bench-scale testing of magnetic-seeding filtration to remove iron-containing precipitates was completed. The results indicated that seeding with magnetic particles is necessary for removal of the iron hydroxide precipitates. It was shown that, under proper conditions, essentially complete removal of iron precipitates by magnetic-seeding filtration is possible. It was also shown that magnetic-seeding filtration can be employed to significantly reduce the buildup of pressure drop across a packed bed and, thus, enhance the lifetimes of zeolite ion-exchange beds. However, due to the limitations imposed by the specific application at a groundwater seep at ORNL (including very low liquid head, small size constraints, and remote, unattended operations), it is not likely that magnetic-seeding filtration will be immediately applied. The technology should be considered for planned future groundwater treatment facilities.

Significant strides were made in the modeling work conducted in collaboration with Professor Sotira Yiacoumi and her research group at Georgia Institute of Technology. Fundamentally sound, yet practical, models of the magnetic-seeding filtration process were developed. Previously developed models for particle flocculation and magnetic filtration are limited to flocculation and filtration of particles having uniform size and magnetic susceptibility. Furthermore, the existing models are highly dependent on experimental data for the calculation of empirical coefficients. A modeling approach that systematically combines flocculation and magnetic filtration models has been developed in this work. This modeling approach provides several significant results: (1) enhanced ability of predictive models from homogeneous to heterogeneous flocculation and magnetic filtration, (2) more accurate particle size prediction by the fractal dimension correction, (3) prediction of the magnetically seeded filtration process without using fitting parameters, and (4) design and optimization of such treatment processes without the use of experimental data.

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

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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. An experimental apparatus for ozonation studies has been set up. Included in this setup are (1) ozone generation from air or oxygen; (2) ozone spraying in an aqueous phase containing an organic solute, such as phenol, by means of an electric field; and (3) collection of gas and liquid samples for chemical analysis. Ozone is generated by two mechanisms: (1) corona discharge and (2) electrochemical reaction. Corona discharge can produce up to 6% (by volume) ozone in oxygen, while the electrochemical method can produce up to 18% ozone. Ozonation experiments have just been initiated, and preliminary data are reported here.

6.5.1 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, which 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, pharmaceutical, and other industries; municipal potable water production; and wastewater treatment.

6.5.2 Progress

A corona-discharge ozone-generator system has been set up. Ozone concentration is monitored either by uv (gas phase) or by colorimetry (liquid phase). The feed gas is oxygen utilized via a syringe pump. Aqueous samples are taken at various time intervals using a syringe to measure the concentration of phenol by gas chromatography. An electrochemical-cell ozone generator, which produces higher concentrations of ozone than the corona-discharge ozone generator, is also used in this project. In the electrochemical method, water is used for ozone generation instead of oxygen. The products are ozone, oxygen, and hydrogen. The experimental setup with the electrochemical-cell ozone generator is basically the same as that for the corona-discharge ozone generator.

A method for ozone concentration measurements using an indigo colorimetric method has been set up and will be employed in the testing. This method is based on light absorbance differences caused by color deterioration of indigo dye by ozone. The analysis of phenol is being performed using solid-phase microextraction (SPME), followed by analysis using a gas chromatograph with a flame ionization detector. This approach is employed due to the low concentrations of phenol used in the experiments. SPME involves the sorption of analytes to a phase-coated fiber (polyacrylate coating) contained within a syringe.

Preliminary results of phenol oxidation by ozone via electrostatic spraying showed a higher reaction rate than that observed with a bubble diffuser system, which is the conventional method of producing small bubbles of ozone in water. Currently, the focus is to determine the accuracy and the error of the various methods used in the analysis. Once the error bars are established, systematic experiments will be conducted to demonstrate the potential of electrostatic spraying for the enhancement of ozonation efficiency.

Additional progress was made in the submission of a possible invention disclosure on a technology development related to this project.

6.6 DEVELOPMENT PROGRAM IN ELECTRODISTILLATION (C. Tsouris, D. W. DePaoli, and K. D. Blankenship)

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Summary: The enhancement of distillation efficiency by using electric fields is investigated in this task. A three-stage distillation column has been designed and constructed, which allows high-intensity electric fields to be applied. Experiments will be conducted to determine whether electric fields can enhance the separation efficiency of binary mixtures.

6.6.1 Purpose and Scope

The primary objective of this project is to enhance the separation factor of distillation of liquid mixtures by using electric fields. It is expected that transport effects on pumping, spraying, and mixing of bubbles in the liquid, as well as equilibria effects, will enhance the separation. These expectations are supported by earlier work on phase equilibria modification by electric fields, batch distillation experiments, and electrohydrodynamic experiments using gas-liquid systems. The work may significantly impact industrial separations by distillation, which consume 2.4 quadrillion British thermal units per year in the United States alone.

6.6.2 Progress

We have designed a distillation column consisting of special arrangements of glassware and metal plates. The column has a boiling flask, four compartments (each 10 cm in length), a condenser, and metal plates separating the compartments. In the next quarter, the column will be tested for the distillation of binary mixtures under high-intensity electric fields.

6.7 ELECTROCOAGULATION (C. Tsouris, D. W. DePaoli, J. T. Shor, M. Z.-C. Hu, M. R. Chattin, and M. A. Spurrier)

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Summary: Bench-scale testing was conducted for the EM-50 Mixed Waste Program to determine the feasibility of application of electrocoagulation for treatment of wastewaters generated by incinerator off-gas scrubbers. A novel process that utilizes electrocoagulation was developed and proven. Tests of this process, conducted with a surrogate solution for Central Neutralization Facility (CNF) wastewater that contained elevated copper levels but no uranium, showed that it was possible to remove copper to levels below detection limits. Given these positive results, it is recommended that further investigations be conducted into the capability of this process for removal of heavy metals and radionuclides.

6.7.1 Purpose and Scope

Electrocoagulation is a wastewater treatment technology that may provide several distinct advantages when used for heavy metal and radionuclide removal, including reduced waste volume, lower cost, and improved solid-liquid separation. The purpose of the limited amount of bench-scale testing conducted in this work was to determine the feasibility of applying this technology to the CNF wastewater.

6.7.2 Progress

The task consisted of the following steps: (1) laboratory tests were conducted to identify process conditions under which magnetic particles are formed; (2) the solids produced by electrocoagulation were characterized in terms of their size, structure, magnetic susceptibility, and other physical properties; (3) the separation of heavy metals either by coprecipitation or sorption during the formation of particulates was measured; and (4) a novel, potentially patentable combined process of electrocoagulation and high-gradient magnetic filtration (HGMF) for the separation of metal ions (electrocoagulation) and solid particles (HGMF) was demonstrated in the laboratory using surrogate solutions.

This work has uncovered some aspects of electrocoagulation that provide promise for improved wastewater treatment. It was shown that magnetite can be formed by the process, most readily in deionized water but also in simulated CNF wastewater under controlled conditions. It was shown that heavy metals can be effectively removed by (1) formation of magnetic solids by electrocoagulation, (2) pH control, and (3) magnetic filtration. Given these positive results, it is recommended that further investigations into the capability of this process for heavy metals and radionuclide removal be conducted. We have identified several steps that should be undertaken to explore the feasibility of the process: (1) experiments with nonradioactive surrogate solutions for optimization of process conditions for waste volume, materials usage, and contaminant removal; (2) testing and adjustment of process conditions with real wastewater; (3) testing on actual wastewater with small-scale commercial equipment; and (4) evaluation of feasibility for full-scale operations.

