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Quarterly Progress Report for the Chemical and Energy Research Section of the Chemical Technology Division: April–June 1997

R. T. Jubin

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ORNL/M-6504

Chemical Technology Division

QUARTERLY PROGRESS REPORT FOR THE CHEMICAL AND ENERGY RESEARCH SECTION OF THE CHEMICAL TECHNOLOGY DIVISION: APRIL–JUNE 1997

R. T. Jubin

Date Published–June 1998

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CONTENTS

ACRONYMS

BES	Basic Energy Sciences (DOE)
CMC	carboxymethyl cellulose
CsRD	Cesium Removal Demonstration
CST	crystalline silicotitanate
CV	column volumes
DBA	design basis accident
DLS	dynamic light scattering
DNS	dinitrosalicylic (acid)
DOE	U.S. Department of Energy
DTA	differential thermal analysis
ED/IX	electrodialysis–ion exchange
EIX	electrochemical ion exchange
ESP	Efficient Separations and Processing Crosscutting Program (DOE)
FDP	fructose 1,6-diphosphate
FDPase	fructose 1,6-diphosphatase
G6P	glucose-6-phosphate
HLW	high-level waste
IES	inverse electrostatic spraying
LDRD	Laboratory Director's Research and Development (ORNL program)
MVST	Melton Valley Storage Tank
NRC	U.S. Nuclear Regulatory Commission
ORNL	Oak Ridge National Laboratory
PCT	product consistency test
PNPC	*p*-nitrophenyl D-(+)-cellobioside
PNP	*p*-nitrophenol
PPP	pentose phosphate pathway
PSI	Photosystem I
PSII	Photosystem II
R-F	resorcinol-formaldehyde
R5P	ribulose-5-phosphate
RCRA	Resource Conservation and Recovery Act
RESS	rapid expansion of supercritical (fluid) solution
SANS	small-angle neutron scattering
SAXS	small-angle X-ray scattering
TCLP	Toxicity Characteristic Leaching Procedure
TFA	Tank Focus Area
TGA	thermogravimetric analysis
XRD	X-ray diffraction

EXECUTIVE SUMMARY

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

The report describes the various tasks performed within six major areas of research: Hot Cell Operations, Process Chemistry and Thermodynamics, Separations and Materials Synthesis, Solution Thermodynamics, 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 column testing of Amberlite IRC-718 resin to remove strontium from ORNL Melton Valley Storage Tank (MVST) supernatant, analyses of leachates and residues from leaching tests on samples of sludge from Hanford tanks, hot cell testing of candidate sorbents and ion exchangers under continuous flow conditions using MVST supernatant, and development and batch testing of spherical sorbents containing sodium titanate to remove strontium. Another task in this area involved conversion of MVST sludge to soda-lime glass using precipitated silica and powdered limestone.

Within the area of *Process Chemistry and Thermodynamics*, testing of Hanford sludge confirmed the efficiency of hydrofluoric acid treatment using an excess of fluoride (i.e., a fluoride-to-silicon ratio of greater than six) to prevent silica deposition. Other initiatives included support offered 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.

In the area of *Separations and Materials Synthesis*, fundamental studies that were in progress explored the use of electromagnetic fields to enhance transport processes in multiphase separations; investigated the mechanisms, kinetics, and thermodynamics of nucleation and particle growth in systems for the synthesis of ultrafine inorganic particles; and examined the use of electric fields to modify phase equilibria in multiphase separations processes. Other efforts involved the application of magnetic-seeding filtration to remove solids from waste streams and the enhancement of oxidation of organic pollutants in aqueous solutions by using electric fields to form microbubbles containing ozone.

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

Within the area of *Biotechnology Research*, experiments continued with Photosystem I–deficient mutants of *Chlamydomonas reinhardtii*, and chromatically adapted *C. reinhardtii* were used 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, and efforts were made to maximize the efficiency of the enzymatic production of hydrogen from glucose. Also within the area of Biotechnology Research, funding was received to support the programmatic development effort to establish the Oak Ridge Complex as the recognized center for the newly emerging area of biomimetics and biomaterials.

In the final area—*Molecular Studies*—as part of an initiative to enhance our microscopic-level understanding of aqueous electrolyte solution, efforts continued on the development of a new intermolecular potential model for water. Related tasks included the investigation of simulation algorithms for nonequilibrium systems and a study of mixed-solvent electrolytes by integral equation methods. Further progress was made on the development of two-dimensional finite-element codes for modeling in situ bioremediation processes at macroscopic and field levels. A new project combines molecular theory/simulation with experimental measurements to investigate supercritical water oxidation.

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: An Amberlite IRC-718 column was used to remove strontium from Oak Ridge National Laboratory (ORNL) Melton Valley Storage Tank (MVST) W-27 supernatant. Efforts to find an efficient method of eluting the strontium from the column are continuing. Preliminary results indicate that the strontium can be stripped from the column using 6 *M* nitric acid.

Batch tests and column tests on cesium, technetium, and strontium removal have been completed. The results are being evaluated and documented. Work has been initiated on a report summarizing the results and comparing them with results from other studies at different U.S. Department of Energy (DOE) sites.

1.1.1 Purpose and Scope

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

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

1.1.2 Progress

In a previous column test, strontium was removed from supernatant from MVST W-27 using a column containing approximately 3 mL of Amberlite IRC-718. In tests to strip strontium from the column, the column was eluted successively with 0.1 and 1 *M* nitric acid solutions using a flow rate of about 2.3 column volumes per hour (CV/h). After the elution was completed, approximately 15% of the strontium that was sorbed onto the IRC-718 remained on the column. In batch tests, a total of

95% of the strontium could be eluted from the sorbent by using higher concentrations of nitric acid. Therefore, after establishing a flow rate of 2.3 CV/h using deionized water, about 6 CV of 6 *M* nitric acid was pumped through the column using a downward flow. Fractions were collected at predetermined times into preweighed tubes, which contained approximately 1.8 mL each. The collected fractions were analyzed by measuring the strontium radioactivity. The sorbent was also monitored, and triplicate samples were transferred into preweighed tubes for radiochemical analysis. Sorbent analysis indicated that most of the strontium had been removed. Analysis of the eluates is continuing. These preliminary results indicate that the higher concentration of nitric acid would effectively remove the strontium from the sorbent. The long-term stability of the sorbent in 6 *M* nitric acid has not been determined.

Work is continuing on a draft report summarizing the results from column tests obtained in FY 1996–1997 and comparing the results with the batch tests. This report includes comparisons of batch and column results obtained at ORNL, including hot cell studies on cesium removal. Results from some of the studies conducted at other DOE facilities using simulants and supernatants are also discussed with respect to the needs and potential applications at various DOE sites. Some of the tests and results are summarized below.

Several sorbents have been evaluated in batch tests for removing cesium, technetium, and strontium from MVST supernatants. Based on these batch tests, sorbents were selected for column tests to demonstrate sorption and elution in a continuous-flow system. Sorbents evaluated in hot cell column tests for cesium removal from MVST W-27 supernatant included IONSIV IE-911, Superlig 644C, resorcinol-formaldehyde (R-F) resin, Duolite CS-100, and potassium cobalt hexacyanoferrate. IONSIV IE-911 was selected for use in the ORNL Cesium Removal Demonstration (CsRD) project for treating about 100,000 L of supernatant.

Removal of technetium as pertechnetate from MVST supernatant was successfully demonstrated using a column of Reillex HPQ. The technetium was eluted from the column using an eluant containing stannous chloride and ethylenediamine. Strontium removal was accomplished using a column of Amberlite IRC-718. Elution of the strontium was more difficult than indicated by the batch tests. It was necessary to use 6 *M* nitric acid to strip the strontium from the Amberlite IRC-718.

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

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Summary: Caustic leach tests have been completed on Hanford tank C-104 sludge at three temperatures: 50, 80, and 93 °C. A sample of S-101 sludge was leached with 4 *M* NaOH for 67 h at 93 °C. Analyses of residues, leachates, and rinse solutions resulting from the leaching tests have been completed. Evaluation of the analytical results is continuing.

1.2.1 Purpose and Scope

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

1.2.2 Progress

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

Efforts are being made to determine the effect of temperature on the caustic dissolution behavior of Hanford tank sludge. Samples of Hanford tank C-104 sludge were leached for 67 h at 50, 80, and 93 °C with 4 *M* NaOH and then rinsed three times with a solution containing 0.01 *M* sodium nitrite and 0.01 *M* sodium hydroxide. Analyses of samples of the sludge residues, leachates, and rinse solutions have been completed, and the data are being evaluated. Due to difficulties in obtaining good material balances, some of the phosphorous analyses are being repeated using a different procedure.

