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Quarterly Progress Report for the Chemical and Energy Research Section of the Chemical Technology Division: April–June 1998

R. T. Jubin

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FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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Chemical Technology Division

QUARTERLY PROGRESS REPORT FOR THE CHEMICAL AND ENERGY RESEARCH SECTION OF THE CHEMICAL TECHNOLOGY DIVISION: APRIL–JUNE 1998

R. T. Jubin

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CONTENTS

ACRONYMS

ACB	auxiliary charcoal bed
AFM	atomic force microscopy
AIChE	American Institute of Chemical Engineers
BES	Basic Energy Sciences (DOE)
CRADA	cooperative research and development agreement
CWRU	Case Western Reserve University
DLS	dynamic light scattering
DOE	U.S. Department of Energy
DTA	differential thermal analysis
ESP	Environmental Simulation Program
ESW	Enhanced Sludge Washing
FTIR	Fourier transform infrared
G-6-P	glucose-6-phosphate
HFIR	High-Flux Isotope Reactor
HPLC	high-performance liquid chromatography
IMP	Mexican Petroleum Institute
IPP	Industrial Partnering Program (DOE)
MMTF	Molecular Modeling Task Force
MSRE	Molten Salt Reactor Experiment
ORNL	Oak Ridge National Laboratory
PSI	Photosystem I
PSII	Photosystem II
SAM	self-assembled monolayer
SANS	small-angle neutron scattering
SAXS	small-angle X-ray scattering
SEM	scanning electron microscopy
TGA	thermogravimetric analysis
USDA-ARS	U.S. Department of Agriculture–Agricultural Research Service
XRD	X-ray diffraction

EXECUTIVE SUMMARY

This report summarizes the major activities conducted in the Chemical and Energy Research Section of the Chemical Technology Division at Oak Ridge National Laboratory (ORNL) during the period April–June 1998. The section conducts basic and applied research and development in chemical engineering, applied chemistry, and bioprocessing, with an emphasis on energy-driven technologies and advanced chemical separations for nuclear and waste applications.

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

Activities conducted within the area of *Hot Cell Operations* focused on efforts to optimize the processing conditions for Enhanced Sludge Washing of Hanford tank sludge, with emphasis shifting to facility decontamination and preparation of the final report on Hanford tank sludges.

Within the area of *Process Chemistry and Thermodynamics*, the problem of solids formation in process solutions from caustic treatment of Hanford sludge and the issue of solution conditions required to dissolve Hanford saltcake were addressed. Attempts to interpret chemical thermodynamics in applied-technology ceramic systems continued with preparation of thin films of barium/cerium and cerium/zirconium compounds using sol-gel processing.

MSRE Remediation Studies focused on recovery of ^{233}U and its transformation into a stable oxide, passivation of fluorinated charcoal in the auxiliary charcoal bed, and radiolysis experiments to permit remediation of MSRE fuel salt.

Within the area of *Chemistry Research*, activities included studies relative to molecular imprinting for use in several areas of separations technology and attempts to define the thermodynamics of uranium compounds in molten salts.

In the area of *Separations and Materials Synthesis*, fundamental studies explored the use of electromagnetic fields to enhance transport processes in multiphase separations; investigated nucleation and particle growth in systems for the synthesis, characterization, application, and processing of ultrafine particles; and examined the use of electric fields to modify phase equilibria in multiphase separations processes. Other efforts involved the enhancement of oxidation of organic pollutants in aqueous solutions by using electric fields to form microbubbles containing ozone, and the use of electric fields to improve distillation efficiency.

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

Within the area of *Biotechnology Research*, experiments on the simultaneous photoevolution of hydrogen and oxygen were performed, the capability of photosynthetic systems for renewable

hydrogen production was investigated, and instrumentation modifications were made to enable measurement of the absolute voltage of a single Photosystem I reaction center. New initiatives included the use of an iron-filing catalyst to generate hydrogen under anaerobic conditions and a proposed process to convert fossil fuel emissions into fertilizers that could support additional photosynthetic fixation of CO_2. In enzyme-related work, studies have continued on the synergy between mesophilic and thermophilic cellulases, preliminary results were reported for transaldolase expressed from the thermophile *Methanococcus jannaschii*, and promising results were achieved for the enzymatic production of hydrogen from sucrose and by means of the pentose phosphate pathway. Lastly, in collaboration with scientists from the Republic of Kazakhstan, plans were made to test a promising microbial consortium that has the potential to inhibit the growth of *Salmonella* in chicken.

In the final area—*Molecular Studies*—as part of an effort to enhance our microscopic-level understanding of aqueous electrolyte solutions, development of a simulation code for water with a flexible potential was continued. Also in progress were the investigation of simulation algorithms for nonequilibrium systems, preliminary work on an integral equation theory for such systems, and preparation of a final report on mathematical modeling of in situ bioremediation processes. Significant progress was made in parallel implementations of the Geocore algorithm, with the goal of developing more rapid, less exhaustive algorithms for very large proteins.

1. HOT CELL OPERATIONS

E. C. Beahm

1.1 SLUDGE-PARTITIONING CHEMISTRY (R. D. Hunt, J. L. Collins, and C. W. Chase)

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Summary: An 83-g sludge sample from Hanford tank C-103 was washed three times (22–143 h) with inhibited water at ambient temperature. The sludge sample was also washed at 85°C for approximately 2 h. The initial weight of the sludge solids was 83.19 g, and the total weight of the inhibited water in the four washes was 481 g. The weights of the washed solids after the first, second, third, and fourth washes were 90.54, 85.48, 84.00, and 80.66 g, respectively. It is important to note that the initial wash increased the weight of the solids by 9%. After the third water wash, the weight of the washed solids was still higher than the initial weight of the sludge sample.

Due to the reductions in FY 1998 funding, the caustic leaches of the washed sludge sample from Hanford tank C-103 were not performed. Therefore, the focus of this task shifted to facility decontamination, waste disposal, and preparation of the final report. Nearly all of the decontamination and waste disposal activities have been completed. Finally, the initial draft of the final report on the water washes and caustic leaches of sludge from Hanford tank S-101 and on the water washes of sludge from Hanford tank C-103 was prepared.

1.1.1 Purpose and Scope

Many underground storage tanks at Hanford contain high concentrations of nonradioactive materials such as aluminum and sodium that can significantly increase the volume of the final high-level waste (HLW) for disposal. Other less abundant, inert components, such as chromium and phosphate, can also determine the volume of the HLW product from vitrification processes. The U.S. Department of Energy (DOE) can reduce the costs of long-term storage and disposal of HLW if these nonradioactive components can be removed from the HLW before it is immobilized. DOE has selected Enhanced Sludge Washing (ESW) as its baseline technology to separate key inert components from the radionuclides in the HLW sludges. ESW refers to the simple sludge washing, which is followed by caustic leaching with 2–3 *M* NaOH at an elevated temperature. The leached solids are then washed with the dilute NaOH to remove the dissolved components and the added NaOH. ESW is effective due to the increased solubility of some of these inert components under very caustic conditions, which can be used to partition the radioactive and nonradioactive components.

The primary objective of this task is to optimize the processing conditions for the ESW of sludges from Hanford tanks S-101 and C-103. The effects of process variables such as NaOH

concentration, temperature, and leaching time on the efficacy of the caustic leaching process will be determined under more realistic processing conditions.

1.1.2 Progress

This task continues to study the potential of caustic solutions (ESW) to remove aluminum and other nonradioactive components from Hanford tank sludges so that the volume of the HLW stream can be reduced. Parametric studies on sludge samples from Hanford tanks S-101 and C-103 will determine the effects of two different temperatures (70 and 95°C), two different NaOH concentrations (1 and 3 *M*), and four different leaching times (5, 24, 72, and 168 h) on the performance of the ESW procedure.

An 83-g sludge sample from Hanford tank C-103 was washed three times (22–143 h) with inhibited water at ambient temperature. The sludge sample was also washed at 85°C for approximately 2 h, and then the wash solution and sludge were allowed to cool to ambient temperature. At the end of each water wash, the sample was centrifuged and the liquid was decanted. The weights of the washed solids and the decanted wash solutions were determined. The initial weight of the sludge solids was 83.19 g, and the total weight of the inhibited water in the four washes was 481 g. The weights of the washed solids after the first, second, third, and fourth washes were 90.54, 85.48, 84.00, and 80.66 g, respectively. It is important to note that the initial wash increased the weight of the solids by 9%. Apparently, the heat that was generated from the high concentrations of ^{90}Sr and ^{137}Cs led to a dehydration of the sludge sample. After the third water wash, the weight of the washed solids was still higher than the initial weight of the sludge sample. The 85°C wash was slightly more effective than the last wash at ambient temperature.

Due to the reductions in FY 1998 funding, the caustic leaches of the washed sludge sample from Hanford tank C-103 were not performed. Therefore, the focus of this task shifted to facility decontamination, waste disposal, and preparation of the final report. The hot fume hood has been sufficiently cleaned so it is now available for other projects. Most of the contaminated wastes from the parametric study have been processed. Finally, the initial draft of the final report on the water washes and caustic leaches of sludge from Hanford tank S-101 and on the water washes of sludge from Hanford tank C-103 was completed, and it will be issued in the next quarter.

