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LOCKHEED MARTIN



**Quarterly Progress Report for the
Chemical and Energy Research Section
of the Chemical Technology Division:
January–March 1998**

R. T. Jubin

MANAGED AND OPERATED BY
LOCKHEED MARTIN ENERGY RESEARCH CORPORATION
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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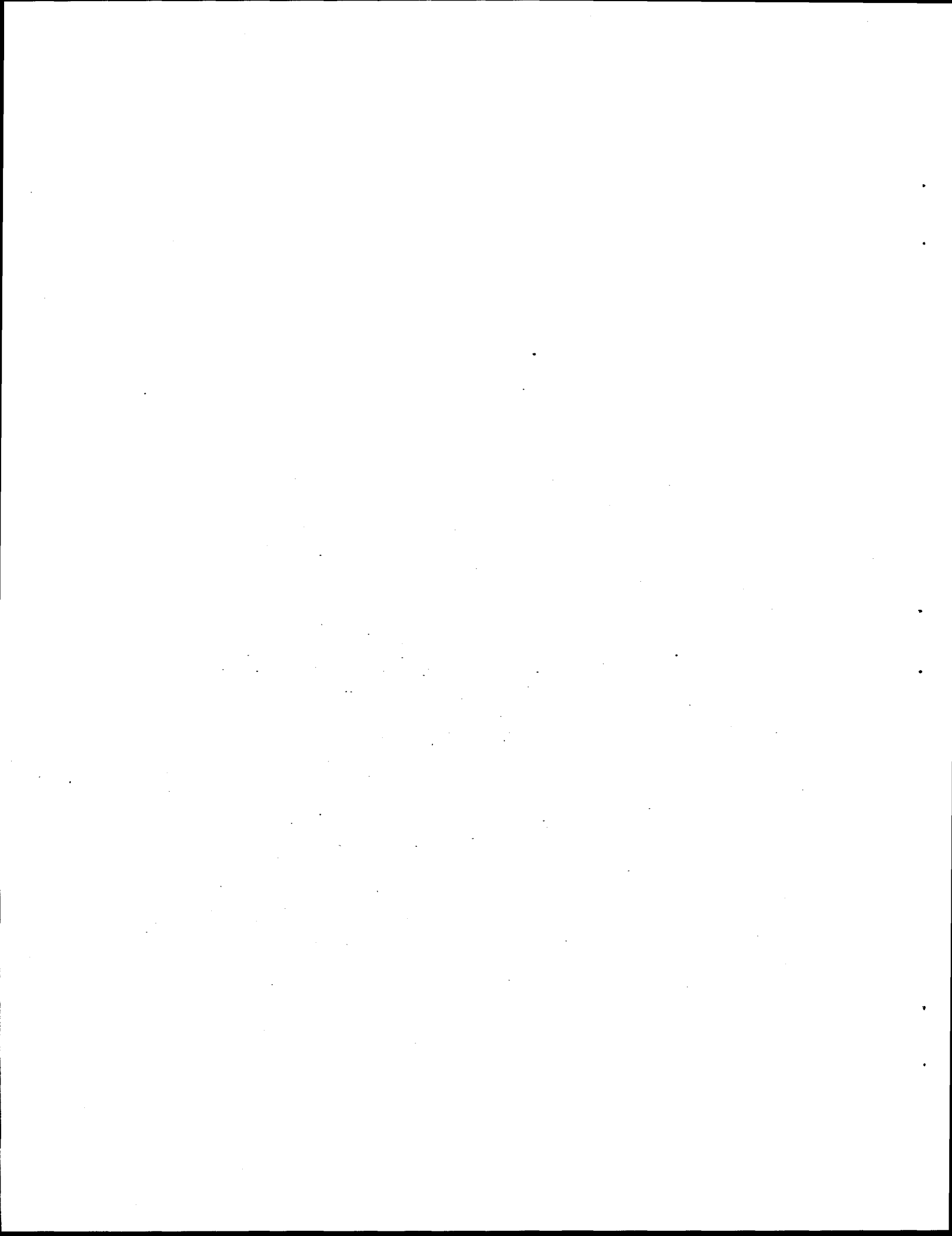
Chemical Technology Division

QUARTERLY PROGRESS REPORT FOR THE
CHEMICAL AND ENERGY RESEARCH SECTION OF
THE CHEMICAL TECHNOLOGY DIVISION:
JANUARY-MARCH 1998