6.8 PARTICLE INTERACTIONS IN REACTIVE SYSTEMS (C. Tsouris, S. Yiacoumi, and K. Subramaniam)

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Summary: In this task, we investigate the effect of sorption of metal ions from aqueous solutions on interparticle forces. Sorption of metal ions by colloidal particles changes the surface properties of the particles, as well as the chemical speciation of the sorbing species. Sorption of copper and cadmium ions by ferric oxide particles was studied using batch equilibrium and kinetics experiments. Changes in the size distribution of the aggregates of ferric oxide particles during uptake of ions were observed in the sorption kinetics studies. These findings indicate a potential role of metal ion uptake in particle flocculation kinetics through alteration of the surface electrostatic potential.

6.8.1 Purpose and Scope

Heavy metal ions are commonly encountered and are difficult-to-treat environmental pollutants. They are introduced into the environment through industrial and domestic wastes. The geochemical fate of these metals is controlled by their reactions with surfaces at the solid-water interface. Most colloidal phases in aqueous solutions are effective sorbents of such contaminants. As metal ions are sorbed on the surface of colloidal particles, the surface properties of the particles change. These changes may cause stable particles to become unstable with respect to flocculation.

The purpose of this work is to determine the conditions under which sorption of metal ions destabilizes the colloidal phase. A unified theoretical approach of metal ion sorption and flocculation of colloidal particles is expected to be developed in this work.

6.8.2 Progress

Work has been conducted in collaboration with Professor Sotira Yiacoumi and her student, Ph.D. candidate Kavitha Subramaniam of the Georgia Institute of Technology, who visited ORNL during the summer. Equilibrium and kinetics experiments of copper and cadmium ion sorption on ferric oxide particles were conducted. During these experiments, the pH of the solution, particle zeta potential, particle size, and metal ion concentration were periodically measured. The sorption process is pH dependent, with the uptake increasing at high pH values. In both copper and cadmium sorption, an increase in the equilibrium pH was observed when the initial pH was in the acidic range and a decrease from initial values was observed in the basic range. A large increase in the zeta potential of the particles was observed during sorption. This increase occurs as a result of surface charge neutralization due to metal ion uptake. Particle destabilization occurs as a result of metal ion sorption. Kinetics experiments indicate that the uptake of copper by ferric oxide particles is a slow process. The pH histories were similar to those obtained in the sorption equilibrium experiments. Changes in the size distribution of the aggregates of ferric oxide particles during uptake of ions are observed in the sorption kinetics studies. These findings indicate a potential role of metal ion uptake in particle flocculation kinetics through alteration of the surface electrostatic potential. These studies are currently continued at the Georgia Institute of Technology under the supervision of S. Yiacoumi and C. Tsouris.

During the summer, Professor Yiacoumi also worked on the hydrodynamics of particle interactions under various flow regimes, with the objective of helping in the initiation of a new research program at ORNL in this area.

6.9 CHEMICAL LEACHING OF MERCURY-CONTAMINATED SOILS (M. Z. Hu and K. T. Klasson)

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Summary: Work was conducted to support EM-50 Mixed Waste Program efforts on the remediation of mercury-contaminated soils. A user-friendly spreadsheet was developed to predict the

results of varying process parameters in a flow sheet of 14 unit operations. The flexibility provided by this program will be valuable in optimization of DOE waste treatment operations.

6.9.1 Purpose and Scope

Chemical leaching is considered a potential technology for remediation of soils contaminated with mercury. For effective implementation of the process, it was determined that a design tool that provides the EM-50 Mixed Waste Program with a means of evaluating of the effects of a broad range of process variables would be highly valuable. This task, conducted at the request of K. T. Klasson of the Engineering Development Section, involved the development of a user-friendly spreadsheet to predict the impact of varying process parameters in the chemical leaching process.

6.9.2 Results

A computer simulation program was developed in Microsoft Excel to predict the chemical leaching process for remediation of mercury-contaminated soils. A total of 14 unit operations were included in the flow sheet of the simulated chemical leaching process. For each unit operation, material balances were made with respect to the liquid stream volume (in liters), solid weight (in grams), and each possible chemical species (in moles) in the stream. The computer calculation is flexible for simulation of different scenarios by variation of input process parameters, with automatic recalculation of results. The capabilities provided by this tool will guide the optimization of chemical-leaching soil-remediation processes.

6.10 INDUSTRIAL INTERACTION (D. W. DePaoli)

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Summary: D. W. DePaoli was one of four ORNL employees who spent 3 weeks in an off-site assignment at the R&D centers of a major industrial firm. Several topics were identified that are of interest for possible collaboration.

6.10.1 Purpose and Scope

In March of this year, the Senior Vice President for Science and Technology of PPG Industries visited Oak Ridge with his staff. At the conclusion of a 3-day visit, it was decided that an exchange of personnel would be initiated for the express purpose of identifying Oak Ridge technologies that could contribute to the improvement of PPG's processes and products. PPG has four major business units—glass, fiberglass, coatings and resins, and specialty chemicals. Four ORNL staff members were assigned to cover these business units in the technical areas of chemistry, analytical chemistry, metallurgy, and instrumentation and controls.

6.10.2 Results

D. W. DePaoli spent 3 weeks in an off-site assignment at the PPG's R&D centers, focusing mainly on the coatings and resins group. Several topics were identified that are of interest for possible collaborative research, including at least three that would primarily involve the Chemical Technology Division. A list of potential topics for collaboration was prepared by each of the ORNL visitors to PPG and compiled into a report that has been delivered to each division director.

6.11 PUBLICATIONS

C. Tsouris and D. W. DePaoli, "Special Issue: Electroseparations; Guest Editors' Note," *Sep. Purific. Technol.* **11**, 143 (1997).

S. E. Burns, S. Yiacoumi, and C. Tsouris, "Microbubble Generation for Environmental and Industrial Separations," *Sep. Purific. Technol.* **11**, 221 (1997).

W.-T. Shin, S. Yiacoumi, and C. Tsouris, "Experiments on Electrostatic Dispersion of Air in Water," *Ind. Eng. Chem. Res.* **36**, 3647 (1997).

7. FLUID STRUCTURE AND PROPERTIES

H. D. Cochran

7.1 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.

7.1.1 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.

7.1.2 Progress

With our new parallel code for solving the inhomogeneous Ornstein-Zernike equation on the Paragon, we have recalculated one of the state points of our earlier study of adsorption from dilute supercritical solutions. The recalculations with longer range normal to the surface, with longer range parallel to the surface, and with finer grid spacing in each direction have confirmed our earlier conclusions. However, we note, as expected, that as the grid for discretizing the correlation functions is further refined, small quantitative changes in the correlation functions are observed. We can approximately quantify the small errors in our prior work using these new calculations and plan to prepare a manuscript for publication describing the parallel calculational technique and the sensitivity of results to the discretization.

The student performing the extractions of ω-3 fatty acid from fungal biomass with supercritical CO_2 has completed his Ph.D. and taken a faculty position at Louisiana State University. A manuscript describing both the equilibrium solubility measurements and the mass-transfer-rate measurements is nearing completion.