A leach test was also performed on a sample of Hanford tank S-101 sludge. The leach time was 67 h; the NaOH concentration was 4 *M*; and the temperature was 93 °C. The mass of the original sample was 1.90 g. After the leach test, the mass of the residue was 0.42 g, indicating that a significant portion of the sample was dissolved under these conditions. (For comparison, under similar conditions the C-104 sludge sample containing 2.14 g produced a residue of 1.69 g.) Partitioning of the sludge components will be determined after the analyses are completed, and the results will be compared with those obtained from other Hanford sludge samples.

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

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Summary: This task covers work in the continuous removal and concentration of radioactive components of supernatant at the various DOE sites. The primary objective is to test candidate absorbers and ion exchangers under continuous-flow conditions using actual supernatant from the MVSTs. An experimental system contained in a hot cell facility is used to test the materials in columns or modules using the same batch of supernatant so that all of them can be compared on the same basis. The system was used in support of the CsRD program to qualify crystalline silicotitanate (CST) sorbent and MVST supernatant processed by the CsRD. It would also determine if the CST removes other radionuclides or Resource Conservation and Recovery Act (RCRA) metals, provide performance data from a small-scale column to compare directly with the larger CsRD columns for the determination of scale-up parameters, and determine if the spent sorbent is a hazardous waste under the RCRA regulations (40 CFR 261 Subpart C). These objectives were all met, and the CsRD completed its operation.

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 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 Area (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 the electrodialysis–ion-exchange (ED/IX) system from AEA Technology as part of this ESP program because ORNL was the only site with a sufficient amount of available supernatant for testing this multiple-cycle 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.

1.3.2 Progress

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

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

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

These objectives were all met, and the CsRD completed its operation. Final analytical results are presented below.

CST6—Second CsRD Support Experiment. The second test on the cesium removal sorbent and supernatant used in the CsRD was completed using the commercial preparation of UOP IONSIV IE-911 CST to treat more than 12.6 L MVST supernatant from tank W-29. The test was conducted at a flow rate of 6 CV/h using a 1.45-cm-ID column containing 10.1 mL of the CST. The W-29 feed was fed continuously to beyond the 90% cesium breakthrough point. After the column was loaded, it was transferred to analytical services for Toxicity Characteristic Leaching Procedure (TCLP) testing.

CST7—Third CsRD Support Experiment. The third experiment in support of the CsRD was conducted concurrently with a run of the CsRD under the same conditions. The test was conducted at 3 CV/h for 550 CV and resulted in a 50% cesium breakthrough at 475 CV. The CsRD 50% cesium breakthrough was within 1% of the small-column breakthrough.

CST8—Fourth CsRD Support Experiment. The fourth test in support of the CsRD began March 17, 1997, and concluded March 25, 1997, after 190 h of continuous operation and the treatment of more than 12 L of W-29 supernatant. This test was conducted under conditions similar to those used concurrently during the CsRD run using two columns in series at a 6-CV/h flow rate. Results showed that the first column was loaded to >80% of cesium breakthrough at 6 CV/h flow rate and that the second column was loaded to beyond the 50% cesium breakthrough level. No problems were encountered during the operation of the columns during either test, and the results were again consistent with all previous results obtained using CST preparations. Feed samples from both tests were sent for analytical determinations.

In comparing the breakthrough curves from the full-scale CsRD and the bench tests, it was found that the data on cesium breakthrough agreed very well. Fifty-percent breakthrough for the full-scale system occurred at approximately 500 CV processed. The difference in the full-scale and bench-scale data can be attributed to differences in the flow rate per unit cross-sectional area of the two systems.

1.3.2.2 Continuation of the AEAT EIX Technology Testing

Preparations were completed for the operation of the AEA Technology's electrochemical ion-exchange (EIX) rig to test the electrochemical elution of cesium from R-F resin and compare it with the standard nitric acid elution. Some of the W-29 feed previously characterized and used in the CsRD tests will be used for the comparison. The R-F resin was batch tested to make sure it was still in good condition for the EIX tests.

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

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Summary: Samples of hydrous zirconium oxide microspheres were prepared using a binary organic solvent as a replacement for silicone oil. Experimental work to optimize the conditions for converting hydrous titanium oxide to sodium titanate microspheres is continuing. Several preparations of hydrous titanium oxide microspheres have been prepared for use in processes to chemically convert them to pure sodium titanate microspheres. Several sodium titanate preparations were made using different mole ratios of reactants. License agreements have been executed with Eichrom Industries, Inc., for the transfer and utilization of technology developed in this program.

1.4.1 Purpose and Scope

The general objectives of this task are to develop, prepare, and test new and unique inorganic ion exchangers made as microspheres by the internal gelation process to remove fission products, actinides, and other metals (such as the RCRA metals) from waste streams occurring at 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. Composite microspheres containing varying amounts of sodium titanate homogeneously embedded in microspheres of hydrous titanium oxide have been prepared utilizing the internal gelation process.

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

1.4.2 Progress

The 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 radionuclides from waste streams occurring at the various DOE sites. Initially, microspheres will be made of materials that have already been shown to be highly effective as cesium and strontium sorbents.

Sodium titanate is an excellent sorbent for strontium. Experimental work has continued to try to optimize the conditions for converting hydrous titanium oxide microspheres to pure sodium titanate microspheres using an alkoxide conversion process. This process involves preparing hydrous titanium oxide microspheres and making adjustments in the alkoxide conversion parameters (temperature and reaction time) to convert the titanium oxide to sodium titanate.

Zirconium oxide microspheres are also being considered as a matrix material for preparing composite sorbents containing sodium titanate and other ion exchangers. A preparation of hydrous zirconium oxide microspheres was made using a binary mixture consisting of 60% isoamyl alcohol and 40% perchloroethylene as a replacement for silicone oil. The binary mixture eliminates a secondary organic washing step that is needed when silicone oil is used. Their function is to serve as immiscible organic media that are used as heat sources during gel-sphere formation.

Several preparations of hydrous titanium oxide microspheres were made for use in the conversion process. One of the variable reaction parameters is the mole ratio of sodium to titanium. Several conversion preparations were made in which the mole ratio of sodium ethoxide to titanium was varied. Optimization of the conversion is continuing. Attempts will also be made to convert hydrous titanium oxide microspheres to sodium titanate microspheres hydrothermally by reaction of the hydrous titanium oxide microspheres with sodium hydroxide in a Parr reactor. The sodium titanate products will then be tested for their effectiveness for removing strontium in batch tests using MVST supernatant simulant.

License agreements have been completed with Eichrom Industries, Inc., to allow the transfer of technology developed in this program and disclosed in an ORNL patent application, "Internal Gelation Process for Making Hydrous Oxide Spherules." Interest has been expressed in additional sorbents being developed. The technology disclosed in the patent application includes the optimum formulations and conditions for making hydrous titanium oxide microspheres, composite microspheres of hydrous titanium oxide containing fine particles of other inorganic or organic sorbents, and titanium monohydrogen phosphate microspheres.

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

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Summary: Both surrogate sludge and actual MVST W-25 sludge were successfully converted to soda-lime glass using precipitated silica and powdered limestone. Product consistency tests (PCTs) are under way to evaluate the glasses.

1.5.1 Purpose and Scope

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

1.5.2 Progress

Actual actinide-based sludge from MVST W-25 and a surrogate sludge representing this waste were successfully immobilized in our hot cell into both cement-based grout and soda-lime glass for testing purposes. All equipment that was modified to enable us to set up a dedicated cell for the purpose of waste immobilization and testing worked as planned. Grout prepared with both the surrogate and actual waste appeared to have similar properties with the exception that the actual waste set faster than the surrogate. Both grouts were shown to be free of bleed water upon preparation and both hardened rapidly, with the actual waste-containing grout setting marginally faster.

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[*] ORNL Chemical Technology Division, Engineering Development Section.

Samples of grout submitted to the TCLP leach test showed that they were able to pass this test, while the raw waste failed due to mercury. Testing of samples of glass prepared and submitted for the same tests has not been completed.