R. T. Jubin

Date Published- March 1999

Prepared by the
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U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-96OR22464



CONTENTS

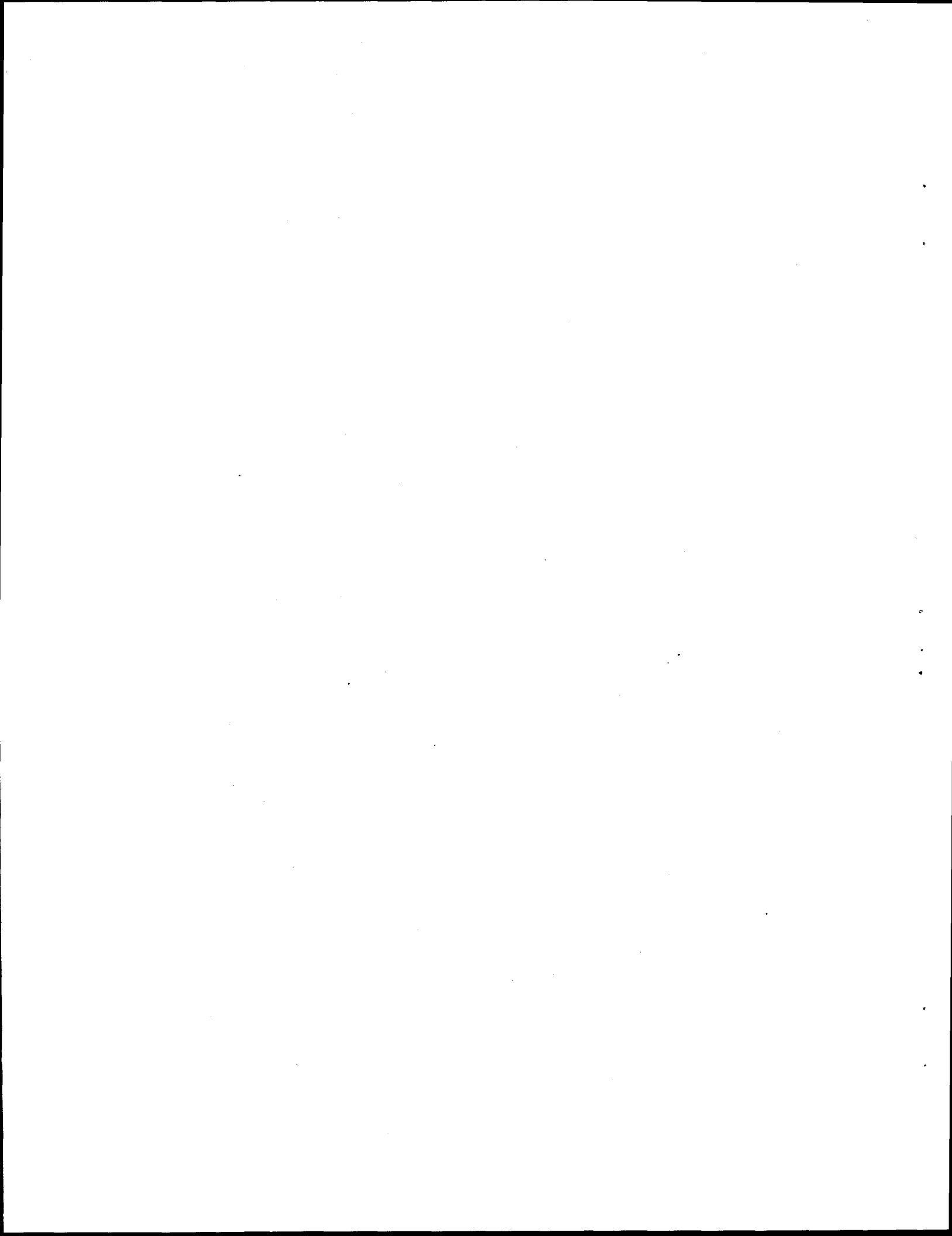
ACRONYMS	ix
EXECUTIVE SUMMARY	xi
1. HOT CELL OPERATIONS	1
1.1 SLUDGE-PARTITIONING CHEMISTRY	1
1.1.1 Purpose and Scope	1
1.1.2 Progress	2
1.2 DEVELOPMENT AND TESTING OF INORGANIC SORBENTS	3
1.2.1 Purpose and Scope	3
1.2.2 Progress	4
2. PROCESS CHEMISTRY AND THERMODYNAMICS	5
2.1 SLUDGE TREATMENT STUDIES	5
2.1.1 Purpose and Scope	5
2.1.2 Progress	5
2.1.2.1 Control of Solids in Enhanced Sludge Washing	5
2.1.2.2 Acid Treatment	6
2.2 SALTCAKE DISSOLUTION	7
2.2.1 Purpose and Scope	7
2.2.2 Progress	7
2.3 THERMODYNAMICS AND KINETICS OF ENERGY-RELATED MATERIALS	7
2.3.1 Purpose and Scope	8
2.3.2 Progress	8
2.3.2.1 Solidification of the Y-Ba-Cu-O System	8
2.3.2.2 Oxidation States of Copper and Oxygen in 1:2:3:n	8
2.3.2.3 Collaboration	9
3. MSRE REMEDIATION STUDIES	9
3.1 URANIUM CONVERSION	9
3.1.1 Purpose and Scope	10
3.1.2 Progress	10
3.2 URANIUM DEPOSIT REMOVAL AND PASSIVATION OF FLUORINATED CHARCOAL	11
3.2.1 Purpose and Scope	11
3.2.2 Progress	11
3.3 SALT DISPOSITION STUDIES	12
3.3.1 Purpose and Scope	12
3.3.2 Progress	12
4. CHEMISTRY RESEARCH	13