Dr. Paul Smith of the Chemical Sciences Division has approved our continuing the Seed Money project (reported in Sect. 7.2) for up to 1 year with one graduate student while seeking funding from a sponsor interested in applications. Next quarter, electrodispersion results will be reported.

Plans have been completed for study of the radius of gyration of chain molecules (polydimethylsiloxane) in supercritical CO_2 by small-angle neutron scattering (SANS). These experiments are scheduled for the next quarter.

7.2 ELECTRODISPERSION OF H_2O IN SUPERCRITICAL CO_2 (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.

7.2.1 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.

7.2.2 Progress

With the new, larger pressure cell, we were successful in producing submicron-sized aqueous dispersions in supercritical CO_2 using pulsed high-intensity electric fields. We had good results with an electrode geometry employing a tapered capillary for water feed as one electrode (ground) and a wire mesh about 2.5 cm below the orifice as the other (high-voltage) electrode. A 12 vol % solution of ethanol in water was readily dispersed as well, and the extract condensed from the supercritical CO_2 has been collected for analysis.

Future reports on work in this area will appear under the heading "Interactions of Solutes, Solvents, and Surfaces."

7.3 MOLECULAR-BASED STUDY OF REVERSE MICELLES IN SUPERCRITICAL CO_2 (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.

7.3.1 Objective

The aim of this multi-institutional project is 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.

7.3.2 Progress

Simulations of alkane chains in supercritical CO_2 have shown good agreement with experimental solubility data. Simulations of perfluoroalkane chains in supercritical CO_2 have been completed, but there are scant data available for comparison. We are striving to test agreement between simulations of these systems and SAXS data we obtained earlier. However, to date we have not succeeded in performing both simulations and experiments on the same systems at the same conditions because of technical difficulties. We have now succeeded in molecular simulations of a preformed micelle without surrounding solvent. This new code will be adapted to add solvent molecules. We are scheduled to perform SANS experiments with surfactants from the University of Pittsburgh group during the next quarter.

7.4 STRUCTURE AND PROPERTIES OF CHAIN MOLECULE SYSTEMS UNDER SHEAR (H. D. Cochran, P. T. Cummings, S.-T. Cui, and M. D. Dadmun)

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Summary: This program employs experiments, molecular simulations, and theory to understand the structure and properties of systems of long-chain molecules under homogeneous shear (planar Couette flow).

7.4.1 Objective

The aim of this program is to develop techniques for quantitative, molecular-based prediction of the structure and properties of systems of long-chain molecules undergoing shear flow through coarse graining of accurate, atomistic simulations of shorter-chain systems, as well as coarse graining based on theory and verified by careful small-angle light scattering (SALS), SAXS, and SANS experiments on sheared systems.

7.4.2 Progress

We continue simulations on the Paragon of linear and branched alkanes under shear. The systems we have studied so far include *n*-decane; *n*-hexadecane; *n*-tetracosane; 7-hexyl-nonadecane; 9-octyl-docosane; and 2,6,10,15,19,23-hexamethyl-tetracosane (squalane). Where experimental (Newtonian) viscosity data are available, our results have shown excellent agreement.

We have continued the conceptual design of a shear cell capable of strain rates in the range of 10^8–10^{10} s^{-1}. With sapphire disk and slider, the cell should be suitable for SALS and SANS studies. With beryllium disk and slider, it should be suitable for SAXS. We have been discussing with vendors the possibility of producing these critical components to our (very demanding) specifications.

We have executed a personal services subcontract with Yurij Kaluzhnyi in Ukraine to work in collaboration with us to develop integral equation theories of chain molecule systems under shear. Literature review and definition of our technical approach are essentially complete.

7.5 PUBLICATIONS

7.5.1 Accepted

S. T. Cui, P. T. Cummings, H. D. Cochran, J. D. Moore, and S. A. Gupta, "Nonequilibrium Molecular Dynamics Simulation of the Rheology of Linear and Branched Alkanes," *Int. J. Thermophys.*, accepted (1997).

J. D. Moore, S. T. Cui, H. D. Cochran, and P. T. Cummings, "Lubricant Characterization by Molecular Simulation," *AIChE J.*, accepted (1997).

S. T. Cui, P. T. Cummings, and H. D. Cochran, "Configurational Bias Gibbs Ensemble Monte Carlo Simulation of Vapor-Liquid Equilibria of Linear and Short-Branched Alkanes," *Fluid Phase Equilib.*, in press (1997).

S. A. Gupta, H. D. Cochran, and P. T. Cummings, "Shear Behavior of Squalane and Tetracosane Under Extreme Confinement. I. Model, Simulation Method, and Interfacial Slip," *J. Chem. Phys.* **107**, in press (1997).

S. A. Gupta, H. D. Cochran, and P. T. Cummings, "Shear Behavior of Squalane and Tetracosane Under Extreme Confinement. II. Confined Film Structure," *J. Chem. Phys.* **107**, in press (1997).

S. A. Gupta, H. D. Cochran, and P. T. Cummings, "Shear Behavior of Squalane and Tetracosane Under Extreme Confinement. III. Effect of Confinement on Viscosity," *J. Chem. Phys.* **107**, in press (1997).

7.5.2 Submitted

J. D. Londono, D. D. Wignall, H. D. Cochran, J. B. McClain, D. E. Betts, D. A. Canelas, J. M. DeSimone, E. T. Samulski, and R. Triolo, "Small Angle Neutron Scattering from Polymers in Supercritical Carbon Dioxide," *Neutron News*, submitted (1997).

S. A. Gupta, H. D. Cochran, and P. T. Cummings, "Nanorheology of Liquid Alkanes," *Int. J. Thermophys.*, submitted (1997).

S. T. Cui, P. T. Cummings, H. D. Cochran, J. D. Moore, and S. A. Gupta, "Nonequilibrium Molecular Dynamics Simulation of the Rheology of Linear and Branched Alkanes," *Int. J. Thermophys.*, submitted (1997).

8. BIOTECHNOLOGY RESEARCH

E. Greenbaum

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

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Summary: Further characterization of Photosystem II (PSII) photosynthesis was performed during the quarter. J. W. Lee traveled to Brookhaven National Laboratory to conduct experiments in collaboration with Dr. Paul Falkowski. Significant progress has been made. PSII photosynthesis was demonstrated in wild-type *Chlorella* by photosynthetic quantum requirement measurements, using an original apparatus for making precise measurements of O_2 evolution and light absorption.

8.1.1 Purpose and Scope

This research program is a study of the fundamental reactions of photosynthesis and conversion of light energy into chemical energy. Sustained simultaneous photoevolution of molecular hydrogen and oxygen is studied as a model photosynthetic reaction in which the energy-rich product produced is molecular hydrogen, rather than a carbon dioxide fixation compound. Basic issues such as the molecular mechanisms of gas evolution, thermodynamic limits of photosynthesis, and minimum number of light reactions required to split water to hydrogen and oxygen are studied. Fundamental studies on the enzymology of cellulase are also being performed.