Both the surrogate sludge and actual tank sludge were converted to soda-lime glass at 1300°C over 4 h. The glass formula that was utilized centered on the addition of precipitated silica and powdered limestone to both sludges. The glasses that were formed appeared dark in color and were friable enough to pulverize and screen in preparation for the PCT, in which samples are leached at 90°C for 7 d in ASTM Type 1 water followed by analysis of the acidified leachates. This leaching phase of the testing program is currently in progress and should be completed this fiscal year.

1.6 PUBLICATIONS AND PRESENTATIONS

The Comprehensive Supernatant Treatment, Development and Testing of Inorganic Sorbents, and the Hot Demonstration of Proposed Commercial Nuclide Removal Technology programs were reviewed at the ESP Crosscutting Program Midyear Review in Gaithersburg, Maryland. Technical Task Plans were prepared for FY 1998 and 1999.

A paper entitled "Tank Waste Treatment R&D Activities at Oak Ridge National Laboratory," written by R. T. Jubin, E. C. Beahm, J. L. Collins, D. J. Davidson, B. Z. Egan, D. D. Lee, A. J. Mattus, R. D. Spence, and J. F. Walker, Jr., was presented at the Organization for Economic Cooperation and Development/Nuclear Energy Agency Nuclear Science Committee Workshop on Long-Lived Radionuclide Chemistry in Nuclear Waste Treatment on June 18–20, 1997, Avignon, France.

A paper entitled "Cesium Removal Flow Studies Using Ion Exchange," written by D. D. Lee, J. F. Walker, Jr., and P. A. Taylor of ORNL and D. W. Hendrickson of SGN Eurisys Services Corp., was accepted for publication in *Environmental Progress*.

Two draft reports were prepared and are undergoing review before being distributed as ORNL reports. The first report is *Characterization and Leaching Study of Sludge from Melton Valley Storage Tank W-25*, and the second is *Removal of Actinides from Dissolved MVST Sludge Using the TRUEX Process*.

A paper by B. B. Spencer, R. M. Counce, and B. Z. Egan, "Extraction of Nitric Acid from Aqueous Media with OφD(iB)CMPO-*n*-Dodecane," *AIChE Journal* **43**, 555–64, 1997, was published.

A paper entitled "Partitioning of Actinides from Dissolved ORNL Melton Valley Storage Tank Sludge Using the TRUEX Process" was presented at the 21st Annual Actinide Separations Conference, Charleston, South Carolina, June 23–26, 1997.

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: In acid treatment of sludge, hydrofluoric acid must be mixed with nitric acid to avoid the formation of silica gel in leachates and wash solutions and to enhance the dissolution of silicaceous materials. Leaching the SX-113 sludge with an excess of fluoride beyond what was necessary to convert all of the silica to SiF_6^{-2} (a ratio >6) resulted in essentially complete dissolution of the sludge solids and no transport of silica. Only a small amount of residue remained.

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

In acid treatment of sludge, hydrofluoric acid must be mixed with nitric acid to avoid the formation of silica gel in leachates and wash solutions and to enhance the dissolution of silicaceous materials. Hydrofluoric acid will convert silica to SiF_6^{-2}, which is soluble. This requires six fluoride ions for each silicon. In a test with Hanford underground storage tank SX-113 sludge, a fluoride-to-silicon ratio of four was used. The sludge was leached at 75 °C using 10 mL/g of sludge. The leaching solution was 3 *M* in both hydrofluoric acid and nitric acid. As a result of this treatment, a porous material identified as silica formed in the airspace above the liquid. It is likely that this vapor-assisted deposition of silica occurs when the fluoride in solution is consumed by reaction with silica in the sludge. This would result in conversion of some of the SiF_6^{-2} to SiF_4, which is a gas. This gas would decompose to silica and hydrofluoric acid in a cooler region.

To prevent the transport and deposition of silica out of the sludge/leachate, a fluoride-to-silicon ratio of at least six should be required. To demonstrate this, two additional tests were run with sludge from SX-113. In one test, a fluoride-to-silicon ratio of eight was used; in the other test, the sludge was leached with nitric acid only. The temperature and solution volume per gram of sludge and the nitric acid concentration were the same as in the previous test.

Leaching the SX-113 sludge with an excess of fluoride beyond what was necessary to convert all of the silica to SiF_6^{-2} (a ratio >6) resulted in essentially complete dissolution of the sludge solids and no transport of silica. Only a small amount of residue remained.

Leaching the SX-113 sludge with 3 *M* nitric acid alone was not effective in dissolving sludge solids. A mass of solids remained after treatment.

This series of tests revealed what is required in the use of hydrofluoric acid in acidic sludge treatment. First, hydrofluoric acid must be used to enhance dissolution of sludge solids. It will also prevent the formation of silica gel in leachates. Second, it is necessary to have an excess of fluoride, a fluoride-to-silicon ratio of greater than six, to prevent transport of silica out of solution and prevent deposition in unwanted places such as tank domes, ventilation systems, and sample lines. This excess of fluoride must be preserved in all parts of the system (tank) to avoid local regions of low fluoride concentration.

Alternatively, limited addition of hydrofluoric acid during nitric acid treatment could be used in a controlled system to remove silica from sludge by chemical vapor transport from the sludge and leachate.

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

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Summary: A report entitled *Iodine Volatility and pH Control in the AP600 Reactor* was prepared and sent to the U.S. Nuclear Regulatory Commission (NRC) Technical Monitor. In this report, a design basis accident (DBA) for the AP600 reactor was formulated and evaluated.

2.2.1 Purpose and Scope

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

2.2.2 Progress

A report entitled *Iodine Volatility and pH Control in the AP600 Reactor* was prepared and sent to the NRC Technical Monitor. In this report, a DBA for the AP600 reactor was formulated and evaluated. In this DBA there was a significant bypass of the pH control system. Some iodine released from the primary system would be retained in the containment water storage tank and never interact with water that contains pH control chemicals.

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

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Summary: Collaborative work with Dr. Gennady Voronin of Moscow State University continues to be directed toward the determination of the solidification conditions of yttrium, barium, and copper oxides from their melts. 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) as well as $BaCuO_2$ + Y123 at oxygen partial pressure ranging from 0.1 to 0.000006 MPa.

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. Preliminary analyses of 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+}. Future experiments will involve different oxidizers and reductants, and, in some cases, the samples will be reduced before the oxidation step.

2.3.1 Purpose and Scope

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

2.3.2 Progress

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

Experimental work on the two-year collaboration with Dr. Gennady Voronin of Moscow State University continued. The goal of this joint effort is to determine the solidification conditions of yttrium, barium, and copper oxides from their melts. These conditions include temperature, partial oxygen pressure, the chemical composition of the melt, and the phase and chemical composition of the growing solids. The liquidus and solidus surfaces in the four-component Y-Ba-Cu-O (YBCO) system will be determined in terms of temperature, composition, and oxygen chemical potential. In addition, all co-nodes in the heterogeneous areas of the phase diagram and the metastable states of the system will be evaluated.

The experimental phase has been completed on the melts of Y123 + $BaCuO_2$; the mole ratios of Y, Ba, and Cu for YBCO system were 1, 3, and 4, respectively. The Y123 + $BaCuO_2$ melts were prepared at different temperatures under partial oxygen pressures of 0.1, 0.01, 0.001, 0.0001, and 0.000006 MPa. After the melts were allowed to equilibrate, they were reduced with hydrogen in order to determine the oxygen content. The results from the Y123 + $BaCuO_2$ experiments, which are shown in Table 1, are being used by Dr. Voronin to develop a formal description of the Y123 + $BaCuO_2$ melt as well as a thermodynamic simulation of the equilibria and prediction of the composition and thermodynamic functions of the liquid. It is interesting to note that the results for Y123 and Y123 + $BaCuO_2$ are different. With the Y123 + $BaCuO_2$ melts, the oxygen content initially increases with higher temperatures. As soon as the analysis of the Y123 + $BaCuO_2$ results is complete, a manuscript on the melts of Y123 and Y123 + $BaCuO_2$ will be prepared. This experimental technique is currently being applied to another system, which has Y, Ba, and Cu mole ratios of 1, 2, and 7.3, respectively.