2. PROCESS CHEMISTRY AND THERMODYNAMICS

E. C. Beahm

2.1 PREVENTION OF SOLIDS FORMATION (E. C. Beahm, C. F. Weber, T. A. Dillow, and R. D. Hunt)

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Summary: Operating windows for Hanford sludge pretreatment were produced. Operating windows are expressed in terms of phosphate fluoride and aluminate concentrations at which solids do not form in process solutions. These concentrations must be kept quite low in process steps that involve temperature decreases.

2.1.1 Purpose and Scope

Technical support is needed for Hanford Phase I and Phase II privatization initiatives. This effort provides data for process development, evaluation, and design. It is focused on identifying operating envelopes that avoid solids precipitation during retrieval, transport, sludge washing, sludge leaching, and wash and leachate mixing.

2.1.2 Progress

Operating windows for Hanford sludge pretreatment were produced from a combination of tests with sludge, simulant tests, and modeling. Thermochemical data for modeling gel formation by sodium phosphate and sodium phosphate fluoride were assessed and put into a form to generate operating windows. *Operating windows* are defined as process conditions where solid formation can be avoided. The operating windows are expressed in terms of the concentrations of phosphate, fluoride, and aluminate at given hydroxide concentrations and temperatures where solids do not form in process solutions.

Pretreatment of sludge with caustic at temperatures above ambient followed by a cooldown to ambient results in very narrow operating windows. This means that the concentrations of phosphate, fluoride, and aluminate must be quite low. The potential for formation of solids containing phosphate or phosphate fluoride increases with caustic concentration, and the potential for forming alumina solids increases with decreasing caustic concentration. This opposition means that a compromise will have to be made in selecting process operating conditions. For example, when the sum of the concentrations of phosphate, fluoride, and aluminate is 0.3 *m*, the operating window at 3 *m* caustic is a small region with less than approximately 0.03 *m* phosphate and less than

approximately 0.15 *m* fluoride. On the other hand, in 1 *m* caustic the operating window is low in alumina while fluoride and moderate amounts of phosphate can be tolerated.

2.2 SALTCAKE DISSOLUTION (E. C. Beahm)

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Summary: A methodology for validating the Environmental Simulation Program (ESP) code has been designed. The validation includes a combination of data assessment, comparison calculations, and thermochemical techniques to evaluate consistency of data.

2.2.1 Purpose and Scope

This effort provides coordination and thermochemical evaluations for a team effort on Hanford saltcake dissolution. Tests on Hanford saltcake are run at Numatec Hanford, and calculations using the ESP are being run at Mississippi State. Some of the key issues that are being addressed include the solution conditions required to dissolve saltcake and validation of the ESP code.

2.2.2 Progress

A systematic approach to validate the ESP code has been designed. The validation will include (1) calculations based on the results of experimental tests to compare calculated predictions with actual results, (2) comparison calculations using ESP at Mississippi State and the SOLGASMIX code at Oak Ridge National Laboratory (ORNL), (3) assessment of standard thermochemical values for approximately 100 key chemical species compared with data that are known to be consistent, and (4) evaluation of the consistency of the activity coefficients for key species using thermochemical techniques employing the Gibbs-Duhem equation.

A Saltcake Dissolution Workshop was held at Mississippi State on May 5, 1998. This workshop provided the basis for the interactions involving Saltcake Dissolution Project participants from ORNL, Mississippi State, and Numatec Hanford with the users.

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

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Summary: Thin films of $BaCeO_3$ and $Ce_{0.75}Zr_{0.25}O_2$ were prepared using sol-gel processing techniques. Results from differential thermal analysis (DTA) and thermogravimetric analysis (TGA) indicate that $BaCeO_3$ and $Ce_{0.75}Zr_{0.25}O_2$ form at 800 and 400°C, respectively. These results were included in a manuscript entitled "Low Temperature Preparation of $BaCeO_3$ and $Ce_{0.75}Zr_{0.25}O_2$ Thin Films Using Sol-Gel Processing Techniques." This paper was submitted to the *Material Research Bulletin* for peer review and publication.

2.3.1 Purpose and Scope

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

2.3.2 Progress

This project has continued its collaborative effort with the Basic Energy Sciences (BES) project, which is led by Mariappan Paranthaman. Thin films of $BaCeO_3$ and $Ce_{0.75}Zr_{0.25}O_2$ were prepared from sol-gel precursor solutions using the standard Schlenkware and inert atmosphere technique. DTA and TGA were performed on the dried gels. With the Ba/Ce samples, two exothermic events at 200–400°C and at 800–1000°C were detected with the DTA and the TGA. The 200–400°C exotherm is due to the loss of residual solvent and the formation of cerium oxide at 400°C. The 800–1000°C exotherm corresponds to the formation of $BaCeO_3$. For the Ce/Zr samples, only one exothermic event at 200–400°C was observed with the DTA and the TGA. The Ce/Zr exotherm is due to the loss of residual solvent and the formation of $Ce_{0.75}Zr_{0.25}O_2$. These results were included in a manuscript entitled "Low Temperature Preparation of $BaCeO_3$ and $Ce_{0.75}Zr_{0.25}O_2$ Thin Films Using Sol-Gel Processing Techniques." This paper was submitted to the *Material Research Bulletin* for peer review and publication.

3. MSRE REMEDIATION STUDIES

D. F. Williams

3.1 URANIUM CONVERSION (G. D. Del Cul, A. S. Icenhour, D. W. Simmons, and J. Caja)

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Summary: Fissile ^{233}U is presently being recovered, trapped, and removed as an essential part of the remediation and decommissioning activities presently under way at the Molten Salt Reactor Experiment (MSRE). Uranium hexafluoride trapped in NaF, along with uranium-laden activated charcoal, represents the bulk of the inventory. For permanent storage, all of the ^{233}U needs to be recovered and transformed into a stable oxide. In this period, preparation of charcoal deposit surrogate was completed, and the conversion of this material in a prototypical apparatus was begun. The myriad activities that are required to prepare the facility in Building 4501 for MSRE remediation conversion operations continue on schedule.

3.1.1 Purpose and Scope

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

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

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

3.1.2 Progress

Surrogate fluorinated uranium-laden charcoal was prepared and passivated by treatment with ammonia. This material, similar to that in the auxiliary charcoal bed (ACB) at the MSRE, was then

used in full-scale testing of the conversion prototype. The processing of the uranium-laden charcoal in the prototype was initiated.

Draft designs for conversion process equipment and process layout were prepared based on input from the process developers, hot cell operators, and designers. A specification for the in-cell crane has been prepared. Drawings for all key equipment, vessels, instrumentation, and electrical supply were prepared and reviewed. The draft safety analysis report and technical safety requirements document for conversion operation were completed and are under review. These documents will serve as the basis for the upgrade of a segment of Building 4501 to a Category 2 nuclear facility. All equipment was removed from hot cell D in Building 4501, and the cell was decontaminated to the maximum extent practical in preparation for the installation of the conversion equipment.

3.2 URANIUM DEPOSIT REMOVAL AND PASSIVATION OF FLUORINATED CHARCOAL (G. D. Del Cul, D. W. Simmons, and L. D. Trowbridge)

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Summary: The passivation process of the ACB charcoal deposit was successfully completed. This event constituted a major milestone for the remediation activities of the MSRE. At present, the ACB is being prepared for the actual removal and recovery of the about 2.6 kg of ^{233}U deposited in the charcoal. These recovery activities are possible only because of the removal of the potentially explosive conditions of the fluorinated charcoal bed.

The MSRE ACB contains a volume of approximately 506 L of activated charcoal (6–16 mesh). The top 12 in. of the ACB is known to have about 2.6 kg of uranium as intercalated fluoride and oxyfluoride. In addition, a few feet of fluorinated charcoal is believed to extend beyond the uranium front. The rest of the ACB, about 90 ft of 6-in. pipe, is believed to consist of unreacted charcoal.

Fluorinated charcoal, when subjected to rapid heating, can decompose to generate gaseous products (CF_4, C_2F_6, etc.). Under confined conditions, the abrupt, exothermic decomposition (deflagration) can produce high temperatures and pressures of near-explosive characteristics.

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

transform this reactive fluorinated charcoal into a more stable material prior to the removal of the uranium in the ACB.

3.3 RADIOLYSIS AND MATERIALS DISPOSITION STUDIES (D. F. Williams, A. S. Icenhour, L. D. Trowbridge, and L. M. Toth)

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Summary: Radiolysis experiments in support of establishing a fluoride standard for the conversion oxide product were conducted, and preparations have been made for irradiation of passivated charcoal in order to answer questions regarding the interim storage of this material. The assessment and analysis of the radiolysis that is occuring in the NaF traps have been completed, and this issue is being followed closely.

3.3.1 Purpose and Scope

Understanding the radiolysis of MSRE fuel salt and uranium oxides that derive from conversion of the recovered UF_6 is necessary in order to proceed with remediation, interim storage, and permitted storage of the MSRE radioactive materials. The most significant remediation activities for the MSRE include (1) removal and recovery of uranium from the off-gas system, (2) removal of the uranium-laden charcoal from the charcoal bed, and (3) removal of the stored fuel salt. All of these retrievable intermediate materials are not suitable for long-term storage and must be converted to a more stable form. In the case of the MSRE fuel salt, it is also necessary to understand the chemical consequences of the radiolysis in order to safely melt and treat the salt. A recent addition to the scope of this work has included short-term tests and analyses to support the interim storage of materials before they are converted into stable oxides.