4.1	MOLECULAR IMPRINTING APPROACH TO SMART INORGANIC/ORGANIC HYBRID SORBENTS	13
4.1.1	Purpose and Scope	13
4.1.2	Progress	14
4.2	URANYL ADSORPTION CAPACITY ON MESOPOROUS SORBENTS	14
4.2.1	Purpose and Scope	14
4.2.2	Progress	15
4.3	FAA PROJECT ON EXPLOSIVE DETECTION	15
4.4.	SOLUBILITIES OF UO_3 IN CARBONATE BUFFER SOLUTIONS AT HIGH TEMPERATURE ($>1000^\circ C$)	16
4.4.1	Purpose and Scope	16
4.4.2	Progress	16
4.5	PUBLICATIONS	16
5.	BIOTECHNOLOGY	17
5.1	ADVANCED BIOREACTOR SYSTEMS FOR ALCOHOL FUEL PRODUCTION	17
5.1.1	Purpose and Scope	17
5.1.2	Progress	17
5.1.3	Publication	18
5.2	ALTERNATIVE FEEDSTOCKS FOR CHEMICALS AND PETROLEUM REFINING INDUSTRIES: PLASTICS, FIBERS, AND SOLVENTS FROM BIOLOGICALLY DERIVED SUCCINIC ACID	18
5.2.1	Purpose and Scope	18
5.2.2	Progress	18
5.2.2.1	Programmatic and Industrial Partnering	18
5.2.2.2	Biocatalyst and Fermentation Development.	19
5.3	BIOFILTRATION OF VOLATILE POLLUTANTS: FUNDAMENTAL MECHANISMS FOR IMPROVED DESIGN, LONG-TERM OPERATION, PREDICTION, AND IMPLEMENTATION	19
5.3.1	Progress	19
5.3.2	Publications	20
5.4	CHARACTERIZATION OF CHEMICALLY MODIFIED ENZYMES FOR BIOREMEDIATION REACTIONS	20
5.4.1	Purpose and Scope	20
5.4.2	Progress	21
5.4.3	Publications	22
5.5	FUNDAMENTAL BIOPROCESSING RESEARCH FOR COAL APPLICATIONS	22
5.5.1	Purpose and Scope	22
5.5.2	Progress	23