8.1.2 Progress

Further characterization of PSII photosynthesis was performed during the quarter. J. W. Lee traveled to Brookhaven National Laboratory to conduct experiments in collaboration with Dr. Paul Falkowski. Significant progress has been made. PSII photosynthesis was demonstrated in wild-type *Chlorella* by photosynthetic quantum requirement measurements, using an original apparatus for making precise measurements of O_2 evolution and light absorption. The system uses a polarographic oxygen electrode and an optically thin algal cell suspension. The rate of photon absorption was calculated based on the absorption spectra of the algal suspension, the intensity, and the emission spectrum of the actinic light source. The experimental data indicated that the quantum requirement was about 6 photons/O_2 evolved in wild-type *Chlorella*. This result is consistent with some previously reported quantum requirement of less than 8 photons/O_2 evolved in wild-type green algae. This result indicates the existence of our newly discovered PSII photosynthesis in wild-type photosynthetic organisms. Based on the measured photosynthetic quantum requirement, PSII photosynthesis contributed about 50% of the total photosynthesis under the experimental conditions.

Recently we discovered that the simple sugar glucose could be converted enzymatically into molecular hydrogen using two enzymes, glucose dehydrogenase and hydrogenase. Several years ago, it was shown that chloroplast membranes when platinized were capable of the simultaneous photoproduction of hydrogen and oxygen (E. Greenbaum, *Science*, December 1985). The significance of these data was that electrons produced by these membranes were capable of reducing metallic platinum, which catalyzed the production of hydrogen.

We investigated whether enzymes that catalyzed oxidation reactions would be capable of hydrogen production if they were platinized. Such a premise is based on the example of glucose dehydrogenase, which catalyzes the oxidation of glucose to gluconic acid. This enzyme requires an electron acceptor, a molecule called nicotinamide adenine dinucleotide phosphate ($NADP^+$), which upon the oxidation of glucose accepts two electrons and a proton to become NADPH. In our original work on the enzymatic production of hydrogen from sugar, the enzyme hydrogenase then oxidizes NADPH to form molecular hydrogen.

We felt that the obligate need for $NADP^+$ by glucose dehydrogenase could be overcome. The enzyme was platinized, and the platinum atoms were capable of accepting electrons directly from glucose. In other words, platinized glucose dehydrogenase might be able to oxidize glucose with resulting hydrogen evolution without the need for $NADP^+$ or hydrogenase.

The reaction catalyzed by platinum would be as follows:

$$4e^- + 4H^+ \rightarrow 2H_2 .$$

The objectives of this research, therefore, are to platinize oxidase enzymes such as glucose dehydrogenase and to determine whether novel catalysts could be generated that could produce hydrogen from abundant environmental sources such sugar.

Platinization of *Bacillus megaterium* glucose dehydrogenase (purchased commercially from Sigma Chemical Company) was carried out by dissolving 250 units of enzyme activity in phosphate buffer, pH 7.0, containing 2 m*M* sodium hexachloroplatinic acid. Hydrogen gas was bubbled through this solution for 2 h until the solution turned black, an indication that platinum had precipitated from the $[Pt(Cl)_6]^{2-}$ ions in the solution.

As a control, the inert protein bovine serum albumin (with no catalytic activity) was also platinized. This was done by dissolving 10 mg of protein in 10 mL of buffer, pH 7.0, followed by the addition of hexachloroplatinic acid to the solution to a final concentration of 2 m*M*. Platinization was achieved as described for glucose dehydrogenase.

The platinized enzyme or bovine serum albumin was placed in the reaction vessel used for the measurement of hydrogen production and the reaction initiated by the addition of glucose (250 mmol). The experiments were carried out at room temperature. Using platinized glucose dehydrogenase, hydrogen evolution was observed 6 h after the addition of glucose, and a maximum rate of hydrogen evolution of 650 nmol/h was observed. Based upon the stoichiometry of the reaction (1 mol of glucose yields 1 mol of hydrogen), the yield of hydrogen was low (6.6%). However, this was an exciting first result, because it showed for the first time that platinized glucose dehydrogenase was capable of accepting electrons from glucose without the need for $NADP^+$ or hydrogenase.

To confirm that the catalytic activity of platinized glucose dehydrogenase was responsible for the oxidation of glucose and the subsequent transfer of electrons to platinum and the resulting hydrogen evolution, platinization of an inert protein, bovine serum albumin, with no capability for oxidizing glucose, was carried out. Upon addition of glucose to platinized bovine serum albumin, hydrogen evolution was observed after about 2 h at a maximum rate of 550 nmol/h . Again, the yield of hydrogen was low (3.4%,). However, it appeared that the evolution of molecular hydrogen resulting from the addition of glucose to platinized glucose dehydrogenase or bovine serum albumin was unrelated to any catalytic activity of the protein but rather to a direct reduction of platinum by glucose. When glucose was incubated with bovine serum albumin that had not been platinized, no hydrogen evolution occurred, indicating the requirement for the platinum metal or atoms on the protein.

The result with the platinized bovine serum albumin has been repeated, and hydrogen was evolved at a maximum rate of 4.8 mmol/h and a yield of 7.4%. In other words, it appears that glucose can donate electrons to platinum directly with the concomitant evolution of molecular hydrogen. In this regard, it is interesting to note that platinized asbestos was prepared by heating a solution of platinic acid at 90°C in the presence of glucose (W. M. Clark, *Oxidation-Reduction Potentials of Organic Systems*, Williams and Wilkins, Baltimore, 1960). Clearly the reducing potential of glucose (−0.362 V) is sufficient for electron transfer to metallic platinum precipitated on the protein molecules. It is expected that other reducing sugars such as galactose and sucrose will have sufficient reducing potential to effect the same reaction.

8.2 BIOMOLECULAR ELECTRONICS (E. Greenbaum, J. W. Lee, I. Lee, S. Zhang, and R. Collins)

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Summary: Further progress has been made in nanofabrication for molecular optoelectronics. A 10- to 20-Femtometer thin film of dried thylakoid membranes was layered between parallel electrodes consisting of a smooth gold plate and a tin oxide conductive glass plate.

8.2.1 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 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, ORNL. 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.

8.2.2 Progress

Further progress has been made in nanofabrication for molecular optoelectronics. A 10- to 20-Femtometer thin film of dried thylakoid membranes was layered between parallel electrodes consisting of a smooth gold plate and a tin oxide conductive glass plate. The dried thylakoid film typically had an impedance of about 500 kW over a 3 × 3 cm area. When energized by microsecond pulses of about 600 V, photon emission from the thylakoid film was detected through the transparent conductive glass by a Hamamatsu photosensor (Module H5783-01). The photosensor has a nanosecond response time and detection sensitivity in the wavelength range 300 to 800 nm. Experiments showed that an active thylakoid film was required for electroenergized photon emission. A thylakoid film that had been stored for 3 months at room temperature in air completely lost its activity. These preliminary results suggest that photosynthetic reaction centers may act like light-emitting diodes.

8.3 RENEWABLE HYDROGEN PRODUCTION (E. Greenbaum, J. W. Lee, C. V. Tevault, and S. L. Blankinship)

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Summary: During the current reporting period, we focused on the simultaneous photoevolution of hydrogen and oxygen in *Chlamydomonas reinhardtii* mutant B4-PsaA-Δ-2, kindly provided by Dr. Kevin Redding of the University of Geneva. In mutant B4-PsaA-Δ-2, the genetic coding for one of the major structural proteins of the Photosystem I (PSI) reaction center has been deleted. We have observed simultaneous photoevolution of hydrogen and oxygen in this class of mutants.