3.3.2 Progress

Currently, one of the major uncertainties is the maximum acceptable fluoride content for the long-term storage of the converted oxide. There are two bases for a fluoride limitation: (1) pressure buildup due to radiolysis and (2) corrosion due to HF if H_2O is also present. Investigations of the rationale of establishing a fluoride limit for $^{233}U_3O_8$ in the final package for long-term storage are being conducted. Experimental irradiations of (1) the converted oxide and (2) surrogate samples of known fluoride and water content are being used to simulate long-term storage conditions. A variety of metal coupons (e.g., SS304, SS304L, SS316, SS316L, carbon steel, and aluminum) placed in contact with uranium oxide samples are being irradiated under very high radiation fields (i.e., using

a ^{60}Co source). During this period, samples of UO_2F_2 and $UO_2F_2 \cdot 3H_20$ were irradiated in the division's ^{60}Co irradiator. Gas and solid samples were taken and analyzed for radiolytic products, but results were not available for this reporting period. Materials for the second set of experiments were prepared.

The plans for irradiation of a large plug of simulant salt (~1 kg) have been changed due to fabrication delays and delays related to the approval of the experiment by High Flux Isotope Reactor (HFIR) personnel. This will probably delay insertion of salt into a cooling fuel element until late summer.

An instrumented NaF trap loaded with $^{233}UF_6$ from MSRE is showing an accelerating pressure rise. A preliminary analysis of the rate of pressure rise was conducted and reported to MSRE program management. The best explanation of the observed rate is that the NaF-UF_6 complex, after an induction period, appears to be subject to alpha radiolysis at an efficiency (i.e., G-factor) that is a moderate fraction (30 to 50%) of literature-reported gas-phase alpha radiolysis rates. Some degree of radiolysis of UF_6 and NaF was anticipated during planning, but the uncertainty in the magnitude of the phenomenon was fairly large. Most of the deposited decay energy in these traps is due to alpha particles, and no quantitative alpha radiolysis data were available on condensed-phase UF_6. Beta and gamma radiolysis may also be occurring, but it seems unlikely that they are responsible for much of the pressure rise. The current rate of rise is within (though toward the high end of) the range predicted during project planning. The pressure rise continues to be monitored and evaluated.

4. CHEMISTRY RESEARCH

D. F. Williams

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

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Summary: A novel method for introducing template-selective recognition sites in mesoporous sorbents through molecular imprinting has been developed. This method makes use of the unique surface environment of hexagonally packed mesopore surfaces of selected pore size and coats these surfaces with ligands by binding them to a target metal-ion template. The procedure produces much more uniform imprints that exhibit the ideal size and stereochemical requirements for binding target ions and has led to the preparation of mesoporous sorbents that exhibit

significantly greater binding selectivities than sorbents prepared by conventional coating methods. This development has resulted in a new class of ordered mesoporous sorbents with molecular-recognition capabilities. The design principles illustrated by these results offer opportunities for application of imprint-coated mesoporous materials in such areas as selective sorption, chemical sensing, and catalysis.

4.1.1 Purpose and Scope

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

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

4.1.2 Progress

One major drawback associated with bulk molecular imprinting is that the kinetics of the sorption-desorption process are unfavorable, as the template and ligand are totally embedded in the bulk polymer matrix and, thus, require mass transfer through nonpolar, microporous channels. Furthermore, molecular imprinting studies have thus far been conducted in disordered polymers or amorphous sol-gel matrices, where the inhomogeneity of the cavities produced by the molecular imprinting reduces the selectivity of the final imprinted materials.

These issues in molecular imprinting were addressed in our research by development of surface imprinting in *ordered* mesoporous materials. The functional groups are introduced to the pore surface of mesoporous silica through *imprint coating*. The key to the current design is to coat

the mesopore surface with complexes between ligands and target metal ions rather than just the free ligands. After removal of the metal ions, ligand imprints of the template metal ions are created on the mesopore surfaces. This organization reflects both the size and stereochemical signature of the template ion and ultimately should lead to future ion recognition and selective rebinding of the target ion from ion mixtures. We have found that such functionalized ordered mesoporous materials exhibit significantly greater target-ion-binding selectivities than sorbents prepared by conventional coating methods. The success of our approach is built upon the unique and beneficial environment of ordered, hexagonally packed mesopore surfaces for conducting surface imprinting. These beneficial characteristics include (1) circularly curved, extremely rigid pore surfaces, with optimum pore diameters (20–100 Å) that match the stereochemical requirements for surface imprinting of four or six coordinated metal ions, and (2) a very uniform pore size distribution, which allows the generation of the uniform imprints and limits the possible choices of coordination environments.

The mesoporous ordered silica hosts used in this study were prepared by a neutral surfactant-assembly pathway that involves hydrogen-bonding interactions between a neutral primary amine surfactant and inorganic silica precursors. Calcined, ordered mesoporous silica samples prepared by this procedure have surface areas of over 1000 m^2/g and average pore sizes of ~25 Å. Both powder X-ray diffraction (XRD) and small-angle X-ray scattering (SAXS) show a peak around $2\lambda = 2°$, which agrees with the pore size determined by the BJH method.

In order to illustrate the potential of this imprinting methodology, Cu^{2+}-selective, ordered mesoporous sorbents were chosen to demonstrate both the basic principles of the concept and the ease with which imprinted sorbents may be prepared. Furthermore, an extensive literature study already exists concerning imprinted polymers for copper separation. A critical comparison of the binding properties of our sorbents with imprinted organic polymeric matrices shows the unprecedented advantages of our imprint-coated mesoporous sorbents. To test the selectivity of our new sorbents, we conducted competitive-ion-binding experiments using aqueous Cu^{2+}/Zn^{2+} mixtures. This system constitutes one of the most stringent tests for ion-binding selectivity because both ions have identical charge, similar sizes, and exhibit high affinities for amine ligands.

4.2 MOLTEN SALT RESEARCH (S. Dai, Y. H. Ju, and Y. S. Shin)

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Summary: Our investigation of uranium compounds in $AlCl_3$-EMIC (1-ethyl-3-methylimidazolium chloride) room-temperature melts and high-temperature molten salts such as $CaCl_2$ and $MgCl_2$ indicated that the second-shell complexation by solvents plays an important role in defining thermodynamics of uranium compounds in these media. In this quarter, we have synthesized a new class of room-temperature melt systems to further investigate the second-shell coordination effect in uranium chemistry. These melts are stable in aqueous solutions. This work may lead to new solvent extraction systems involving ionic liquids.

4.2.1 Purpose and Scope

The basic focus of our research is the relationship between the molecular-scale speciation and the macroscopic thermodynamic properties of uranium compounds in molten salts. Specifically, through spectroscopic techniques, we have given physical meaning to activity coefficient changes as they relate to coordination stabilization of species in solution.

4.2.2 Progress

A method for synthesizing 1-isobutyl-3-methylimidazolium bromide has been established. This compound is a liquid at room temperature, and two phases form when it is mixed with water. Some preliminary spectroscopic experiments are conducted using this new room-temperature melt.

4.3 PUBLICATIONS

Y. S. Shin, M. C. Burleigh, S. Dai, C. E. Barnes, and Z. L. Xue, "Uranyl Adsorption on Mesoporous Titanium-Based Sorbents Prepared by the Sol-Gel Procedure: A Significant Improvement of Kinetics and Capacity," *Radiochimica Acta*, submitted.

5. SEPARATIONS AND MATERIALS SYNTHESIS

D. W. DePaoli

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

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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. The triennial program review was successfully completed during this quarter. In addition, progress was made in several areas, including (1) spraying and mixing in electrohydrodynamic flows and (2) aggregation of colloidal particles in reactive solutions and under magnetic fields.

5.1.1 Purpose and Scope

This program is comprised of several fundamental studies that explore transport processes in multiphase separations, with particular emphasis placed on the application of electromagnetic fields for enhancement. Experimental, theoretical, and computational methods are employed to investigate the effect of electromagnetic fields on transport processes in liquid-liquid, gas-liquid, and solid-liquid systems. This work will provide information necessary to devise novel means to dramatically improve transport rates in these systems and, thus, will have widespread benefit for separations processes such as solvent extraction and distillation, as well as applications in environmental and biotechnology areas. The areas of current focus are (1) interface deformation and breakup, including electrostatic spraying (both "normal" and "inverse"), drop formation, drop oscillations, stretching liquid bridges, and drop impact; (2) interactions and coalescence of drops; (3) enhancement of transport processes through electrohydrodynamic flows; and (4) interactions and aggregation of particles.

5.1.2 Progress

The triennial program review was held on April 21–22, 1998. The main external reviewer was Professor Jan Miller of the University of Utah; attending from DOE/BES were Dick Gordon and Paul Maupin. The review appeared to be successful; the reviewers commented positively on the areas of publications, the computational work, the interplay between computations and experiments, and the outreach to applied programs and industry. Some areas the reviewers identified for further work included the following:

- parallel computations of drop formation, both with and without a modulated electric field;
- understanding inverse spraying in more-conductive fluids;
- development of a more realistic electrocoalescence model; and
- electrohydrodynamic pumping and mixing in microdevices.

Investigations of electrohydrodynamic micromixing have continued. We have resumed work with the model sol-gel system for producing ultrafine particles. During this period, we adjusted the zirconium alkoxide chemistry and experimental operating conditions for steady operation. Dynamic light scattering (DLS) measurements and scanning electron microscopy (SEM) results show that the production of relatively uniform nanoparticles is possible.