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

Oxygen partial pressure (MPa)	Temperature (°C)	Oxygen content
0.1	1052.4	7.60
0.1	1118.1	7.82
0.1	1187.6	7.54
0.1	1251.6	7.48
0.01	1048.6	7.27
0.01	1152.0	7.39
0.01	1214.5	7.15
0.01	1249.4	7.02
0.001	1026.6	7.22
0.001	1091.9	7.32
0.001	1151.9	7.07
0.001	1226.6	6.94
0.0001	1003.4	7.04
0.0001	1047.8	7.12
0.0001	1091.7	7.10
0.0001	1142.4	6.85
0.0001	1199.7	6.74
0.000006	986.9	7.00
0.000006	1029.3	7.07
0.000006	1084.1	7.03
0.000006	1132.4	6.92
0.000006	1202.8	6.72

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 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 repesentation of Y123 at its different oxygen stoichiometries. Examples of possible stoichiometries 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. $Y^{(+3)}Ba_2^{(+2)}Cu_3^{(+1)}O_{3.8}^{(-1)}O_{3.1}^{(-2)}$

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. 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. Preliminary analyses of 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. Results obtained with $YBa_2Cu_3O_{6.64}$, and $YBa_2Cu_3O_{6.9}$

imply the presence of Cu^{+3}. Future experiments will involve different oxidizers and reductants, and in some cases, the reductant will be added before the oxidizer.

2.3.2.3 *Collaborations*

This project is collaborating with three other Basic Energy Sciences (BES) projects at ORNL. This project continues to perform the final sample preparation, which involves the manipulation of the oxygen content in crystals of Y123 in our vacuum TGA equipment. After the final sample preparation, the BES project that is led by Herbert Mook, Pengcheng Dai, and Mohana Yethiraj performs magnetic dynamics experiments on the Y123. 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. The third BES collaboration is with Michael Hu's project, which is preparing spherical and cubic ZrO_2 from $ZrOCl_2 \cdot 8H_2O$ salt. Our DTA/TGA equipment is being used to characterize the reaction.

3. SEPARATIONS AND MATERIALS SYNTHESIS

D. W. DePaoli

3.1 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, and (3) investigation of mixing in electrohydrodynamic flows.

3.1.1 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, thus providing widespread benefit for separations processes such as solvent extraction and distillation as well as applications in environmental and biotechnology areas. The areas of current focus are (1) interface deformation and breakup, including electrostatic spraying (both "normal" and "inverse"); drop formation, drop oscillations, stretching liquid bridges, and drop impact; (2) interactions and coalescence of drops; and (3) enhancement of transport processes through electrohydrodynamic flows.

3.1.2 Progress

3.1.2.1 Drop Deformation and Breakup

A volume-of-fluid model has been developed for drop deformation and breakup from a capillary tube in liquid-air and liquid-liquid systems. Extensive computations have been carried out to simulate drop formation in liquid-air systems at different physical conditions. This study is particularly important in exploring the velocity field in the drop that is essential for predicting mass transfer during drop formation. A manuscript is in preparation for submission to the *Journal of Fluid Mechanics*.

3.1.2.2 Wetting and Stability of Drops on Solid Surfaces

Fundamental studies have continued with the object of understanding and improving the wettability and stability of liquid drops on solid surfaces. Different surfactants and pH values of aqueous solutions are used to determine their effects upon removal of oil or organic contaminants from solid surfaces. The research is of significant importance in industrial and environmental cleaning and degreasing, and in oil recovery processes.

3.1.2.3 Mixing in Electrohydrodynamic Flows

Our studies of inverse electrostatic spraying (IES) have indicated that significant electrohydrodynamic flows can be generated in immiscible gas-liquid and liquid-liquid systems (see C. Tsouris et al., "Spraying, Pumping, and Mixing of Fluids by Electric Fields," submitted to *AIChE Journal*). These flows can be effective for efficient micromixing of fluids. During this reporting period, the studies were extended to soluble and miscible systems. The experimental approach that was developed to investigate electrohydrodynamic micromixing involves 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. Through experiments involving the dispersion/dissolution of alcohols (butanol, isopropanol, ethanol, etc.) into deionized water, it was learned that the miscibility between the phases greatly affects the spraying/dispersing pattern. Additionally, it was determined that effective mixing can be achieved for homogeneous systems (e.g., ethanol into ethanol). For all systems, rapid mixing of the fluids was achieved with appropriate system design and applied voltage. Further studies are aimed at quantification of mixing and at evaluating the effectiveness of this technology for application to reaction systems, including particle production.

3.2 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 five distinct areas of materials synthesis: (1) synthesis and characterization of nanosized, monodispersed ceramic precursor particles by forced hydrolysis; (2) homogeneous precipitation in aqueous-alcohol mixtures; (3) sol-gel processing for advanced materials synthesis in alkoxide systems; (4) supercritical fluids processing in preparation of ultrafine particles and inorganic membranes; and (5) ultrafine particle synthesis by a new electrically driven method.

3.2.1 Purpose and Scope

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

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

The results of this work will impact the development of advanced materials, such as nanophase ceramics, that have dramatically improved properties compared with traditional ceramics. These advanced ceramics are potential candidates for structural ceramics, electroceramics, catalysts, nanocrystalline thin films, coatings, and nanostructured inorganic membranes.

3.2.2 Progress

3.2.2.1 Forced Hydrolysis in Aqueous Solutions

We recently focused on the thermal hydrolytic homogeneous precipitation in concentrated aqueous zirconium salt solutions. Preliminary results have been obtained on the effect of salt concentration on the particle sizes by DLS measurements. We also observed that urea-aided thermal hydrolytic precipitation resulted in gel materials with uniform milky turbidity. Under the same incubation temperature, higher urea concentration corresponds to an earlier gelling time.

3.2.2.2 Homogeneous Precipitation in Aqueous-Alcohol Mixtures

Experiments have been conducted using the High Temperature Materials Laboratory facilities for characterization of zirconia precursor powder materials (i.e., high-temperature XRD and DTA/TGA). In the absence of alcohol solvent in the solution, thermal incubation at 100 °C produced nanocrystalline (monoclinic) cube-shaped particles, which start to transform to tetragonal phase at 1200 °C. The XRD data are under analysis to determine the size of crystallites in each crystalline particle. The phase transformation of typical sphere-shaped particles was found to be very different from that of cube-shaped particles. In general, it appears that higher temperature (>100 °C) and longer incubation time will give more thermal energy to cause the crystallization of particles during homogeneous precipitation. Further XRD experiments will be designed to confirm the effect of incubation conditions (temperature, incubation time, salt concentration, and alcohol/water ratio) on the crystallization and the behavior of high-temperature microstructure transformation of sphere-shaped particles.

3.2.2.3 Sol-Gel Processing in Alkoxide Systems

Batch solution experiments were conducted to optimize the reaction conditions by adjusting the concentration of zirconium tetrabutoxide and water in alcohol, pH (hydrochloric acid), aging temperature, and aging time, as well as the type of the alkoxide and alcohol solvent (ethanol, propanol, isopropanol, butanol, hexanol). Molar ratio of alkoxide over water (0.1 *M*/0.2 *M*), aging temperature, and type of solvent were found to be major factors that affect the reaction kinetics, size, and morphology. Strategies based on the use of surfactant (sodium dodecyl sulfate), polymeric dispersant (hydroxypropyl cellulose), and adjustment of pH and ionic strength are being considered to control the agglomeration state of primary particles.

3.2.2.4 Supercritical Fluids Processing of Ultrafine Particles and Inorganic Membranes

This work is conducted in collaboration with Professor N. Xu at the Nanjing University of Chemical Technology. Experimental equipment has been built that can measure the solubility of inorganic substances in supercritical fluid phase and also prepare ultrafine monosized particles by the rapid expansion of supercritical fluid solution (RESS) technique. The solubility of aluminum isopropoxide in supercritical propane was determined at 388 and 403 K for pressures up to 30.5 MPa. The effects of nozzle structure and preexpansion temperature on the properties of ultrafine particles of aluminum isopropoxide formed by the RESS technique has been studied; a paper describing the results is in preparation.

3.2.2.5 Ultrafine Particle Synthesis by Inverse Electrostatic Spraying (IES)

Work has continued toward the development of a new process of particle synthesis using electrohydrodynamic mixing (see Sect. 3.1.2.3, Mixing in Electrohydrodynamic Flows). Continuous production of very fine particles has been achieved through conventional sol-gel reactions taking place when solvent-containing alkoxides are rapidly dispersed in deionized water. However, the particles produced were readily agglomerated in the deionized water. Alternative reaction conditions have been devised and will be tested during the next quarter. If successful, the developed IES reactive system will offer the following advantages relative to the classical chemical synthesis in batch solutions: (1) faster particle formation rate, (2) continuous production, (3) higher solid fraction, and (4) controllable size and monodispersity.