8.3.1 Purpose and Scope

The purpose of this research program is the production of renewable hydrogen by photosynthetic water splitting. Experiments on the production of hydrogen and oxygen with a view towards the design and development of a real-world process system are being performed. An understanding of the limitations of the photosynthetic process, the light saturation curves, and the long-term stability and endurance of microalgae are under investigation.

8.3.2 Progress

During this period, PSII photosynthesis was demonstrated by simultaneous photoevolution of hydrogen and oxygen using several newly acquired PSI-deficient mutants of *Chlamydomonas*: CC-3362 (A-66-8), CC-3363 (ACC-238), B4-PsaA-Δ-2, and F8-PsaA-Δ-2. Among them, the most noteworthy are B4-PsaA-Δ-2 and F8-PsaA-Δ-2, which were created by deletion of the second exon of the PsaA gene in the chloroplast genome. Recent P700 assays have confirmed that these mutants contain no detectable PSI activity. The first demonstration of the hydrogen and oxygen photoproduction was achieved by steady-state photosynthesis measurements. In this experiment, 35 mL of B4-PsaA-Δ-2 cell suspension containing 10 μg chl/mL was put into our dual-reactor-flow-detection system using helium that contains 700 ppm CO_2 as carrier gas. Actinic illumination (200 $\mu E/m^2 \cdot s$) was provided by an array of light-emitting diodes that emit red light at 660 nm (Q-BEAM 2001, Quantum Devices, Inc., Wisconsin). The onset of actinic illumination resulted in simultaneous photoevolution of hydrogen and oxygen that can be sustained for hours. The photoevolution of hydrogen and oxygen by B4-PsaA-Δ-2 has also been demonstrated in pulsed-light experiments. Consistent results have been obtained.

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

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Summary: Thermophilic enzymes of interest or their clones were obtained from commercial sources and from the ORNL culture collection. Purification and characterization of the enzymes were initiated. A mixed culture from the ORNL collection that originated in a 2.7-km-deep drill hole in Virginiawas examined for potentially useful enzymes. Xylanase and cellulase activities at 701°C were detected in a mixed culture from the same source. Xylanase activity was partially purified from culture supernatant by ion-exchange chromatography, which was carried out with a Pharmacia Mono-P column using 25 m*M* Bis-Tris HCl, pH 7.1. Supernatants or lysates from induced cultures were dialyzed against starting buffer and loaded on the column. Proteins were eluted with a linear gradient from 0.15 to 1.0 *M* sodium chloride. Assays were carried out at 701°C and pH 7.0. Fundamental genetic characterization of the strains present in the culture has been published by the Environmental Sciences Division at ORNL. Several of these unique strains are divergent from any species that has been previously reported. Jizhong Zhou is also designing DNA probes for the isolation of xylanase genes from the mixed cultures.

8.4.1 Purpose and Scope

The absorbance is then used to calculate the quantity (in millimolars) of reducing sugar produced when CEL-001-02 acts on the substrate; from there, the specific activity of CEL-001-02 can be determined. For the *p*-nitrophenol (PNP) assay, a standard curve is prepared from known concentrations of PNP in buffer and a 1 *M* sodium carbonate solution. This mixture absorbs light at 402 nm, with the absorbance directly proportional to the concentration of PNP. After the reaction between CEL-001-02 and the *p*-nitrophenyl D-(+)-cellobioside (PNPC) is allowed to take place in a hot water bath for 5 min, a 100-μL aliquot is removed and added to 1 mL sodium carbonate. The absorbance at 402 nm is then read on the spectrophotometer and used to calculate the quantity of PNP (in millimolars) produced from the PNPC and the specific activity of the CEL-001-02. For the pH-optimization experiments, the test tubes were incubated at 70°C for 5 min. The results of these experiments showed that the optimal pH for all three substrates is 5.0. The temperature optimization for PNPC has also been completed, showing that 75°C is optimal for that substrate.

8.4.2 Progress

Commercial extremozymes from Diversa, Inc., formerly Recombinant BioCatalysis, Inc. (RBI), were examined for suitability for digesting biomass. A β-glucosidase from the RBI collection, GLY-001-02, was found to have high activity on cellobiose and cellooligosaccharides, as well as exceptional thermal stability, remaining active for days at 801°C. The enzyme is extremely thermophilic, with optimal activity at 801°C and pH 4.5. This enzyme also binds very well to crystalline cellulose, although it is unable to hydrolyze the insoluble cellulose.

At the optimal conditions of pH 5.0 and 801°C, the cellulase CEL-001-02 from the RBI collection was found to hydrolyze barley β-glucan five times faster than the mesophilic cellulase endoglucanase II from *Trichoderma reesei*. The cellulase CEL-001-02 readily hydrolyzes cellopentaose and cellotetraose but has very low activity on cellotriose, resulting in accumulation of cellotriose during digestions of cellooligosaccharides or cellulose. This cellulase, which is unique and has only 40% identity with the sequences of previously characterized cellulases, has been crystallized for structural studies by Jerry Bunick and coworkers of the Life Sciences Division at ORNL.

Several clones containing genes of interest from the archaeal organism *Methanococcus janaschii* were obtained from the TIGR/ATCC (The Institute for Genomic Research/American Type Culture Collection). These genes include an endoglucanase, which has been subcloned into an expression vector and the recombinant protein expressed in *Escherichia coli*. Purification of the endoglucanase by heat treatment and affinity chromatography is under way.

8.5 ENZYMATIC CONVERSION OF BIOMASS TO HYDROGEN (J. Woodward and B. R. Evans)

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Summary: During this quarter, we completed our work on the optimization of the rates of hydrogen production. These studies concerned the effect of temperature, $NADP^+$ concentration, and concentration of hydrogenase and glucose dehydrogenase on the rate of hydrogen production from glucose. The maximum rate of hydrogen evolution by this system was observed at a temperature of 50°C, containing glucose (50 m*M*), glucose dehydrogenase (11 units), hydrogenase (64 units), and $NADP^+$ (2 m*M*), although it should be noted that there was little increase in the rate of hydrogen evolution from 0.5 to 2 m*M* $NADP^+$. It is concluded that these reaction conditions are required for optimal rates of hydrogen production from glucose using the glucose dehydrogenase and hydrogenase enzyme couple.