Significant progress was made in the study of particle interactions. Experimental studies on the aggregation of colloidal magnetic particles were continued in collaboration with

Professors S. Grant of the University of California at Irvine and S. Yiacoumi of Georgia Institute of Technology. It was found that magnetic aggregation and formation of chains of initially stable particles occur in the secondary minimum of the energy potential, which means that the particles are not attached to one another. As soon as the field is removed, the particles rapidly diffuse away from each other, leading to breakup of the chains. Investigation of chain breakup was conducted under various conditions of pH, ionic strength, and magnetic field strength by removing the magnetic field.

The behavior of sorbent alumina particles in copper solutions was experimentally investigated in collaboration with Professor Yiacoumi. In these experiments, the objective was to observe surface-charge modifications during sorption and the effect on aggregation kinetics of sorbent particles. A large increase in the zeta potential of the particles was observed during sorption of metal ions. It was also found that by observing the particle behavior with respect to surface charge and aggregation, one may discriminate the mechanism of metal-ion uptake between sorption and precipitation.

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

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Summary: This project aims to develop understanding of nucleation and growth of clusters/particles involved in homogeneous or heterogeneous systems. We extended the mixed-solvent approach to the synthesis of titania. Similar to the zirconia system, we observed interesting sol and gel phenomena using inorganic titanium precursor salt. SAXS experiments were conducted for understanding the nucleation and growth phenomena in two different systems: (1) ceramic film deposition onto self-assembled monolayers (SAMs) and (2) synthesis of homogeneous mixed-solvent solutions of microspheres and nanospheres.

5.2.1 Purpose and Scope

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

Our current emphasis lies with the chemistry, reaction engineering, colloidal/interfacial sciences, and materials sciences in three major wet-chemical systems: (1) homogeneous

precipitation in inorganic salt solutions of mixed solvent; (2) forced hydrolysis via hydrothermal processing of inorganic salt aqueous solutions; and (3) acid- or base-catalyzed hydrolysis and condensation of organometallic compounds (such as alkoxides) in water-alcohol solutions. Experiments utilize several specially developed techniques, including real-time DLS, rapid-mixing flow cell coupled with Fourier transform infrared (FTIR) and SAXS, as well as high-temperature XRD, electron microscopy, Raman spectroscopy, and electrostatic spraying.

It is anticipated that the results of this work will have significant impacts upon development of advanced materials such as nanoscale and nanophase ceramics that have dramatically improved properties over traditional "coarse-grained" ceramics. These advanced ceramics are potential candidates as structural ceramics, electroceramics, catalysts, nanocrystalline thin films, coatings, and nanostructured inorganic membranes.

5.2.2 Progress

The mixed-solvent approach was extended to the titania system. Similar to the zirconia system, we observed interesting sol-gel formation under controlled conditions. Titania microspheres are generally larger than zirconia microspheres. We conducted SAXS experiments and SEM imagings to elucidate the mechanism for microsphere formation. The SAXS experiments on $TiCl_4$ hydrolysis failed because of corrosion problems with the aluminum cells. A new stainless steel cell with Kypton windows was designed and is being prepared for such experiments at 1.5-m geometry.

Interactions continued with DuPont regarding technology transfer of the mixed-solvent synthesis approach. Titania microsphere samples were prepared and shipped to DuPont for testing for their commercial interests.

For the research concerning ceramic (titania) film deposition onto SAMs, we collaborated with Professor Mark DeGuire at Case Western Reserve University (CWRU) and Dr. Stephen Shempp at the Max Planck Institute (Germany) to develop better understanding of the film-deposition mechanisms. Dr. Shempp came to visit ORNL and spent a week here to work with us in collecting SAXS data on the growth kinetics of titania cluster. The data supported the previous atomic force microscopy (AFM) studies by the CWRU researchers.

On the project using electrohydrodynamic micromixing for producing ultrafine particles, we adjusted the zirconium alkoxide chemistry and experimental operating conditions. The DLS measurements and SEM results show that the production of relatively uniform nanoparticles is

possible. We are trying to develop understanding of the electrical effect on the control of particle size and colloidal stability.

In May, Michael Hu attended the 100th Annual Meeting of the American Ceramic Society and gave an oral presentation entitled "Auto Ignition Synthesis of $(Ba,Sr)TiO_3$ and Related Materials." On invitation from Professors George Beaucage and J.-S. Lin, Hu visited his collaborators' research laboratories at the University of Cincinnati and presented a talk entitled "Chemical Synthesis and Characterization of Ultrafine Monodispersed Ceramic Particles." During the same reporting period, Dr. Hu was scheduled to give an invited seminar at the Naval Research Laboratory. The manuscript "Nanocrystallization and Phase Transformation in Monodispersed Ultrafine Zirconia Particles from Various Homogeneous Precipitation Methods" was submitted to the *Journal of the American Ceramic Society*. We have prepared two invention disclosures, "A Sol-Gel Processing for Advanced Materials Synthesis" and "Dielectric Tuning Method for Synthesizing Monodispersed Barium Titanate." Both were selected for filing patent applications.

5.3 PHASE EQUILIBRIA MODIFICATION BY ELECTRIC FIELDS (C. Tsouris, D. W. DePaoli, X. Zhang, 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 transport and thermodynamic effects of electric fields on vapor-liquid and liquid-liquid systems. Batch-distillation, vapor-liquid-equilibria, liquid-liquid-equilibria, and vapor-pressure experiments are in progress, using various liquid mixtures of polar-nonpolar, polar-polar, and nonpolar-nonpolar components. The results obtained to date show that electric fields have an effect on the vapor-liquid equilibria of some systems.

5.3.1 Purpose and Scope

The primary objective of this project is to enhance separations of mixtures by applying an electric field across an interface between two phases. Enhancement in separation may be caused either by increasing transport rates through the interface or by changing the phase equilibria. Electric fields have been known to interact with charge carriers, such as ions and electrons, leading to higher mass- and heat-transfer rates, fluid atomization, mixing, and pumping, which are transport phenomena. In contrast, the effects of electric fields on the

behavior of noncharged molecules and the macroscopic thermodynamic behavior of the system are examined in this project. The behavior of various types of molecules under the influence of electric fields and macroscopic effects of electric fields on such properties as dielectric constant and phase equilibria are investigated.

5.3.2 Progress

Experiments were conducted using mixtures of water and isopropanol at various conditions. The geometry and distance of the electrodes and the strength and direction of the applied voltage were varied to investigate their effects on vapor-liquid equilibria. It was found that the effect is decreased when the electrical current is increased and that the field strength did not play a significant role. The applied voltage, rather than the voltage over distance, controlled the effect. Computations showed that at short electrode distances, the charge density at the interface decreases sharply with increasing electrode distance, while at longer electrode distances, the charge density does not change significantly. In our experiments, in order to prevent liquid masses at the interface from reaching the electrode in the vapor phase, we did not move the electrodes very close to the interface; therefore, all the experiments were conducted in the regime in which the electrode distance did not affect significantly the charge density at the interface. This result also suggests that the mechanism of electric-field effects on vapor-liquid equilibria is related to interfacial effects. Spectroscopic studies were also conducted in which the infrared and Raman spectra were measured in situ under an electric field. It was found that the relative intensity of the peaks did not change but that the intensity of the whole spectrum change with applied voltage. Experiments were also initiated to investigate the effect of electric fields on electrosorption of ions. Preliminary data with copper ions in a solution between two electrodes made of carbon aerogel showed a reversible sorption enhancement, which suggests that under the influence of the electric field, metal ions are accumulated near the surface and then released back to the solution as soon as the field is removed.

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

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Summary: Electric fields are used to form microbubbles containing ozone for the oxidation of organic pollutants in aqueous solutions. An experimental apparatus has been set up

for ozonation studies. Included in this setup are (1) ozone generation from air or oxygen by means of corona discharge; (2) ozone spraying in an aqueous phase containing an organic solute, such as phenol, by inverse electrostatic spraying; and (3) collection of gas and liquid samples for chemical analysis. Experimental results showed an enhancement in the oxidation rate by electrostatically generated microbubbles, as compared with conventional bubble diffusers.

5.4.1 Purpose and Scope

The primary objective of this project is to enhance the efficiency of ozonation processes by inverse electrostatic spraying. 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 enhances the oxidation efficiency by (1) increasing the surface area per unit volume between the gas and liquid phases and (2) increasing the gas volume fraction (since smaller bubbles have a lower rise velocity than larger bubbles). This project is aimed at applying the knowledge gained in our fundamental studies of inverse electrostatic spraying to develop an efficient means for production of ozone-containing microbubbles. The work may significantly impact a wide range of processes, including operations in the pulp and paper industry; ultrapure water production for the semiconductor, pharmaceutical, and other industries; municipal potable water production; and wastewater treatment.

5.4.2 Progress

Experiments including (1) mass transfer of ozone from the bubbles to deionized water, (2) oxidation of a color compound dissolved into water (indigo), and (3) oxidation of phenol were conducted. It was found that microbubbles formed by inverse electrostatic spraying significantly enhance ozone transfer rates to aqueous solutions and, subsequently, ozonation rates of organic compounds.

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

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

5.5.1 Purpose and Scope

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

5.5.2 Progress

Experiments using a three-stage distillation column under electric fields showed a small effect of the electric fields on the separation of isopropanol-water mixtures. A stronger effect was observed with the single-stage, coaxial electrode geometry. The effect of electric fields on bubble size distribution in the column stage will be discussed in the next report.