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

3.3.1 Purpose and Scope

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

3.3.2 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, showed a significant effect of electric fields in both batch distillation and phase equilibria. A specially designed cell has been constructed from Teflon, glass, and stainless steel for vapor pressure measurements of pure liquids and mixtures under the influence of electric fields. These experiments are currently in progress.

The results obtained to date suggest that electric fields may cause modification of vapor-liquid equilibria in some systems, while more experiments are needed to investigate the effects of electric fields on liquid-liquid equilibria. In liquid-liquid systems, it was found that a strong electric field across an interface causes electrohydrodynamic flow that is undesirable for isolating the electric-field effects on phase equilibria. The transport enhancement of a solute between two liquids caused by electrohydrodynamic flows is currently studied in these systems.

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

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

3.4.1 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.

3.4.2 Progress

Bench-scale testing of magnetic-seeding filtration is currently focused on the removal of iron-containing precipitates that have caused significant problems in the treatment of contaminated groundwater by ion exchange. Experiments have indicated that, due to a low magnetic susceptibility for the iron precipitate, seeding will be necessary for removal by magnetic filtration. Experiments have been conducted with iron hydroxide precipitates in pH-adjusted tap water to explore the capabilities of removal with seeding under various conditions of flow rate and field strength. As might be expected, the experiments showed that lower removal was achieved as the flow rate was increased, while application of a 0.8-T magnetic field both increased the removal rate over that with no field by a factor of approximately 3 and increased the time to breakthrough. Interestingly, the ratio of particle removal with an applied field to that without an applied field as a function of the bed volumes passed through the filter appears to lie approximately on the same curve for each flow rate. This suggests that there may be a way to extrapolate the performance of a magnetic filter through the results of a few experiments. In the next reporting period, experiments measuring the capability of this filtration method to reduce pressure drop in a zeolite bed will be conducted, and the results will be compared with those from other filtration methods currently under study by EM-40.

The modeling approach developed to predict the evolution of particle size under turbulent-shear flocculation was further examined. The effects of particle size, particle size ratio, agitation speed, and interparticle forces on collision efficiency were investigated. The results obtained from the model were found to be similar to those of relevant studies available in the literature for cases in which interparticle forces are suppressed. The effect of interparticle forces is also currently being examined by our model, which is unique in accommodating these forces in particle flocculation under a turbulent-shear flow. The flocculation rate, defined as the product of collision efficiency and collision frequency, was incorporated into the population-balance equation and provided direct comparison between modeling results and experimental data. A modeling approach, combining the single-particle/single-wire trajectory model, the particle buildup model, and the breakthrough equation, was developed to predict the performance of a magnetic filter without using adjustable parameters. Also, the bivariate population-balance equation, which is able to provide the size and magnetic susceptibility distributions of particles in suspensions, was employed to predict the behavior of magnetic-seeding processes. Modeling results described well breakthrough experiments conducted with adsorbent particles from Argonne National Laboratory. Current efforts are concentrated on further comparisons between modeling results and experimental data. Results of the modeling work were presented on July 1, 1997, in a paper entitled "Flocculation and Filtration of Paramagnetic Colloidal Particles" at the 71st American Chemical Society Colloid and Surface Science Symposium at the University of Delaware.

3.5 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; no results are reported at this point.

3.5.1 Purpose and Scope

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

3.5.2 Progress

An experimental apparatus has been set up for ozonation studies. 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. The electrochemical ozone generator has been obtained from Lynntech, Inc. The combination of higher concentration of ozone and efficient mass transfer is expected to lead to enhanced ozonation performance. The experimental work is in its initial stages, and at this point no results are reported.

3. 6 PUBLICATIONS

C. Tsouris and S. Yiacoumi, "Particle Flocculation and Filtration by High-Gradient Magnetic Fields," *Sep. Sci. Technol.* **32**, 599–616 (1997).

C. Tsouris, S. H. Neal, V. M. Shah, M. A. Spurrier, and M. K. Lee, "Comparison of Liquid-Liquid Dispersions Formed by a Stirred Tank and Electrostatic Spraying," *Chem. Eng. Comm.*, in press (1997).

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

S. E. Burns, S. Yiacoumi, and C. Tsouris, "Microbubble Generation for Environmental and Industrial Separations," *Sep. Purifi. Technol.*, in press (1997).

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

C. Tsouris, W.-T. Shin, and S. Yiacoumi, "Spraying, Pumping, and Mixing of Fluids by Electric Fields," submitted for publication in *AIChE J.* (1997).

X. Zhang, J. S. Kim, and O. A. Basaran, "Dynamics of Deformation and Breakup of Stretching Liquid Bridges in the Presence of an Axial Electric Field," submitted to *J. Electrostatics* (1997).

3.7 PRESENTATIONS

C. Tsouris, "Pumping and Mixing of Fluids by Electric Fields," presented at Mixing XVI, Williamsburg, Virginia, June 22–27, 1997.

C. Tsouris, W.-T. Shin, and S. Yiacoumi, "Formation of Microbubbles Using Electric Fields for Environmental Applications," presented at the 71st Colloids and Surface Science Symposium, University of Delaware, June 29–July 2, 1997.

S. Yiacoumi, K. Subramaniam, and C. Tsouris, "Influence of Sorption Rates on Particle Flocculation Kinetics," presented at the 71st Colloids and Surface Science Symposium, University of Delaware, June 29–July 2, 1997.

S. Yiacoumi, T.-Y. Ying, S.-C. Lu, C.-J. Chin, and C. Tsouris, "Flocculation and Filtration of Paramagnetic Colloidal Particles," presented at the 71st Colloids and Surface Science Symposium, University of Delaware, June 29–July 2, 1997.

4. SOLUTION THERMODYNAMICS

H. D. Cochran

4.1 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.

4.1.1 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.

4.1.2 Progress

We attended the 4th International Symposium on Supercritical Fluids and presented two papers—"Molecular Adsorption: Repulsive and Attractive Supercritical Fluid Mixtures" and "SAXS and SANS Studies of Surfactants and Reverse Micelles in Supercritical CO_2"—that were published in the proceedings.

With Lloyd Lee of Oklahoma University and Phil LoCascio of the Center for Computational Sciences, we have successfully implemented on the Paragons a parallel version of our code for solving the inhomogeneous Ornstein-Zernike equation, with which we have previously studied adsorption of both attractive and repulsive solutes from a supercritical solution. Parallel calculations on the Paragons will allow us to refine the discretization of the pair correlation functions to finer grid spacing and longer range in each of the three dimensions and, thereby, to test the accuracy of our previous calculations. Ultimately, the parallel code will allow us to extend the calculations to states and systems that were previously inaccessible, such as systems with stronger (more realistic) surface forces.

Our efforts to extract ω-3 fatty acids from biomass with supercritical CO_2 have been quite successful. A large batch of biomass from fermentation of filamentous fungi was sheared to disrupt the cells and freeze dried to ~10 wt % water, and samples have been rehydrated to 30 wt % and 95 wt % water and extracted. The 95 wt % water sample was extracted with the aid of a commercially available Krytox surfactant. Quantitative extraction data have been obtained. Short-time data at the lowest CO_2 flow rate are being analyzed with an equilibrium model, and long-time data at higher flow rates are being analyzed with two mass transfer models.

4.2 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.

4.2.1 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.

4.2.2 Progress

With the existing cell (½-in. ID, limited to 2000 psi), we have assembled and successfully tested the electrodispersion apparatus at The University of Tennessee. The water dispersions produced to date have not been as fine as we hope to achieve because the existing cell limits us to external placement of the counterelectrode and, consequently, to rather small electric field gradients. The new cell (1½-in. ID, certified to 5000 psi) has been received and installed. This cell allows easier access for internal placement of the counterelectrode. The high-pressure electrical feedthroughs for the feed capillary (primary electrode) and the counterelectrode are being installed in the shop at this time.

4.3 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)

Contact: H. D. Cochran
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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.

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[*] University of North Carolina.
[†] University of Pittsburgh.

4.3.1 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.

4.3.2 Progress

J. M. DeSimone and members of his team including J. D. Londono, G. D. Wignall, and H. D. Cochran received the 1997 President's Green Chemistry Challenge Award for previous accomplishments in this program.