5.6	NOVEL DRY-STATE BIOCATALYSIS FOR AIRBORNE HYDROCARBONS	24
5.6.1	Progress	24
5.6.2	Publications and Outside Contacts	25
5.7	REMOVAL OF HETEROATOMS FROM CRUDE OIL	25
6.	SEPARATIONS AND MATERIALS SYNTHESIS	26
6.1	CHEMICAL AND PHYSICAL PRINCIPLES IN MULTIPHASE SEPARATIONS	26
6.1.1	Purpose and Scope	26
6.1.2	Progress	26
6.1.2.1	Drop Deformation and Breakup	26
6.1.2.2	Wetting and Stability of Drops on Solid Surfaces	27
6.1.2.3	Spraying and Mixing in Electrohydrodynamic Flows	27
6.1.2.4	Particle Interactions Under Magnetic Fields	27
6.1.2.5	Particle Interactions in Reactive Systems	27
6.2	NUCLEATION, GROWTH, AND TRANSPORT PHENOMENA	28
6.2.1	Purpose and Scope	28
6.2.2	Progress	29
6.3	PHASE EQUILIBRIA MODIFICATION BY ELECTRIC FIELDS	30
6.3.1	Purpose and Scope	30
6.3.2	Progress	30
6.4	MAGNETIC-SEEDING FILTRATION	31
6.4.1	Purpose and Scope	31
6.4.2	Progress	31
6.5	ELECTROSTATIC OZONATION	32
6.5.1	Purpose and Scope	32
6.5.2	Progress	32
6.6	DEVELOPMENT PROGRAM IN ELECTRODISTILLATION	33
6.6.1	Purpose and Scope	33
6.6.2	Progress	33
6.7	INDUSTRIAL INTERACTION	34
6.7.1	Purpose and Scope	34
6.7.2	Results	34
6.8	PUBLICATIONS	34
7.	FLUID STRUCTURE AND PROPERTIES	35
7.1	INTERACTIONS OF SOLUTES, SOLVENTS, AND SURFACES	35
7.1.1	Objective	35
7.1.2	Progress	35