8.5.1 Purpose and Scope

We first performed assays to determine whether the theoretical yield of 2 mol of hydrogen released from glucose was possible in the NADPH production step. This was done by incubating glucose-6-phosphate (G6P), glucose-6-phosphate dehydrogenase (G6PDH), 6-phosphogluconic dehydrogenase (6PGDH), and $NADP^+$ together in 50 m*M* sodium phosphate buffer, pH 7.5, and monitoring the amount of NADPH formed. In these experiments, it was shown that the NADPH production step produced 2 mol of NADPH per mole of glucose. We then tested to see if more than 1 mol of hydrogen could be extracted by utilizing the entire pentose phosphate pathway (PPP). One unit of each enzyme required for the PPP to run to completion was added, along with G6P and NADP, into 50 m*M* sodium phosphate buffer, pH 7.5, and the amount of NADPH produced was monitored. This experiment did not produce more than 2 mol of NADPH per mole of glucose, and, when all of the enzymes were added at one time, the rate of the NADPH production step was inhibited. In order to determine which enzyme inhibited this pathway and prevented G6P from being regenerated, a test was designed in which the hydrogen production step of the pathway would be performed while each enzyme was added individually. For example, the NADPH production step was performed in the presence of the next enzyme in sequence in the pathway, and the rate of NADPH production was monitored. The next test was performed with all of the enzymes of the previous test plus one more. This was continued until each of the enzymes was present in the reaction mixture. It was not until fructose 1,6-diphosphatase (FDPase) was added that there was a significant drop in the rate of reaction of the NADPH production step. We then tested to see if FDPase or the sugar fructose 1,6-diphosphate (FDP), the product of the enzyme, caused the process to be inhibited. The activity of FDPase was also measured. It was shown that FDP did not inhibit the reaction, while FDPase does. A portion of the FDPase was dialyzed in 50 m*M* sodium phosphate buffer to remove any contaminating substances, and another portion was treated with EDTA.

8.5.2 Progress

8.5.2.1 Optimize Molar Yields

This task involves the determination of whether more than one molecule of hydrogen can be extracted from a glucose molecule. We have derived a formula to determine the number of molecules of hydrogen that will be extracted from a given number of G6P molecules. The total number of hydrogen molecules evolved is divided by the number of G6P molecules (n) present: $(12n-16)/n$ or $12-(16/n)$. When n approaches infinity, the term $16/n$ approaches zero, and so we get closer to the theoretical yield of 12 molecules of hydrogen from 1 molecule of G6P.

8.5.2.2 Utilization of the Pentose Phosphate Pathway for Optimizing Hydrogen Yields from Glucose

We have carried out experiments to determine whether it is practically possible to increase the molar yields of hydrogen from glucose if enzymes of the PPP are utilized. The starting substrate in all experiments carried out was G6P. The experiments were carried out by incubating G6P first with G6PDH and 6PGDH (the first two enzymes of the PPP) and then with all of the enzymes of the pathway. The formation of NADPH was monitored at 340 nm. The maximum amount of NADPH that can be formed from 0.05 mmol of G6P is 0.1 mmol (absorbance of 0.62, based upon the molar extinction coefficient for NADPH of 6.22) if only G6PDH and 6PGDH are present in the reaction mixture. If the PPP results in the formation of approximately 12 mol of NADPH per mole of G6P, then an absorbance of 3.72 is expected. When only G6PDH and 6PGDH were present in the reaction mixture, the yield of NADPH was found to be greater than 90% of theoretical maximum. However, if all the enzymes of the PPP were present in the reaction mixture, the rate of NADPH formation was much lower, and no evidence was obtained to suggest that greater than 2 mol of NADPH per mole of G6P could be achieved. On further experimentation, we discovered that the commercial preparation of FDPase (an enzyme of the PPP converting FDP to fructose-6-phosphate) contained an inhibitor of either G6PDH or 6PGDH. If this enzyme were dialyzed, the inhibitor could be removed. In one experiment, we found that a reaction mixture containing enzymes of the PPP, including dialyzed FDP, obtained a yield of 6.8 mol of NADPH per mole of G6P. A similar result was obtained that showed the rate and yield of NADPH formation from G6P using either undialyzed or dialyzed FDP. A control where G6P was omitted from the reaction mixture indicated that NADPH was not formed. These data show a yield of 6.1 mol of NADPH per mole of G6P.

The conclusion from these experiments is that the enzymes of the PPP can be used to extract more than 1 mol of hydrogen per mole of G6P if hydrogenase were present in the reaction mixture to oxidize NADPH to molecular hydrogen. It is clear from the data that given sufficient time, the theoretical maximum of hydrogen yields (i.e., ~12 mol NADPH/mol G6P) could be obtained. These experiments certainly do not represent conditions for optimal rates and yields of NADPH production, and experiments to determine these conditions are under way.

8.5.2.3 Preliminary Experiments on the Production of Hydrogen from Glucose-6-Phosphate Using Enzymes of the Pentose Phosphate Pathway and Hydrogenase

We have initiated experiments in which G6P was incubated with all the enzymes of the PPP, including hydrogenase, and monitored hydrogen production. The preliminary results are very encouraging in that 7.3 mol of hydrogen per mole of G6P has been obtained. Initially, the rate of hydrogen evolution increased rapidly, then dropped slightly, and rose gradually to a maximum before falling to baseline. These "strange" kinetics cannot be explained at the present time, but we have seen them more than once and are currently trying to understand them. The maximum rate of hydrogen evolution observed was 578 nmol/h. This low rate is due to the low concentration of starting substrate and can be increased by raising the concentration of G6P.

8.5.2.4 Electrical Power Production

In terms of energy, the total hydrogen produced (7.3 mmol) is equivalent to 0.58 MWh. In terms of power, the rate of hydrogen evolution is 46 mW. The theoretical maximum amount of energy produced from 1 mol of G6P is 0.96 MWh. Our calculations are based upon the knowledge that 1 mmol of hydrogen is equivalent to 0.08 MWh of energy and that a rate of hydrogen production of 1 nmol/h is the equivalent of 0.08 mW of power.

It is interesting to note that the glucose dehydrogenase/hydrogenase system used for hydrogen production from sugar has yielded rates of almost 100 mmol/h, which is equivalent to 8 mW of power. This rate and the subsequent power can clearly be increased.

8.6 DEVELOPMENT OF MICROCYCLE TECHNOLOGY FOR THE LARGE-SCALE PRODUCTION OF FUNGAL ENZYMES (B. D. Faison)

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Summary: During the current reporting period, preparations were made to cultivate test fungi under a microcycle regime. Laboratory space and equipment were acquired, as were certified cultures of the test organisms. Multiple replicate cultures were prepared and preliminary experiments conducted to determine the contribution of light to microcycle growth.

8.6.1 Purpose and Scope

Most (~55%) of the enzymes produced by or for U.S. industry are of fungal origin. However, methods for the efficient production of fungal enzymes are lacking. Efficient enzyme production would allow maximal yield from minimal biomass, decrease nutrient supply requirements, and facilitate product recovery. For spore-borne enzymes, efficiency may require the use of microcycle technology (forcing fungi to cycle rapidly between growth and sporulation). Microcycles may be achieved via manipulation of nutrient titers and/or quality, temperature, or irradiation or via addition of specific physiological substrates (e.g., enzyme inducers). This approach has not yet been used for fungal enzyme production. This high-risk experimental work is being conducted with support from the ORNL Seed Money Program.

8.6.2 Progress

This project was initiated in July 1997. New laboratory space, required to avoid contamination of ongoing projects, was located and customized. A list of reagents, supplies, standard equipment, and specialized instrumentation necessary for this work was generated. Most of these materials were acquired and stored for use throughout the project period; efforts are under way to obtain the remainder. Certified cultures of the test organisms C *Aspergillus niger*, *Phanerochaete chrysosporium*, and *Trichoderma reesei* C were purchased and successfully propagated.

A crude preliminary experiment was conducted to determine whether these cultures, like other fungi, would sporulate in response to visible light. White (multiple-wavelength) light was shown to promote sporulation as predicted, validating the proposed study of irradiation with light of specific uv/visible wavelengths. The project work plan has been reorganized to pursue the light phenomenon earlier than originally planned, in tandem with the study of temperature; nutritional and chemical factors will be studied immediately thereafter. This change will not affect overall project length.