5. 6 PUBLICATIONS

M. A. Norato, C. Tsouris, and L. L. Tavlarides, "Phase Inversion Studies in Liquid-Liquid Dispersions," *Canadian Journal of Chemical Engineering* **76**, 486–94 (1998).

C. Tsouris, W.-T. Shin, and S. Yiacoumi, "Spraying, Pumping, and Mixing of Fluids by Electric Fields," *Canadian Journal of Chemical Engineering* **76**, 589–99 (1998).

C. J. Chin, S. Yiacoumi, and C. Tsouris, "Shear-Induced Flocculation of Colloidal Particles in Stirred Tanks," *Journal of Colloid and Interface Science* **206**, 14 (1998).

W.-T. Shin, A. Mirmiran, S. Yiacoumi, and C. Tsouris, "Ozonation Using Microbubbles Formed by Electric Fields," accepted, *Separation and Purification Technology*, June 1998.

K. D. Blankenship, D. W. DePaoli, J. O. Hylton, and C. Tsouris, "Effect of Electrode Configurations on Phase Equilibria with Electric Fields," accepted, *Separation and Purification Technology*, June 1998.

S. E. Burns, S. Yiacoumi, J. D. Frost, and C. Tsouris, "Application of Digital Image Analysis for Size Distribution Measurements of Microbubbles," pp. 100–107 in the Proceedings of the Engineering Foundation Conference, *Imaging Technologies: Techniques and Applications in Civil Engineering*, American Society of Civil Engineers, Reston, Virginia, 1998.

K. Subramaniam, S. Yiacoumi, and C. Tsouris, "A Unified Model for Ion Sorption Kinetics and Colloidal Particle Flocculation Rates," p. 6 in the *Sixth International Conference on Fundamentals of Adsorption*, Giens, France, May 24–28, 1998.

C. Tsouris, C. H. Byers, and S. Yiacoumi, "Charging Up Your Separations: Applications of Electrotechnologies," pp. 153–58 in *1998 Corn Utilization & Technology Conference Proceedings*, St. Louis, Missouri, June 1–3, 1998.

5.7 PRESENTATIONS

D. W. DePaoli, "Electrotechnologies for Chemical Processing," presented at the 3M Tech Fair, May 6, 1998.

M. Z.-C. Hu, "Auto Ignition Synthesis of (Ba,Sr)TiO_3 and Related Materials," presented at the 100th Annual Meeting of the American Ceramic Society, Cincinnati, Ohio, May 3–6, 1998.

M. Z.-C. Hu, "Chemical Synthesis and Characterization of Ultrafine Monodispersed Ceramic Particles," invited presentation at the University of Cincinnati, Cincinnati, Ohio, May 7, 1998.

C. Tsouris, "Flocculation and Filtration of Particles by Magnetic Fields," presented at the Second International Conference on the Scientific and Clinical Applications of Magnetic Carriers, Cleveland, Ohio, May 28–30, 1998.

C. Tsouris, W.-T. Shin, and S. Yiacoumi, "Ozonation Using Electrostatic Spraying," presented at the 72nd Colloid and Surface Science Symposium, Pennsylvania State University, University Park, Pennsylvania, June 21–24, 1998.

C. Tsouris, D. W. DePaoli, J. T. Shor, M. Z.-C. Hu, and T.-Y. Ying, "Electrochemical Methods for Magnetic Seeding of Wastewaters," presented at the 72nd Colloid and Surface Science Symposium, Pennsylvania State University, University Park, Pennsylvania, June 21–24, 1998.

C. Tsouris, K. D. Blankenship, D. W. DePaoli, W.-T. Shin, and J. O. Hylton, "Electric-Field Effects on Gas-Liquid and Liquid-Liquid Systems," presented at the 72nd Colloid and Surface Science Symposium, Pennsylvania State University, University Park, Pennsylvania, June 21–24, 1998.

R. M. Worden, M. D. Bredwell, and C. Tsouris, "Synthesis Gas Fermentations: Mass Transfer Improvement in Butyribacterium Methylotrophicum Fermentations," presented at the 20th Symposium on Biotechnology for Fuels and Chemicals, Gatlinburg, Tennessee, May 3–7, 1998.

S. Yiacoumi, K. Subramaniam, and C. Tsouris, "Stability of Colloidal Particles During Metal Ion Uptake from Aqueous Solutions," presented at the 72nd Colloid and Surface Science Symposium, Pennsylvania State University, University Park, Pennsylvania, June 21–24, 1998.

6. FLUID STRUCTURE AND PROPERTIES

H. D. Cochran

6.1 INTERACTIONS OF SOLUTES, SOLVENTS, AND SURFACES (H. D. Cochran, H.-C. Li, and K. D. Heath)

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

6.1.1 Objective

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

6.1.2 Progress

H.-C. Li completed and defended his M.S. thesis on simplification of the generalized quartic equation of state and its extension to mixtures. Fifteen terms were eliminated from the equation with only minor loss of accuracy. The equation performed satisfactorily in tests with 35 varied binary mixtures and 5 ternary mixtures.

K. D. Heath has assembled components to demonstrate the feasibility of using laser light scattering to characterize the droplet size in microdispersions of water in supercritical carbon dioxide produced by pulsed electric fields. With Li, he has developed an equation-of-state model of the ethanol–water–carbon dioxide system to aid in planning and interpreting experiments.

K. D. Heath is planning density measurements, in collaboration with J. M. Simonson of the Chemical and Analytical Sciences Division, on binary solutions in supercritical carbon dioxide of styrene, methyl methacrylate, and isopropyl alcohol. These density data are needed for quantitative analysis and publication of results of earlier neutron-scattering experiments of reverse micelles in supercritical carbon dioxide that contained these compounds.

6.2 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, Yu B. Melnichenko, S.-T. Cui, S. Salaniwal, and K. D. Heath)

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

6.2.1 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.

6.2.2 Progress

S. Salaniwal and K. D. Heath participated in two periods of experimentation, led by Yu. Melnichenko, involving small-angle neutron (SANS) scattering studies of polydimethylsiloxane in supercritical carbon dioxide. The objective was to observe the variation of the radius of gyration of the chains as a function of carbon dioxide density. The results are undergoing analysis and appear to be of very good quality.

S.-T. Cui has calculated the vapor-liquid phase equilibrium of binary mixtures with carbon dioxide of *n*-hexane and *n*-perfluorohexane from molecular simulations using simple interaction-site models. The simulation results are in reasonable agreement with experimental results. These simulation results give us some confidence in our interaction-site model for perfluoroalkanes in carbon doxide. In addition, they indicate that most of the difference in behavior between alkanes and perfluoroalkanes in supercritical carbon dioxide can be accounted for by conventional van der Waals interactions and that any specific interaction is of minor importance, contrary to claims by others.

S. Salaniwal is making good progress toward an accurate, atomistic simulation of a reverse micelle with an aqueous core in a medium of supercritical carbon dioxide. Currently, the model is complete except that a continuum dielectric is used to represent the aqueous core rather than explicit water molecules.

6.3 STRUCTURE AND PROPERTIES OF CHAIN MOLECULE SYSTEMS UNDER SHEAR (H. D. Cochran, P. T. Cummings, S.-T. Cui, H.-J. Dai, J. D. Moore, Yu. V. Kalyuzhyi, and M. D. Dadmun)

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

6.3.1 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, and coarse graining based on theory and verified by careful small-angle light-scattering (SALS), SAXS, and SANS experiments on sheared systems.

6.3.2 Progress

Yu. Kalyuzhnyi has completed a series of calculations using an integral equation theory proposed by Eu and Gan to model the effects of shear flow on the structure of a fluid. S.-T. Cui has performed molecular simulations for the same systems. The theory employs an approximate nonequilibrium potential in the Ornstein-Zernike equation with the approximate Percus-Yevick closure. Comparison of theoretical results with results from equilibrium molecular dynamics calculations using the nonequilibrium potential shows that the nonequilibrium potential is only crudely effective in representing the effects of flow on structure. However, possible improvements to the potential are being considered. Comparison of the theoretical results with the results of nonequilibrium molecular dynamics using an equilibrium potential indicates that most of the inaccuracy in the theory is due to the nonequilibrium potential, but the Reference Hypernetted Chain closure, which is expected to be quite accurate, has also been programmed.

J. Moore has continued nonequilibrium molecular dynamics simulations of alkane chains of 100 carbons in shear flow. This is, by far, the longest-chain system to be simulated in shear flow with atomistic accuracy. Because it takes very long simulations to ensure that steady state has been achieved, the early results must be considered preliminary; however, it appears that the 100 carbon chains behave in a qualitatively different fashion from shorter chains. If so, these

simulations may allow atomistic exploration of the transition to reptation, the flow mode characteristic of high polymers.

H.-J. Dai joined this project during the quarter. He has been ordering components for a cell capable of light-scattering studies at extremely high strain rates.

6.4 PUBLICATIONS

6.4.1 Submitted

T. H. Walker, H. D. Cochran, G. J. Hulbert, and L. R. Wilhelm, "Supercritical Carbon Dioxide Extraction of Lipids from *Pythium irregulare*," *J. Assoc. Oil Chem. Soc.* (1998).

6.4.2 Published

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.* **146**, 51–61 (1998).