We attended the 13th Symposium on Thermophysical Properties and presented the paper "SAXS and SANS Studies of Surfactants and Reverse Micelles in Supercritical CO_2." Small-angle neutron scattering (SANS) experiments planned for the quarter have been delayed because of the extended shutdown of the High Flux Isotope Reactor. The valving on the SAXS cell has been modified for more efficient operations, and SAXS beam time has been scheduled in the next quarter.

Our manuscript, "Intermolecular Potentials and Vapor-Liquid Phase Equilibria of Perfluorinated Alkanes," has been submitted to *Fluid Phase Equilibria*. The next step in developing models for the complex CO_2–surfactant systems is to develop and test the potential model for the interactions between sites on the CO_2 molecule and sites on the surfactant molecule. To this end, simulations have been initiated of CO_2 with alkane and perfluoroalkane solutes at infinite dilution for determining the infinite dilution chemical potential. Experiments with model solutions have been planned for the next SAXS and SANS beam times to provide data against which to test the models.

We have begun efforts to simulate reverse micelles in solution. As a first step, we plan to reproduce previous simulations by O'Connell and Karaborni; this simulation approach will be used to preform the micelles for our subsequent, more realistic simulations as well. The code to reproduce the O'Connell-Karaborni results has been written, and a simplified version of this code conserves energy successfully. Debugging of the full code continues.

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

Contact: H. D. Cochran
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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).

4.4.1 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, SAXS, and SANS experiments on sheared systems.

4.4.2 Progress

This program was proposed to the DOE Division of Materials Sciences for startup in October. We have invested considerable effort in planning the experimental and theoretical approaches that will complement the ongoing molecular simulation work from our prior Laboratory Director's Research and Development (LDRD) project.

A paper from the previous LDRD effort in this area, "Molecular Dynamics Simulations of the Rheology of Normal Decane, Hexadecane, and Tetracosane," by S. T. Cui, S. A. Gupta, P. T. Cummings, and H. D. Cochran, received an ORNL 1997 Awards Night Award for Technical Publications.

4.5 PUBLICATIONS

4.5.1 Published

L. L. Lee and H. D. Cochran, "Molecular Adsorption: Repulsive and Attractive Supercritical Fluid Mixtures," pp. 347–50 in *Proc. 4th Int. Symp. on Supercritical Fluids,* V. C, Sendai, Japan, May 11–14, 1997.

J. D. Londono, R. S. Dharmapurikar, G. D. Wignall, and H. D. Cochran, "SAXS and SANS Studies of Surfactants and Reverse Micelles in Supercritical CO_2," pp. 667–70 in *Proc. 4th Int. Symp. on Supercritical Fluids,* V. **B,** Sendai, Japan, May 11–14, 1997.

4.5.2 Submitted

S. T. Cui, J. I. Siepmann, H. D. Cochran, and P. T. Cummings, "Intermolecular Potentials and Vapor-Liquid Phase Equilibria of Perfluorinated Alkanes," *Fluid Phase Equilib.*, submitted (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.*, submitted (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.*, submitted (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.*, submitted (1997).

5. BIOTECHNOLOGY RESEARCH

E. Greenbaum

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

Contact: E. Greenbaum
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Summary: During the current reporting period, experiments were continued on the study of photosynthetic reactions using Photosystem I (PSI)–deficient mutants of the green alga *Chlamydomonas reinhardtii*. Absolute measurements of photosynthetic reactions and associated parameters in *Chlamydomonas reinhardtii* mutant Fud26 have been performed and compared with predictions of the Z-scheme.

5.1.1 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 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 that are required to split water to hydrogen and oxygen are studied. Fundamental studies on the enzymology of cellulase are also being performed.

5.1.2 Progress

Whereas the stoichiometric ratio of PSI to Photosystem II (PSII) is 0.081:1, the ratio of hydrogen to oxygen of individual single-turnover saturating flashes is approximately 1:1. This ratio is too large to be explained by a "leaky" Z-scheme model proposed by Boichenko [*Photosyn. Res.* **47,** 291–92 (1996)], in which 10–20 PSIIs operating in parallel send their reducing equivalents to a single PSI. In addition, comparative measurements of oxygen evolution coupled to carbon dioxide reduction in mutant Fud26 and wild-type *C. reinhardtii* 137c have been performed under light-limiting conditions. The rate of oxygen evolution in Fud26 is about 50% of the corresponding rate in wild type. In order to account for these data with Boichenko's model, the antenna size of PSI in mutant Fud26 would have to be 4.5 times larger than its corresponding size in PSII. However, this is not the case. The PSI antenna in mutant Fud26 is *smaller* than the corresponding PSII antenna. The PSI antenna is ≈150 Chl, whereas that for PSII is ≈320 Chl. It is concluded that photosynthetic reactions in mutant Fud26 can occur that conflict with the Z-scheme. In nature these reactions may not occur at all, or they may operate with varying amplitude simultaneously with the Z-scheme.

Synergy experiments were carried out to examine the interactions between the thermophilic enzymes and the mesophilic cellulases. The β-glucosidase GLY-001-02 from *Pyrococcus furiosus* was found to bind strongly to microcrystalline cellulose (Avicel). It also acted synergistically with a cellulase (CBH I) from the mesophile *Trichoderma reesei*. This was a true synergy between a cellobiohydrolase that removes cellobiose from cellulose chains and a β-glucosidase that hydrolyses cellobiose to glucose. The amount of glucose produced by the combination of these enzymes was 50% higher than that expected if the cellobiose produced by CBH I were simply hydrolyzed. As far as is known, β-glucosidase has not previously been shown to demonstrate true synergy with cellulases. We have demonstrated that the common sugar glucose can be used to produce hydrogen using two enzymes: glucose dehydrogenase and hydrogenase. The novel aspect of this work is that no sophisticated or expensive hydrogen detection equipment is required, only a redox dye, benzyl viologen, which turns purple when it is reduced. The color can be detected by a simple colorimeter. Finally, we have platinized bovine serum albumin and found that it is capable of producing a combustible gas upon the addition of glucose. This intriguing result is currently under investigation and is of interest in the context of generating novel hydrogen-producing catalysts. Platinized cellulosic particles did not carry out this reaction.

5.2 BIOMOLECULAR ELECTRONICS (E. Greenbaum, J. W. Lee, and I. Lee)

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Summary: During the current period, we set up electric field–gradient microscopy, scanning Maxwell stress microscopy, and Kelvin probe microscopy to measure local electric-field gradients and surface potentials on the nanometer scale. Detection is comprised of a two-pass system, where surface topography is obtained in the first pass and the electric-field gradient or surface potential is measured in the second. We have tested electric field–gradient detection on a gold substrate with both gold and hydrocarbon particles.

5.2.1 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.

5.2.2 Progress

During the current period, we set up electric field–gradient microscopy, scanning Maxwell stress microscopy, and Kelvin probe microscopy to measure local electric-field gradients and surface potentials on the nanometer scale. Detection is comprised of a two-pass system, where surface topography is obtained in the first pass and the electric-field gradient or surface potential is measured in the second. We have tested electric field–gradient detection on a gold substrate with both gold and hydrocarbon particles. Both have similar topographical images. We can differentiate gold particles from hydrocarbon particles with electric field–gradient detection since their electric-field gradients are different. Very good resolution has been obtained. Particles as small as 10 nm can be well resolved.

Further experiments designed to calibrate the system to obtain quantitative voltage measurements of PSI reaction centers are planned.

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

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Summary: Experiments with chromatically adapted *Chlamydomonas reinhardtii* have been performed. The objective of these experiments is to perform a quantitative measurement of the amount of PSI present in the algae with the amount of carbon dioxide fixed on a per-reaction-center basis. These experiments utilized the technique of single-turnover saturating flashes of light to measure the absolute amount of carbon dioxide taken up per single turnover saturating flash of light. The quantitation of the amount of PSI present in the algal samples is being performed in collaboration with Professor A. Melis, of the University of California, Berkeley. When Professor Melis sends us the results of his analysis, comparison of the two data sets can proceed.

5.3.1 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.

5.3.2 Progress

Experiments with chromatically adapted *Chlamydomonas reinhardtii* have been performed. The objective of these experiments is to perform a quantitative measurement of the amount of PSI present in the algae with the amount of carbon dioxide fixed on a per-reaction-center basis. These experiments utilized the technique of single-turnover saturating flashes of light to measure the absolute amount of carbon dioxide taken up per single-turnover saturating flash of light. The quantitation of the amount of PSI present in the algal samples is being performed in collaboration with Professor A. Melis, of the University of California, Berkeley. When Professor Melis sends us the results of his analysis, comparison of the two data sets can proceed.