8.7 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 was received 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 this complex as the recognized center for work in this emerging new area.

8.7.1 Purpose and Scope

The objective of this task 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 this complex as the recognized center for work in this emerging new area.

8.7.2 Progress

Funding was received into the Chemical Technology Division financial plan in March 1997. The assignments for various members of the planning team, as well as schedules for conducting/completing tasks, continue to be developed. A series of seminars has been established as well as ongoing intradivisional communications.

8.8 PUBLICATIONS

8.8.1 Published

J. W. Lee and E. Greenbaum, "A New Perspective on Hydrogen Production by Photosynthetic Water Splitting," pp. 209–22 in *Fuels and Chemicals from Biomass,* ed. B. C. Saha and J. Woodward, ACS Symposium Series 666, American Chemical Society, 1997.

E. Greenbaum, J. W. Lee, S. L. Blankinship, and C. V. Tevault, "Hydrogen and Oxygen Production in Mutant Fud26 of *Chlamydomonas reinhardtii*," in *Proceedings of the 1997 U.S. DOE Hydrogen Program Review,* NREL/CP-340-23722, Herndon, Virginia, May 21–23, 1997.

8.8.2 In Press

E. Greenbaum and J. W. Lee, "Photosynthetic Hydrogen and Oxygen Production by Green Algae," *Proceedings of the International Conference on Biological Hydrogen Production, BioHydrogen '97*, Waikoloa, Hawaii, June 23–26, 1997, in press.

I. Lee, J. W. Lee, and E. Greenbaum, "Biomolecular Electronics: Vectorial Arrays of Photosynthetic Reaction Centers," *Phys. Rev. Letters*, in press (1997).

J. W. Lee, R. T. Collins, and E. Greenbaum, "Molecular Ionic Probes: A New Class of Hill Reagents and Their Potential for Nanofabrication and Biometallocatalysis," *J. Phys. Chem. B*, in press (1997).

8.8.3 Submitted

B. R. Evans, V. M. Justice, and J. Woodward, "An Acetylesterase from the Peel of Lime (*Citrus aurantifolia*)," submitted, *J. Chem. Technol. Biotechnol.*

8.9 PRESENTATIONS

J. W. Lee and E. Greenbaum, "A New Perspective on Solar Energy Conversion by Photosynthesis," presented at the 25th Annual Meeting of the American Society for Photobiology, St. Louis, Missouri, July 5–10, 1997.

E. Greenbaum, J. W. Lee, and T. G. Owens, "Measurement of H_2 and O_2 Flash Yields in PSI-Deficient Mutants of *Chlamydomonas* and Comparison with Predictions of the Z-Scheme," presented at the 25th Annual Meeting of the American Society for Photobiology, St. Louis, Missouri, July 5–10, 1997.

J. W. Lee, I. Lee, and E. Greenbaum, "Nanofabrication for Optoelectronics and Solar Energy Conversion Using Photosynthetic Reaction Centers," presented at the 25th Annual Meeting of the American Society for Photobiology, St. Louis, Missouri, July 5–10, 1997.

E. Greenbaum, J. W. Lee, T. G. Owens, and L. J. Mets, "A Study of Photosynthetic Reactions in Photosystem I–Deficient Mutants of *Chlamydomonas*," presented at the Gordon Research Conference on Physical Mechanisms of Photosynthesis, Plymouth, New Hampshire, August 3–8, 1997.

J. W. Lee, I. Lee, and E. Greenbaum, "From Physics and Chemistry of Photosynthesis to Its Potential Applications in Nanofabrication and Optoelectronics," presented at the Gorgon Research Conference on Physical Mechanisms of Photosynthesis, Plymouth, New Hampshire, August 3–8, 1997.

I. Lee, B. R. Evans, and J. Woodward, "Atomic Force Microscope Measurements of Enzyme Interactions with Various Cotton Fibers," presented at the 44th Annual National Symposium of the American Vacuum Society, San Jose, California, October 20–24, 1997.

9. MOLECULAR STUDIES

P. T. Cummings

9.1 AQUEOUS ELECTROLYTE SOLUTIONS AT AMBIENT AND SUPERCRITICAL CONDITIONS (P. T. Cummings, A. A. Chialvo, S. H. Lee, and S. A. Gupta)

Contact: P. T. Cummings
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Summary: We continued development of our new intermolecular potential model for water and extended our code for simulating water/alcohol/tetrabutylammonium bromide from conventional constant volume to constant pressure.

9.1.1 Purpose and Scope

This project is aimed at developing microscopic-level understanding of aqueous electrolyte solutions using a combination of molecular simulation, statistical mechanical theory, and experimental measurement of vapor-liquid equilibrium and solution densities. The states of interest range from ambient conditions to high-temperature/high-pressure supercritical conditions (such as those encountered in power plant steam cycles and supercritical water oxidation).

9.1.2 Progress

We have continued development of our new intermolecular potential model for water. Our model features polarizability and has the property that the isolated water molecule has the bare dipole moment of water (1.85 D), unlike almost all other models for water. In the current stage of development, the model has a quadrupole moment in good agreement with the measured quadrupole moment and, via molecular simulation, predicts the thermodynamic and structural properties of water (i.e., revised neutron scattering results) to a high degree of accuracy. Our code for simulating water/alcohol/tetrabutylammonium bromide was extended to constant pressure as a first step towards predicting the apparent molar volume of the salt directly.

During the quarter, no papers related to this project were submitted, but several were accepted for publication. In addition, some of the research performed as part of this project was included in a number of invited talks given by P. T. Cummings and A. A. Chialvo.

9.2 THEORY AND MOLECULAR SIMULATION OF NONEQUILIBRIUM SYSTEMS

(P. T. Cummings, A. Baranyai, S. T. Cui, J. D. Moore, and I. Borzsák)

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Summary: The viscosity and viscosity index of various linear and branched alkanes were in the process of being predicted computationally.

9.2.1 Purpose and Scope

In this project, we study and develop new simulation algorithms for systems away from equilibrium. These algorithms form the basis for the calculation of transport properties using non-equilibrium molecular dynamics.

9.2.2 Progress

We continued production calculations on the Intel Paragons at ORNL of the viscosity of various linear and branched alkanes and in particular focused on the viscosity index of another branched C30 alkane to complement our earlier work on squalane (also a branched C30 alkane, for which excellent agreement with experiment was found).

During the quarter, no papers related to this project were submitted, but several were accepted for publication. In addition, some of the research performed as part of this project was included in a number of invited talks given by P. T. Cummings.

9.3 INTEGRAL EQUATION THEORIES OF MOLECULAR FLUIDS (P. T. Cummings, Yu. V. Kalyuzhnyi, and J. N. Herrera)

Contact: P. T. Cummings
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Summary:. A statistical mechanical approach to model the thermodynamic properties of mixed-solvent electrolytes was refined.

9.3.1 Purpose and Scope

This project involves the use of integral equation methods to describe molecular fluids and polymers in the dense-liquid regime. The emphasis is on analytically solvable integral equation theories.