7. BIOTECHNOLOGY RESEARCH

E. Greenbaum

7.1 KINETICS OF ENZYME-CATALYZED PROCESSES (E. Greenbaum, J. W. Lee, C. V. Tevault, and K. Cordray)

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Summary: Further experiments are under way concerning the potential photoevolution of hydrogen and oxygen from thylakoid membranes of mutant algae. Studies have also continued on the synergy between mesophilic and thermophilic cellulases.

During the current reporting period, thylakoid membranes were prepared from mutant (B4-PsaA delta-2) and wild-type (137c) algae and photoevolution of O_2 and H_2 were assayed with exogenous ferredoxin and hydrogenase. Several interesting observations have been made. In the first of these in vitro experiments, simultaneous photoevolution of O_2 and H_2 was observed in thylakoids of both the mutant (B4-PsaA delta-2) and the wild-type algae. This is an interesting observation. It could provide not only new evidence for the existence of Photosystem II (PSII)–driven H_2 and O_2 production but also a new way to elucidate its mechanism. The thylakoid membrane samples have been sent to our collaborator, Dr. Kevin Redding of the University of Geneva, Switzerland, for detection of Photosystem I (PSI) by antibody assays.

However, as is frequently the case with in vitro reconstitution assays, reproduction of the reactions is problematic. In some of the experiments, only photoevolution of H_2 was observed but no O_2 evolution. In other experiments, no photoevolution of O_2 and H_2 was observed under apparently the same conditions. There is much work to be done in verifying these observations. Further experiments are under way.

During this quarter, we have compared the properties of four β-glucosidases: one from almond, one from *Caldocellum,* and two from *Pyroccocus furiosus* (Gly 02 and Gly 03). Preliminary data suggest that Gly 02 binds to cellulose, unlike the other enzymes. This raises the possibility of investigating the effect of β-glucosidase (cellobiase activity) on the efficacy of enzymatic cellulose hydrolysis when it is bound onto the surface of cellulose instead of existing free in solution. We have also continued our studies on the synergy between mesophilic and thermophilic cellulases. Synergy between CBH I and *T. maritima* cellulase (an endoglucanase) occurs and is dependent upon the concentration of these components. This is in agreement with what we have found previously.

7.2 RENEWABLE HYDROGEN PRODUCTION (E. Greenbaum, J. W. Lee, and S. L. Blankinship)

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Summary: Experimentation to assess the capability of photosynthetic systems for renewable hydrogen production continued.

During this quarter, we have addressed the question of the thermodynamic driving force of photosynthetic hydrogen production. This is an important issue in the development of real-world bioreactors for the production of hydrogen and oxygen by light-activated microalgal water splitting. Working with the green alga *Scenedesmus* D_3, we have developed an indirect method for measuring the effect of external hydrogen at 1-atm pressure on photosynthetic hydrogen production. The experiment was carried out in comparative atmospheres of pure helium and pure hydrogen. Helium is the normal atmosphere for creating anaerobiosis and measuring the simultaneous photoproduction of hydrogen and oxygen. By switching to pure hydrogen as the carrier and measuring its effect on oxygen evolution, it is possible to deduce the rate of hydrogen production in a 1-atm carrier of hydrogen. Significantly, for fresh algae, no difference existed in the rate of oxygen production for helium or hydrogen carriers. This result implies that the

thermodynamic driving force of photosynthetic hydrogen production exceeds the back-pressure of 1 atm of pure hydrogen. This is a major advance in assessing the capability of photosynthetic systems for renewable hydrogen production.

7.3 BIOMOLECULAR OPTOELECTRONIC DEVICES (E. Greenbaum, J. W. Lee, and I. Lee)

Contact: E. Greenbaum
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Summary: A new technique for construction of a calibration device for the electric force microscope should make it possible to measure the absolute voltage generated by a single PSI reaction center.

As described in the last quarterly report, using the technique of electric force microscopy, we have measured relative photovoltages from *single* photosynthetic reaction centers. This is the first time such a measurement has been performed. During the present reporting period, we have turned to the question of absolute voltage measurements from these molecular structures. We have developed a new technique for construction of a calibration device for the electric force microscope. In this method, a mask is used during the thin-film growth process. A well-defined island of gold film grown on an atomically flat insulator can be achieved. We are performing a series of tests to ensure film quality. We have also designed an ultralow-noise circuit to control the calibration device. As previously stated, we have measured the relative potential generated by PSI upon illumination. It is anticipated that this calibration device will enable us to obtain the absolute voltage generated by a single PSI reaction center.

7.4 CO_2 SEQUESTRATION BY CHEMICAL TECHNOLOGY (J. W. Lee)

Contact: J. W. Lee
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Summary: This research proposes a means of converting the CO_2 emissions of fossil fuel-fired power plants into valuable fertilizers that support additional photosynthetic fixation of CO_2.

7.4.1 Purpose and Scope

This newly initiated area of research has great potential. Fossil fuels—coal, oil, and natural gas—have long been a prime "engine" of our industrialized society. They supply

abundant energy at low cost. At the same time, most anthropogenic emissions are related to the use of these fuels. At present, 22 gigatons (Gt) of CO_2 per year (equivalent to 6 Gt C/yr) is emitted as a result of the use of fossil fuels. Coal is the fuel most widely used for the generation of electricity worldwide. Today 70% of all electricity in the United States is generated from coal and natural gas, while oil-derived products dominate transportation fuels. Worldwide, coal-fired power plants alone result in 1.8 of the 6 Gt C/yr of CO_2 emission. The increasing anthropogenic CO_2 emission and global warming (thus climate change) have challenged the United States and other countries to find new and better ways to meet the world's increasing needs for energy while reducing greenhouse gases.

7.4.2 Progress

During this reporting period, we have developed a practical and revolutionary concept to reduce CO_2 emission from fossil fuel–fired power plants and to solve the global greenhouse gas problem. It proposes an innovative application of the NH_4HCO_3 and $(NH_2)_2CO$ production reactions as an effective CO_2-sequestering process that can reduce or eliminate CO_2 emission in fossil fuel–fired power plants without affecting their power-generation performance. The proposed process converts the power plants' flue gas (mainly CO_2 and N_2) into valuable products, NH_4HCO_3 and $(NH_2)_2CO$, using water and renewable H_2 or CH_4. Currently, the United States has an abundant supply of inexpensive natural gas (CH_4). This CO_2-sequestering technology will be able to enter the market immediately after its development. This technology can be further advanced to remove NO_x and SO_x emissions from flue gas by converting these harmful emissions into fertilizers. Utilization of NH_4HCO_3 and $(NH_2)_2CO$ will support agriculture for more photosynthetic fixation of CO_2 from the atmosphere. Therefore, this proposed technology should represent a novel, practical, and revolutionary approach to the global CO_2 problem.

This work has gained much positive recognition, although it is still at an early stage of development. DOE's Office of Fossil Energy is very interested in this project. After details of this work were presented as a seminar last April at DOE Headquarters, a DOE program manager visited ORNL to see our research facilities. Now, the Office of Fossil Energy has agreed to provide $50K funding to accelerate project development. More funding is expected from DOE's field offices.

7.5 ENZYMES FROM EXTREMPHILES (J. Woodward, B. R. Evans, and K. Cordray)

Contact: J. Woodward
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Summary: Preliminary results were reported for transaldolase expressed from the thermophile *Methanococcus jannaschii*, and further experimentation was conducted on an isolate from the ORNL mixed thermophilic culture.

The transaldolase from *Methanococcus jannaschii* was found to have threefold higher activity when expressed without the six-histidine tag. The transaldolase was inhibited by phosphate and Tris-HCl. No inhibition was seen when Hepes, histidine, imidazole, or bis-tris-HCl buffers were used. The highest specific activity for the transaldolase achieved so far, 34 units/mg, was achieved by a combination of two gel-filtration steps on Superdex-75 and ion-exchange chromatography on DEAE Sepharose, followed by ion-exchange chromatography on Mono-Q. Preliminary results from the transaldolase investigation were presented at the 20th Symposium on Biotechnology for Fuels and Chemicals, May 3–7, 1998, Gatlinburg, Tennessee.

The C1 isolate from the ORNL mixed thermophile culture was grown for 7 d anaerobically on microcrystalline cellulose. After the 7-d incubation, the microcrystalline cellulose appeared to have been almost completely consumed, and cellotetraose and cellobiose were detected in the culture supernatant by high-performance liquid chromatography (HPLC). The concentrated culture supernatant and cell lysate were found to contain cellulase activity.

7.6 ENZYMATIC CONVERSION OF BIOMASS TO HYDROGEN (J. Woodward and M. T. Orr)

Contact: J. Woodward
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Summary: Significant results were reported in the area of conversion of sucrose to hydrogen, and additional experiments have suggested a promising yield of hydrogen from the pentose phosphate pathway.

During the last quarter, we have focused our energies on two distinct but related projects. The first is the conversion of sucrose to hydrogen. This work resulted in a manuscript that has been submitted to *Biotechnology Progress*. In addition, this work was reported to the 20th Symposium on Biotechnology for Fuels and Chemicals in Gatlinburg, Tennessee, May 3–7,

1998. The second project is the conversion of glucose-6-phosphate (G-6-P)to hydrogen by the pentose phosphate pathway.

The sucrose work produced several important results, focusing on the kinetics and limiting reagent of the pathway using glucose dehydrogenase. The instability of the $NADP^+$ cofactor was determined to be the limiting factor in hydrogen production experiments that produced less than 1 mol of hydrogen per mole of sucrose. The reason for this instability has not been determined to date, but possible explanations include high temperature, change in pH, and presence of gluconic acid, which is a by-product of the system. Attempts to replace the $NADP^+$ with other cofactors such as NAD^+ and immobilized $NADP^+$ proved unsuccessful. The specifics of this work may be found in the manuscript that has been submitted previously. After the completion of the manuscript, we succeeded in immobilizing invertase from *Candida utilis*. This raised the operational temperature from 50 to 80°C, while remaining active for 24 h. This has the potential to increase the temperature at which the reaction may be carried out, which, in turn, may raise the rates of hydrogen production and the yield of hydrogen.