5.4 ENZYMES FROM EXTREMOPHILES IN BIOPROCESSING AND BIOREMEDIATION (J. Woodward and B. R. Evans)

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Summary: The products from the hydrolysis of cellooligosaccharides, barley β-glucan, and carboxylmethyl cellulose (CMC) by the thermophilic enzymes GLY-001-02 (*Pyrococcus furiosus*) and CEL-001-02, obtained from Recombinant Biocatalysis, Inc., were analyzed by high-performance liquid chromatography and compared with the products obtained from the mesophilic cellulases CBH I and EG II from *Trichoderma reesei*. A quick method to concentrate xylanase activity from the ORNL mixed culture by ion-exchange chromatography was devised. Glucose isomerase activity, as well as invertase activity, was detected in the DEAE-Sepharose ion-exchange fractions from the pure ORNL strain TOR-39. A sixfold increase in invertase activity was achieved by a second ion-exchange step with CM-Sepharose. As part of our study of extremozymes, the kinetics of CEL-001-02 have been studied. We have been working to find the optimal temperature and pH at which to perform reactions of this enzyme on three different substrates: barley β-glucan, *p*-nitrophenyl D-(+)-cellobioside (PNPC), and CMC. The CEL-001-02 is added to a mixture of buffer and substrate that has been allowed to reach reaction temperature in the hot water bath. After reacting with the CEL-001-02, the barley β-glucan and the CMC were assayed with dinitrosalicylic acid (DNS) reducing sugar assay reagent, which detects the reducing sugars, such as glucose, that are the end products of reactions between the cellulase and the substrate. The end product of the reaction between the PNPC and CEL-001-02 is *p*-nitrophenol (PNP). In the case of the DNS reducing sugar assay, 100-μL aliquots are removed from the reaction mixture in the hot water bath and added to 1 mL DNS reagent. This new mixture is then placed in a 90° water bath for 5 min, after which the absorbance of the solution is read at 540 nm, the wavelength at which DNS absorbs light after it has been reduced by the sugars.

5.4.1 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 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 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° 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° is optimal for that substrate.

5.4.2 Progress

Experiments are currently being carried out to determine the optimal temperature at which to react CEL-001-02 with barley β-glucan and CMC. It appears that these two substrates will have an optimal temperature of 80° or higher. Crystals of this enzymes have been generated.

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

Contact: J. Woodward
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Summary: We are currently working to utilize the pentose phosphate pathway (PPP) to obtain greater yields of hydrogen from glucose and determine the kinetics of each step. During the first part of the PPP, which we will call the NADPH production step, glucose-6-phosphate (G6P) is oxidized and a carbon is removed to form ribulose-5-phosphate (R5P), reducing 2 molecules of NADP$^+$ to NADPH in the process. The R5P then continues through the pathway, and the G6P that is regenerated can then be recycled and used in the pathway, producing more NADPH. If the G6P goes through the pathway once, then for every 6 mol of G6P, it is possible to produce only 12 mol of NADPH. However, if the G6P is recycled, then for every 6 mol of G6P, the maximum amount of NADPH that can be produced is 56 mol, or 9.3 mol of NADPH per mole of glucose. Once the NADPH is formed, hydrogenase is used to oxidize the NADPH, forming NADP$^+$ and hydrogen.

5.5.1 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 G6P, glucose-6-phosphate dehydrogenase, 6-phosphogluconic dehydrogenase, 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 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 NAPDH 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.

5.5.2 Progress

These treated enzymes were then used in the PPP and tested for activity. It was shown that the activity of the EDTA-treated and the dialyzed FDPases and the rate of the NADPH production step increased in both cases. The dialyzed FDPase was used in the complete pathway once again to see if more than 2 mol of hydrogen could be extracted from 1 mol of glucose, but the pathway did not seem to work because only 2 mol of NADPH per mole of glucose was produced. The phosphate pathway was then tested using 50 m*M* Hepes, pH 7.5, as the buffer instead of the sodium phosphate, and the rate of the NADPH production step did not increase. However, more than 2 mol of hydrogen could be extracted from 1 mol of glucose. The PPP was put through more tests in order to maximize the amount of NADPH formed.

5.6 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)

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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.

5.6.1 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.

5.6.2 Progress

Funding was received into the Chemical Technology Division financial plan in March 1997. Assignments for the 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.

5.7 AWARDS

J. Woodward received the following awards.

1997 James Van Lanen Distinguished Service Award, presented by the Division of Biochemical Technology, American Chemical Society.

1997 Columbus Scholar Award, presented by the Christopher Columbus Fellowship Foundation, for work on the enzymatic production of hydrogen from sugar.

5.8 PUBLICATIONS

5.8.1 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.

B. C. Saha and J. Woodward (eds.), *Fuels and Chemicals from Biomass*, ACS Syposium Series 666, American Chemical Society, Washington, D.C., 1997.

5.8.2 In Press

B. R. Evans, I. Lee, J. Woodward, and S. V. Fox, "The Effect of Cellulases on the Biodegradation and Morphology of Naturally Colored Cotton Fibers," accepted for publication in the ACS Symposium Series.

5.8.3 Submitted

I. Lee, J. W. Lee, and E. Greenbaum, "Biomolecular Electronics: Vectorial Arrays of Photosynthetic Reaction Centers," submitted (1997).

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

N. Herschlag, I. Turnerm, and J. Woodward, "A Simple Method to Demonstrate the Enzymatic Production of Hydrogen from Sugar," submitted to the *Journal of Chemical Education* (1997).

5.8.4 *In Preparation*

J. Woodward et al., "Enzymatic Hydrogen Production: Conversion of Renewable Resources," manuscript in preparation for *Energy and Fuels*.

5.9 PRESENTATIONS

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 2nd Great Lakes Photochemistry Symposium, London, Ontario, Canada, June 6–8, 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 21st DOE Solar Photochemistry Research Conference, Copper Mountain, Colorado, June 7–11, 1997.

E. Greenbaum, "Recent Advances in Photobiological Hydrogen Production," presented at BioHydrogen '97, Kona, Hawaii, June 23–27, 1997.

E. Greenbaum, "New Photosynthetic Pathways: Renewable Fuels Production and Biomolecular Electronics," research seminar presented to the Photosynthesis Research Group, Melvin Calvin Laboratory, the University of California, Berkeley, June 27, 1997.

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. Woodward, "Utilization of Extremozymes for the Conversion of Renewable Sugar to Molecular Hydrogen," presented at the National American Chemical Society Meeting, San Francisco, California, April 1997.

6. MOLECULAR STUDIES

P. T. Cummings

6.1 AQUEOUS ELECTROLYTE SOLUTIONS AT AMBIENT AND SUPERCRITICAL CONDITIONS (P. T. Cummings, A. A. Chialvo, J. T. Slusher, and E. C. Nielsen)

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Summary: A new and sophisticated water model was further refined using newly published neutron scattering results as benchmark data. Improved methods for calculating the chemical potential were applied to simple fluids such as noble gases. A Gibbs-Duhem molecular simulation code, which was under development, will allow the efficient prediction of the phase envelope of water from a molecular model.

6.1.1 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).

6.1.2 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. Smeared charges were introduced, instead of point charges, as well as an exponential (Huggins-Mayer) form for the repulsion in order to obtain better agreement with experimental neutron scattering results.

David Kofke, a visiting faculty member from SUNY at Buffalo, developed a model for understanding the efficiency of Monte Carlo simulation methods used to predict the chemical potential in liquid. His insights were used to develop an improved methodology for simulation of the chemical potential in simple liquids such as the noble gases. Previously, the method had been tested only for the hard-sphere fluid.

The group began development of a molecular simulation program implementing the Gibbs-Duhem method to calculate the phase envelope of water directly from simulation. The Gibbs ensemble method is used to supplement the Gibbs ensemble method of Panagiotopoulos. The Gibbs-Duhem method, developed by David Kofke, will be the first application to a complex molecular fluid such as water.

6.2 THEORY AND MOLECULAR SIMULATION OF NONEQUILIBRIUM SYSTEMS

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

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Summary: In view of previous success in predicting the viscosity index of squalane, we began a new series of calculations for other alkanes. We continued to study the effect of oscillatory shear on the solidification transition in supercooled water.

6.2.1 Purpose and Scope

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

6.2.2 Progress

We began a new series of molecular simulations of alkane liquids subjected to homogeneous shear. The goal will be to calculate the viscosity index and other rheological properties, as we have previously done for squalane.