9.3.2 Progress

Noe Herrera, a faculty member from Mexico, joined the project in January 1997. He is partially supported by the Mexican equivalent of the National Science Foundation. Herrera and Cummings analyzed the analytic solution of the mean spherical approximation for a model of mixed-solvent electrolytes. A paper discussing this work was accepted for publication.

9.4 MATHEMATICAL MODELING OF BACTERIAL MIGRATION THROUGH POROUS MEDIA WITH APPLICATION TO IN SITU BIOREMEDIATION (P. T. Cummings, R. M. Ford,* K. C. Chen,* and M. Jin*)

Contact: P. T. Cummings
Telephone: (423)241-4779
Internet: u53@ornl.gov

Summary: An efficient code for studying in situ bioremediation processes at the macroscopic and field-scale level was refined.

9.4.1 Purpose and Scope

This project is part of a broad effort at the University of Virginia funded by the IBM Environmental Research Program, with Roseanne Ford and Peter Cummings as coprincipal investigators. The goal of the project is to perform experimental studies and computer simulations of bacterial motion in bulk aqueous phases and in porous media to develop an understanding of the transport processes involved in in situ bioremediation and to subsequently develop mathematical models for these processes.

9.4.2 Progress

Progress was made on the development of two-dimensional finite-element codes for modeling in situ bioremediation processes at the macroscopic and field level. During the quarter, one paper was accepted for publication.

9.5 FUNDAMENTAL CHEMISTRY AND THERMODYNAMICS OF HYDROTHERMAL OXIDATION PROCESSES (J. M. Simonson, R. E. Mesmer, D. J. Wesolowksi, P. T. Cummings, and A. A. Chialvo)

Contact: P. T. Cummings
Telephone: (423)241 4779
Internet: u53@ornl.gov

Summary: The Chialvo-Cummings formalism for studying supercritical fluid mixtures has been extended to reaction kinetics in supercritical fluid solvents.

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*University of Virginia.

9.5.1 Purpose and Scope

This three-year project, supported by the new DOE EMSP, began September 1, 1996. The goal is to use a combination of molecular theory/simulation and experimental measurements to develop a fundamental understanding of the thermophysical properties, phase equilibrium, and reaction processes involved in supercritical water oxidation (a new and promising technique for transforming hazardous organic waste).

9.5.2 Progress

The focus during the current quarter has been on extending the Chialvo-Cummings molecular formalism for studying solvation and partial molar thermodynamic properties in supercritical fluid mixtures to reaction kinetics in supercritical fluid solvents. The extended formalism is being used to explain recent experimental data published by Brenneke and Roberts. A paper detailing this work was submitted for publication.

9.6 MOLECULAR-BASED STUDY OF REVERSED MICELLES IN SUPERCRITICAL CARBON DIOXIDE FOR SOLVENT SUBSTITUTION IN THE U.S. CHEMICAL INDUSTRY (P. T. Cummings, H. D. Cochran, S. T. Cui, D. Londono, G. Wignall, A. Habenschuss, E. J. Beckman,[*], and J. M. DeSimone,[†])

Contact: H. D. Cochran and P. T. Cummings
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Internet: hdc@ornl.gov and u53@ornl.gov

Summary: See research description reported in Sect. 7.3.

9.7 PUBLICATIONS

9.7.1 Submitted

A. A. Chialvo, Y. V. Kalyuzhnyi, and P. T. Cummings, "Molecular-Based Interpretation of Solvation Effects on the Reaction Kinetics of Dilute Reactants in Supercritical Solvents," *AIChE J.* (1997).

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[*] University of Pittsburgh.

[†] University of North Carolina.

9.7.2 Accepted

K. J. Duffy, P. T. Cummings, and R. M. Ford, "Residence Time Calculation for Chemotactic Bacteria Within Porous Media," *Biophys. J.*

J. N. Herrera, L. Blum, and P. T. Cummings, "Thermodynamic Properties of an Asymmetric Fluid Mixture with Adhesive-Hard-Sphere Yukawa Interaction in the Mean Spherical Approximation," *Molec. Phys.*

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," *Molec. Phys.*

J. D. Moore, S. T. Cui, P. T. Cummings, and H. D. Cochran, "Lubricant Characterization by Molecular Simulation," *AIChE J.*

S. T. Cui, H. D. Cochran, and P. T. Cummings, "Configurational Bias Gibbs-Ensemble Monte Carlo Simulation of Vapor-Liquid Equilibria of Linear and Short-Branched Alkanes," *Fluid Phase Equilibria.*

A. A. Chialvo, P. T. Cummings, J. M. Simonson, and R. E. Mesmer, "Molecular Simulation Study of Ion Speciation in Supercritical Aqueous Solutions," *J. Molec. Liquids*, in press (1996).

D. A. Kofke, and P. T. Cummings, "Quantitative Comparison and Optimization of Methods for Evaluating the Chemical Potential by Molecular Simulation," *Molec. Phys.*, in press (1997)

9.8 PRESENTATIONS

P. T. Cummings, "Molecular Simulation of Complex Systems Using Massively Parallel Supercomputers," presented at the Knoxville–Oak Ridge AIChE Local Chapter Meeting, Knoxville, Tennessee, September 16, 1997.

P. T. Cummings, "Molecular Modeling and Simulation: Present and Future Tools for Physical Properties Prediction," presented at the Department of Chemical Engineering, University of Florida, Gainesville, Florida, September 22, 1997.

P. T. Cummings, "Molecular Modeling and Simulation: Present and Future Tools for Physical Properties Prediction," presented at the Exxon Research and Engineering, Florham Park, New Jersey, September 29, 1997.

P. T. Cummings, "Molecular Simulation of Complex Systems Using Massively Parallel Supercomputers," presented at the American Society for Engineering Education Workshop for Chemical Engineering Faculty, Snowbird, Utah, August 9–14, 1997.

S. A. Gupta, S. T. Cui, J. D. Moore, H. D. Cochran, and P. T. Cummings, "Nonequilibrium Molecular Dynamics Simulations of the Rheology of Confined and Bulk Alkane Liquids Using

Massively Parallel Supercomputers," presented at the Second Pacific Rim Conference on Rheology, Melbourne, Australia, July 27–31, 1997.

A. A. Chialvo, P. T. Cummings, J. M. Simonson, and R. E. Mesmer, "Behavior of the Hydration Shell Around Ions in Supercritical Aqueous NaCl Solutions: A Molecular Based Study," presented at the Fifth International Symposium on Hydrothermal Reactions, Gatlinburg, Tennessee, July 20–24, 1997.

A. A. Chialvo, P. T. Cummings, J. M. Simonson, and R. E. Mesmer, "Molecular Simulation Study of the Thermodynamics and Kinetics of Ion Speciation in Supercritical Aqueous Solutions," presented at the 25th International Conference on Solution Chemistry, Vichy, France, August 26–31, 1997.

P. T. Cummings, "Molecular Simulation of Supercritical Water and of Ionic Association in Supercritical Aqueous Solutions," presented at MIT Energy Laboratory, Cambridge, Massachusetts, September 23, 1997.

P. T. Cummings, "Molecular Simulation of Supercritical Water and of Ionic Association in Supercritical Aqueous Solutions," plenary lecture presented at the Fifth International Symposium on Hydrothermal Reactions, Gatlinburg, Tennessee, July 20–24, 1997.

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