While the bulk of the work was carried out on the sucrose project, we have carried out several experiments with the pentose phosphate pathway. We returned to this project after discovering a systemic error that may have led to lower-than-accurate results. Further experimentation showed that this error had only a marginal impact on the results. As has been shown in previous reports, the theoretical yield of hydrogen from G-6-P by this method is 12 mol of hydrogen per mole of G-6-P. The highest result we achieved was 11.6 mol of hydrogen per mole of G-6-P.

With the submission of the sucrose results for publication and the promising yield of hydrogen from the pentose phosphate pathway, this has been a very successful quarter. The possibility of raising the operational temperature of the sucrose experiments gives us several areas to work on with that project. Determining the reason for less than 100% hydrogen yield from the pentose phosphate pathway continues to be a challenge.

7.7 HYDROGEN PRODUCTION (J. Woodward and J. P. Getty)

Contact: J. Woodward
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Summary: Research has focused on the nonenzymatic production of hydrogen, specifically the optimization of hydrogen generation by an iron-filing catalyst under anaerobic conditions.

The discovery of hydrogen evolution by nonenzymatic methods, specifically the utilization of iron as a metallic catalyst, has become the focal point of our research. Our current work has encompassed identifying and optimizing the mechanism by which the iron catalyst generates hydrogen gas under anaerobic conditions. Each individual parameter that influences the rate of production and overall hydrogen yield has been investigated separately. Initially, our studies incorporated the effects of an iron alloy magnet (limited surface area); since then, we have converted to iron filings to maximize the area of contact between the iron catalyst and the fueling solution of choice.

Our studies incorporated various masses of iron filings into established experimental conditions. The conclusion drawn from the data is that masses of 1 and 5 mg of iron filings are sufficient to generate hydrogen production. However, 10 mg of iron filings optimizes the rate and yield of hydrogen production in our scaled reaction vessel. The second parameter that we investigated was the fuel solution utilized in conjunction with the iron-filing catalyst. We examined several solution standards, such as tap water, nanopure water, Hepes buffer solution, gluconic acid, and combinations thereof. The solutions were tested in their gaseous and degassed states at various molar concentrations. From the data, normal tap water acted as an inhibitor to hydrogen evolution. However, nanopure water, Hepes buffer, and gluconic acid promoted the generation of hydrogen in the presence of the iron-filing catalyst. From these experiments, we conclude that 0.5 to 1 *M* gluconic acid is the optimal fueling solution for the production of hydrogen gas. The highest peak was produced by 0.5 *M* gluconic acid, which then decreased to a steady-state rate of 2000 nmol/h, while 1.0 *M* gluconic acid reached a steady-state rate of 4200 nmol/h. (The high peak is attributed to oxygen influx at the time of injection.) In addition to the aforementioned parameters, we are currently evaluating the influential parameters of temperature and velocity of stirring.

These parameters have significant bearing on the overall production of hydrogen gas attributed to the iron-filing catalyst mechanism for hydrogen evolution. We have begun additional experiments to upscale the hydrogen production; however, mechanical difficulties have hindered this effort thus far. Our efforts and determination to achieve such goals are promising based on preliminary experiments that analyze each aspect of the upscaling project.

7.8 DEVELOPMENT OF A PROCESS FOR A NOVEL THERAPEUTIC PRODUCT FOR THE PREVENTION OF FOOD CONTAMINATION (J. Woodward)

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Summary: In a collaborative project between ORNL and the Academy of Sciences of the Republic of Kazakhstan, plans were made to test a promising microbial consortium that has the potential to inhibit the growth of *Salmonella* in chicken.

7.8.1 Purpose and Scope

This is a collaborative project between ORNL, the U.S. Department of Agriculture–Agricultural Research Service (USDA-ARS), and the Ministry of Science–Academy of Sciences, Republic of Kazakhstan. It is funded by the DOE Industrial Partnering Program (IPP).

7.8.2 Progress

A joint meeting was held between ORNL, USDA-ARS, and the Academy of Sciences, Republic of Kazakhstan, concerning the IPP project (IPP-ORS-057), "Development of a Process for a Novel Therapeutic Product for the Prevention of Food Contamination." The purpose of this meeting was to establish a research and development collaboration between ORNL, USDA-ARS, and the Academy of Sciences, Republic of Kazakhstan, for the production of commercial products that, when added to animal feed, would have application worldwide for the prevention of food contamination. This collaboration would be based upon natural microbial products developed by institutions of the Academy of Sciences. The major result of this meeting was the report by the Academy of Sciences of a microbial culture isolated from wheat flour that is antagonistic to pathogenic bacteria. The culture consists of 33 strains of lactic acid bacteria, all of which produce a small-molecular-weight peptide that reportedly possesses the ability to inhibit the growth of pathogenic bacteria. It was also reported that mice fed the microbial consortium and then given the pathogenic bacterium *Salmonella* were protected from being infected, unlike the control mice that did not receive the consortium. Based upon these apparently exciting results, a 2-year program of research was proposed (IPP Thrust 2 Project) that could ultimately result in the commercial development of this product by U.S. industry (MS BioScience, Inc.), which would eventually oversee the deployment of this technology in Kazakhstan. A cooperative research and development agreement (CRADA) between Lockheed Martin Energy Systems, Inc., and MS BioScience, Inc., will be implemented to effect the commercial

development of this product. MS BioScience, Inc., would also set up operations at ORNL for this purpose. It was further decided that David Nisbet of USDA-ARS will spend a month in Kazakhstan during August 1998, testing the efficacy of the Kazakh microbial consortium in chicks, as has been shown with PREEMPT, a novel product commercially produced by MS BioScience, Inc., and approved by the U.S. Food and Drug Administration for use with chickens.

7.9 PUBLICATIONS/PATENTS

E. Greenbaum and J. W. Lee, "Photosynthetic Hydrogen and Oxygen Production by Green Algae: An Overview," in *BioHydrogen*, ed. O. R. Zaborsky et al., Plenum Publishing, New York, 1998.

J. W. Lee, R. T. Collins, and E. Greenbaum, "Molecular Ionic Probes: A New Class of Hill Reagents and Their Potential for Nanofabrication and Biometallocatalysis," *J. Phys. Chem. B* **102**, 2095–100 (1998).

N. Hershlag, I. Hurley, and J. Woodward, "A Simple Method to Demonstrate the Enzymatic Production of Hydrogen from Sugar," *J. Chem. Educ.* **75**, 1–5 (1998).

B. R. Evans, I. Lee, J. Woodward, and S. V. Fox, "The Effect of Cellulases on the Biodegradation and Morphology of Naturally Colored Cotton Fibers," *ACS Symposium Series* **687**, 228–45 (1998).

A. Subramanian, S. J. Kennel, P. I. Oden, K. B. Jacobson, J. Woodward, and M. J. Doktcyz, "Comparison of Techniques for Enzyme Immobilization on Silicon Supports," *Enzyme Microb. Technol.* (in press).

J. Woodward and M. Orr, "Enzymatic Conversion of Sucrose to Hydrogen," *Biotechnol. Prog.* (submitted).

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

J. Woodward et al., U.S. Patent 5,637,502, issued June 10, 1998.

7.10 PRESENTATIONS

E. Greenbaum, "Hydrogen Production by Photosynthetic Water Splitting," presented at the 1998 DOE Hydrogen Program Technical Peer Review," Alexandria, Virginia, April 28–30, 1998.

I. Lee, J. W. Lee, and E. Greenbaum, "Immobilization of Oriented Photosystem I Reaction Centers," presented at the 20th Symposium on Biotechnology for Fuels and Chemicals, Gatlinburg, Tennessee, May 3–7, 1998.

E. Greenbaum, I. Lee, and J. W. Lee, "New Photosynthetic Pathways: Atmospheric CO_2 Reduction, Renewable H_2 Production and Molecular Electronics," presented at the 22nd DOE Solar Photochemistry Research Conference, Chantilly, Virginia, June 7–11, 1998.

8. MOLECULAR STUDIES

P. T. Cummings

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

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Summary: Development of a simulation code for water with a flexible potential was continued. Preparation of a major invited review article on water and supercritical solutions was completed. Simulations of limiting conductance in supercritical aqueous electrolyte solutions were continued.

8.1.1 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 state conditions 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).

8.1.2 Progress

Thomas Driesner continued development of a molecular dynamics code for simulating water that employs the flexible BJH model of water. The goal of this work will be to simulate isotope effects in supercritical and ambient water, as well as make contact with EXAFS (extended X-ray absorption fine structure) measurements of the hydration shell of supercritical water around ions, and the spectroscopic properties of water.

Chialvo and Cummings have been invited to write a review article on molecular simulation of supercritical water and aqueous solutions for the journal *Advances in Chemical Physics*. During the current quarter, the review article was completed and submitted.