Further study was made concerning evidence from molecular simulation that the application of oscillatory shear, along with an external electric field, can dramatically decrease the solidification time of water. While further study showed that the effect of oscillatory shear was always positive (i.e., it accelerated solidification), we found that it did not consistently yield order-of-magnitude increases in the rate of solidification.

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

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Summary: A new study of mixed-solvent electrolytes by integral equation methods was initiated.

6.3.1 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.

6.3.2 Progress

Noe Herrera, a faculty member from Mexico who is partially supported by the Mexican equivalent of the National Science Foundation, began to develop and study an integral equation formulation of mixed-solvent electrolytes.

6.4 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
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Internet: u53@ornl.gov

Summary: Considerable effort was expended on developing macroscale two-dimensional finite-element codes to model in situ bioremediation processes.

6.4.1 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.

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*University of Virginia.

6.4.2 Progress

Further progress was made on the development of two-dimensional finite-element codes for modeling in situ bioremediation processes at the macroscopic and field level. Manuscripts describing this work were initiated. An analysis of the swimming behavior of motile bacteria confined to cylindrical pores was initiated.

6.5 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.

6.5.1 Purpose and Scope

This three-year project, supported by the new DOE Environmental Management Science Program, 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).

6.5.2 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.

6.6 MOLECULAR-BASED STUDY OF REVERSED MICELLES IN SUPERCRITICAL CO_2 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,[*] J. M. DeSimone[†])

Contact: H. D. Cochran and P. T. Cummings
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Summary: See research description reported in Sect. 4.3.

6.7 PUBLICATIONS

6.7.1 Published

J. T. Slusher and P. T. Cummings, "Molecular Simulation Study of Tetraalkylammonium Halides. I. Solvation Structure and Hydrogen-Bonding in Aqueous Solutions," *J. Phys. Chem. B* 101, 3818–26 (1997).

M. J. Stevens, M. Mondello, G. S. Grest, S. T. Cui, H. D. Cochran, and P. T. Cummings, "Comparison of Shear Flow of Hexadecane in a Confined Geometry and in Bulk," *J. Chem. Phys.* **106**, 7303–14 (1997).

S. T. Cui, H. D. Cochran, P. T. Cummings, and S. K. Kumar, "Structural and Mixing Properties of Polymer Blends from Molecular Dynamics Simulation," Macromolecules **30**, 3375–82 (1997).

6.7.2 In Press

A. A. Chialvo, P. T. Cummings, J. M. Simonson, and R. E. Mesmer, "Molecular Simulation Study of Ion Speciation in Supercritical Aqueous Solutions," *J. Mol. Liq.*, accepted for publication (1997).

S. T. Cui, P. T. Cummings, and H. D. Cochran, "The Calculation of Viscosity of Liquid *n*-Decane and *n*-Hexadecane by the Green-Kubo Method," *Mol. Phys.* accepted for publication (1997).

P. T. Cummings, "Molecular Simulation of Complex Systems Using Massively Parallel Supercomputers," *Fluid Phase Equilib.*, accepted for publication (1997).

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," *Mol. Phys.*, accepted for publication (1997).

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[*] University of Pittsburgh.
[†] University of North Carolina.

6.7.3 Submitted

A. A. Chialvo, P. T. Cummings, J. M. Simonson, R. E. Mesmer, and H. D. Cochran, "The Importance of the Interplay Between Molecular Simulation and Neutron Scattering in Developing New Insights into the Structure of Water," *J. Am. Chem. Soc.*, submitted (1997).

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

A. A. Chialvo and P. T. Cummings, "Simple Transferable Intermolecular Potential for the Molecular Simulation of Water over Wide Ranges of State Conditions," *Fluid Phase Equilib.*, submitted (1997).

D. A. Kofke and P. T. Cummings, "Precision and Accuracy of Staged Free Energy Perturbation Methods for Computing the Chemical Potential by Molecular Simulation," *Fluid Phase Equilib.*, submitted (1997).

D. A. Kofke, "Semigrand Canonical Monte Carlo Simulation: Integration Along Coexistence Lines," *Adv. Chem. Phys.*, submitted (1997).

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

S. A. Gupta, H. D. Cochran, and P. T. Cummings, "Nanorheology of Liquid Alkanes," *Fluid Phase Equilib.*, submitted (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.*, submitted (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.*, submitted (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.*, submitted (1997).

S. T. Cui, J. I. Siepmann, H. D. Cochran, and P. T. Cummings, "Intermolecular Potentials and Vapor-Liquid Phase Equilibria of Perfluorinated Alkanes," *Fluid Phase. Equilib.*, submitted (1997).

A. A. Chialvo, P. T. Cummings, J. M. Simonson, and R. E. Mesmer, "Thermodynamics and Kinetics of Ion Speciation in Supercritical Aqueous Solutions: A Molecular Based Study," *Fluid Phase Equilib.*, submitted (1997).

6.8 PRESENTATIONS

P. T. Cummings, "The Structure of Ambient and Supercritical Water and the Interplay Between Neutron Scattering and Simulation," invited talk presented at Special Topics in Statistical Mechanics (A Symposium in Honor of Raymond D. Mountain), April 10–11, 1997.

P. T. Cummings, "Molecular Simulation of Supercritical Water and of Ionic Association in Supercritical Aqueous Solutions," invited talk presented at the 5th Mid-Western Thermodynamics and Statistical Mechanics Meeting, Lake Geneva, Wisconsin, May 14–16, 1997.

P. T. Cummings, "Molecular Simulation: A Present and Future Tool for Physical Properties Prediction," keynote lecture presented at the Second Sino-American Conference on Chemical Engineering, Beijing, People's Republic of China, May 19–22, 1997.

P. T. Cummings, "Molecular Simulation of Complex Systems Using Massively Parallel Supercomputers," seminar presented at the Department of Chemical Engineering, Seoul National University, Seoul, South Korea, May 26, 1997.

P. T. Cummings, "Rapidly Emerging Capabilities in Computational Molecular-Based Engineering and Science," Oak Ridge National Laboratory Showcase Lecture, June 12, 1997.

P. T. Cummings, "Molecular Modeling and Simulation: Present and Future Tools for Physical Properties Prediction and Molecular Product Design,"plenary lecture presented at the 13th Symposium on Thermophysical Properties, Boulder, Colorado, June 22–27, 1997.

A. A. Chialvo and P. T. Cummings, "Simple Transferable Intermolecular Potential for the Molecular Simulation of Water over Wide Ranges of State Conditions," presented at the 13th International Thermophysical Properties Symposium, Boulder, Colorado, June 22–27, 1997.

J. T. Slusher and P. T. Cummings, "Simulation Studies of Mixed-Solvent Organic Electrolyte Solutions," presented at the 13th International Thermophysical Properties Symposium, Boulder, Colorado, June 22–27, 1997.

D. A. Kofke and P. T. Cummings, "Optimal Weighting Functions for Measuring the Chemical Potential by Molecular Simulation," presented at the 13th International Thermophysical Properties Symposium, Boulder, Colorado, June 22–27, 1997.

S. A. Gupta, H. D. Cochran, and P. T. Cummings, "Nanorheology of Liquid Alkanes," presented at the 13th International Thermophysical Properties Symposium, Boulder, Colorado, June 22–27, 1997.

S. T. Cui, P. T. Cummings, H. D. Cochran, J. D. Moore, and S. A. Gupta, "Nonequilibrium Molecular Dynamics Simulation of Rheology of Linear and Branched Alkane," presented at the 13th International Thermophysical Properties Symposium, Boulder, Colorado, June 22–27, 1997.

I. Borzsák and P. T. Cummings, "Effect of Oscillatory Shear on the Fluid-Solid Phase Transition of Supercooled Water," presented at the 13th International Thermophysical Properties Symposium, Boulder, Colorado, June 22–27, 1997.

R. M. Ford and P. T. Cummings, "Quantitative Characterization of Bacterial Migration Through Porous Media," presented at the conference In Situ and On Site Bioremediation, New Orleans, Louisiana, April 28–May 1, 1997.

A. A. Chialvo, P. T. Cummings, J. M. Simonson, and R. E. Mesmer, "Thermodynamics and Kinetics of Ion Speciation in Supercritical Aqueous Solutions: A Molecular Based Study," presented at the 13th International Thermophysical Properties Symposium, Boulder, Colorado, June 22–27, 1997.

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