Visiting Professor Song Hi Lee extended molecular dynamics simulations of ions in supercritical water to calculate the limiting conductance as a function of density. The purpose of

this study is to understand the change in slope of the limiting conductance with decreasing density. During the current quarter, additional alkali halide ions, beyond NaCl, were studied.

8.2 THEORY AND MOLECULAR SIMULATION OF NONEQUILIBRIUM SYSTEMS (P. T. Cummings, A. Baranyai, S. T. Cui, J. D. Moore, and I. Borzsák)

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Summary: The viscosity and viscosity index of various linear and branched alkanes were in the process of being predicted computationally. A large-scale simulation of C_{100} was continued. An invited talk was presented at a symposium on molecular modeling at the Mexican Petroleum Institute (IMP), probably leading to funding from the IMP.

8.2.1 Purpose and Scope

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

8.2.2 Progress

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

During the current quarter, we continued a simulation of liquid C_{100} using the massively parallel Cray T3E supercomputer located at the National Energy Research Supercomputing Center at Lawrence Berkeley National Laboratory, as well as Cray T3Es located at Cray headquarters in Minnesota. The goal of the C_{100} simulation will be to test the current limits of feasible calculation of equilibrium and transport properties. It will also provide a set of data that can be used for coarse-graining studies at a future date.

During the quarter, the research performed as part of this project was described in an invited presentation at an international workshop at the IMP in Mexico City. The purpose of the workshop was to launch a new initiative in molecular modeling at IMP. The plan is that the invited external speakers, including P. T. Cummings, will become part of an international advisory board for the initiative, which will involve the IMP funding students and postdoctoral

researchers to conduct research outside Mexico and then return to the IMP, bringing with them skills in molecular modeling.

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

Contact: P. T. Cummings
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Summary: Study of an integral equation theory for nonequilibrium systems was initiated.

8.3.1 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.

8.3.2 Progress

Yu. Kalyuzhnyi began a detailed study and evaluation of the integral equation theory of Eu and Gan. The theory offers the possibility of calculating structural and rheological properties of systems away from equilibrium. Preliminary work involved programming integral equation calculations in the form required by the Eu-Gan theory.

8.4 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*)

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Internet: u53@ornl.gov

Summary: Preparation of a final report to the sponsors was continued.

8.4.1 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

*University of Virginia.

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. The project funding ended on December 31, 1997.

8.4.2 Progress

This project is no longer funded and is being concluded. A final report to the sponsors (IBM) is in preparation.

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

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Internet: u53@ornl.gov

Summary: No progress is reported for this quarter.

8.5.1 Purpose and Scope

This 3-year project, supported by the new DOE Environmental Management Science Program, began September 1, 1996. The goal of the project 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).

8.5.2 Progress

The main technical effort of this quarter involved responding to referees' comments on two manuscripts submitted during the previous quarter.

8.6. DEVELOPMENT AND APPLICATION OF FAST COMPUTATIONAL PROTEIN-FOLDING ALGORITHMS USING MASSIVELY PARALLEL SUPERCOMPUTERS (P. T. Cummings, P. H. LoCascio, K. Dill,* and Kai Yue*)

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Internet: u53@ornl.gov

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*University of California-San Francisco.

Summary: Significant progress was made in the parallelization of the Geocore algorithm.

8.6.1 Purpose and Scope

This 3-year project, supported by the Laboratory Director's Research and Development fund, began October 1, 1997. The goal of the project is to develop parallel implementations of the Geocore ab initio exhaustive-search protein-folding algorithm and use the parallel version to predict the structures of larger proteins; to improve the performance of the Geocore algorithm; and to develop much faster, less exhaustive algorithms for very large proteins.

8.6.2 Progress

During this quarter, Kai Yue and Phil LoCascio continued development of the Geocore ab initio protein-folding algorithm. Excellent progress is being made. A strategy for the parallelization of Geocore has been developed, in addition to a mechanism whereby Yue and Ken Dill could continue to make enhancements to the Geocore algorithm simultaneously with parallelization.

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

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Internet: hdc@ornl.gov and u53@ornl.gov

Summary: See research description reported under H. D. Cochran.

8.8 OTHER IMPORTANT ACTIVITIES

With Thom Dunning from the Environmental Molecular Sciences Laboratory at Pacific Northwest National Laboratory, Cummings cochaired a DOE Council on Chemical Sciences Workshop, Research Frontiers in Molecular Simulation and Computational Chemistry: Extending the Accuracy and Scale of Molecular-Based Calculations, at the Hotel Loretto, Santa Fe, New Mexico, May 17–21, 1998. A report is being prepared for the Council on Chemical

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*University of Pittsburgh.

†University of North Carolina.

Sciences. At the workshop, Cummings presented a talk entitled "Overview of Classical Molecular Simulation Methods."

Cummings is also at the forefront of educational efforts in molecular modeling and simulation. These efforts include chairing the Molecular Modeling Task Force (MMTF) of the nonprofit educational CACHE corporation and heading a group of researchers developing, with National Science Foundation funding, a web-based text on molecular simulation. In relation to these activities, Cummings organized and chaired a meeting of the MMTF in Golden, Colorado, May 14–16, 1998.

Also, during this quarter, Cummings received notification that he had been awarded the 1998 Alpha Chi Sigma award from the American Institute of Chemical Engineers (AIChE). This is the AIChE's most prestigious award for research and is based on each candidate's past decade of research. It consists of a plaque and a check for $5000. The award will be presented at the 1998 Annual Meeting of the AIChE in November 1998 in Miami Beach, Florida.

8.9 PUBLICATIONS

8.9.1. Submitted

A. A. Chialvo and P. T. Cummings, "Molecular-Based Modeling of Water and Aqueous Solutions at Supercritical Conditions," *Adv. Chem. Phys.* (1998).

8.9.2 Accepted

K. C. Chen, R. M. Ford, and P. T. Cummings, "Spatial Effect of the Tumbling Frequencies for Motile Bacteria on Cell Balance Equations," *Chem. Eng. Sci.* (1998).

K. C. Chen, R. M. Ford, and P. T. Cummings, "Mathematical Models for Motile Bacterial Transport in Cylindrical Tubes," *J. Theor. Biol.* (1998).

8.9.3 Published

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.* **146**, 51–61 (1998).

P. T. Cummings, "Molecular Simulation of Complex Systems Using Massively Parallel Supercomputers," *Fluid Phase Equilib.* **144**, 331–42 (1998).

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.* **93**, 73–78 (1998).

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," *Int. J. Thermophys.* **19**, 449–59 (1998).

8.10 PRESENTATIONS

8.10.1 Invited Seminars

P. T. Cummings, "Molecular Modeling and Simulation: Present and Future Tools for Physical Properties Prediction," presented at the Department of Nuclear Engineering, The University of Tennessee, Knoxville, Tennessee, April 15, 1998.

P. T. Cummings, "Frontiers in Molecular Design of New Materials," presented at The University of Tennessee, Arts and Sciences Board of Visitors, Oak Ridge, Tennessee, April 24, 1998.

P. T. Cummings, "Molecular Modeling and Simulation: Present and Future Tools for Physical Properties Prediction and Molecular Product Design," presented at the Department of Chemical Engineering, Universitat Rovira i Virgili, Tarragona, Spain, May 5, 1998.

P. T. Cummings, "Molecular Modeling and Simulation: Present and Future Tools for Physical Properties Prediction and Molecular Product Design," presented at the Department of Chemistry, Eötvös University, Budapest, Hungary, June 2, 1998.

P. T. Cummings, "Molecular Simulation of Supercritical Water and of Ionic Association in Supercritical Aqueous Solutions," presented at the Institut fuer Theoretische Physik Technische Universitaet Wien, Vienna, Austria, June 16, 1998.

8.10.2 Invited Conferences

P. T. Cummings, "Molecular Simulation of Transport and Thermodynamic Properties Relevant to the Petroleum Industry," presented at the Mexican Petroleum Institute (IMP) Workshop: Computer Simulations and Experimental Techniques in Oil Problems, Mexico City, Mexico, April 6–7, 1998.

P. T. Cummings, "The CACHE Molecular Modeling Task Force: Bringing Molecular Modeling into the Undergraduate Classroom," presented at the First Annual Symposium, Ohio Molecular Computation and Simulation Network, Cincinnati, Ohio, April 17, 1998.

P. T. Cummings, "Overview of Classical Molecular Simulation Methods," presented at the DOE Council on Chemical Sciences Workshop on Research Frontiers in Molecular Simulation and Computational Chemistry: Extending the Accuracy and Scale of Molecular-Based Calculations, Santa Fe, New Mexico, May 17–21, 1998.

P. T. Cummings, "Molecular Simulation of Supercritical Water and Aqueous Solutions," presented at the 5th Liblice Conference on the Statistical Mechanics of Liquids, Zelezna Ruda, Czech Republic, June 7–12, 1998.

P. T. Cummings, "Molecular Simulation of Supercritical Aqueous Systems," presented at the Eighth International Conference on Properties and Phase Equilibria for Product and Process Design, Noordwijkerhout, The Netherlands, April 26–May 1, 1998.

8.10.3 Contributed Conferences

P. T. Cummings, H. D. Cochran, J. J. dePablo, D. J. Evans, D. A. Kofke, A. Z. Panagiotopoulos, and R. L. Rowley, "A World Wide Web Based Textbook on Molecular Simulation," presented at the 1998 American Society of Engineering Education Annual Conference & Exposition, Seattle, Washington, June 28–July 1, 1998.

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