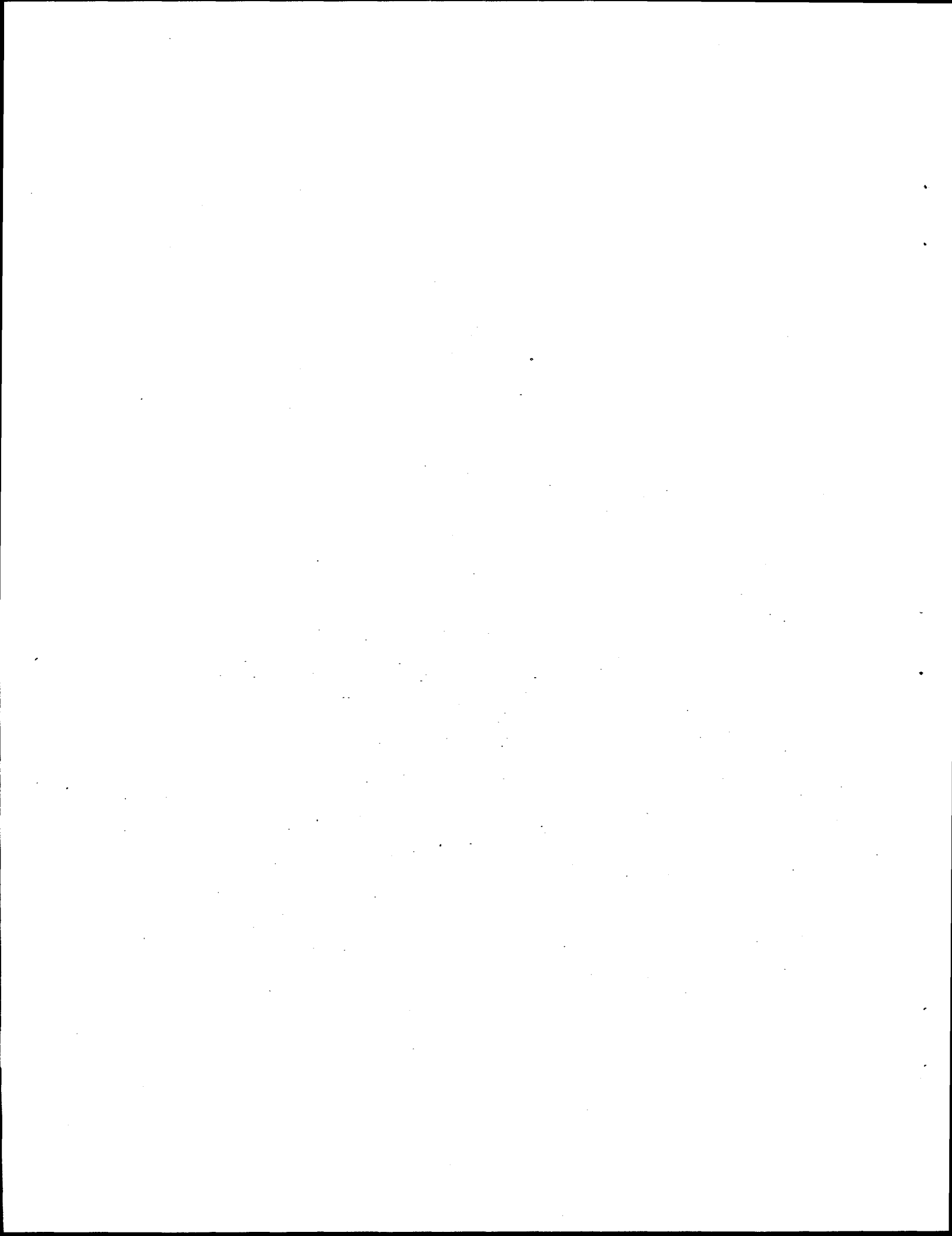
7.2	MOLECULAR-BASED STUDY OF REVERSE MICELLES IN SUPERCRITICAL CO ₂	36
7.2.1	Objective	36
7.2.2	Progress	36
7.3	STRUCTURE AND PROPERTIES OF CHAIN MOLECULE SYSTEMS UNDER SHEAR	37
7.3.1	Objective	37
7.3.2	Progress	37
7.4	PUBLICATIONS	37
7.4.1	Submitted	37
7.4.2	Accepted	38
7.4.3	Published	38
8.	BIOTECHNOLOGY RESEARCH	38
8.1	KINETICS OF ENZYME-CATALYZED REACTIONS	38
8.1.1	Purpose and Scope	38
8.1.2	Progress	39
8.2	BIOMOLECULAR ELECTRONICS	40
8.2.1	Purpose and Scope	40
8.2.2	Progress	40
8.3	RENEWABLE HYDROGEN PRODUCTION	41
8.3.1	Purpose and Scope	41
8.3.2	Progress	41
8.4	ENZYMES FROM EXTREMOPHILES IN BIOPROCESSING AND BIOREMEDIATION	41
8.4.1	Progress	42
8.4.2	Publications	43
8.5	ENZYMATIC CONVERSION OF BIOMASS TO HYDROGEN	43
8.6	DEVELOPMENT OF MICROCYCLE TECHNOLOGY FOR THE LARGE- SCALE PRODUCTION OF FUNGAL ENZYMES	44
8.6.1	Purpose and Scope	44
8.6.2	Progress	44
8.7	PUBLICATIONS	45
8.7.1	Published	45
8.7.2	In Press	45
8.8	PRESENTATIONS	45
9.	MOLECULAR STUDIES	46
9.1	AQUEOUS ELECTROLYTE SOLUTIONS AT AMBIENT AND SUPERCRITICAL CONDITIONS	46

9.1.1	Purpose and Scope	46
9.1.2	Progress	46
9.2	THEORY AND MOLECULAR SIMULATION OF NONEQUILIBRIUM SYSTEMS	47
9.2.1	Purpose and Scope	47
9.2.2	Progress	47
9.3	INTEGRAL EQUATION THEORIES OF MOLECULAR FLUIDS	48
9.3.1	Purpose and Scope	48
9.3.2	Progress	48
9.4	MATHEMATICAL MODELING OF BACTERIAL MIGRATION THROUGH POROUS MEDIA WITH APPLICATION TO IN SITU BIOREMEDIATION	48
9.4.1	Purpose and Scope	48
9.4.2	Progress	49
9.5	FUNDAMENTAL CHEMISTRY AND THERMODYNAMICS OF HYDROTHERMAL OXIDATION PROCESSES	49
9.5.1	Purpose and Scope	49
9.5.2	Progress	49
9.6	DEVELOPMENT AND APPLICATION OF FAST COMPUTATIONAL PROTEIN-FOLDING ALGORITHMS USING MASSIVELY PARALLEL SUPERCOMPUTERS	49
9.6.1	Purpose and Scope	50
9.6.2	Progress	50
9.7	MOLECULAR-BASED STUDY OF REVERSED MICELLES IN SUPERCRITICAL CARBON DIOXIDE FOR SOLVENT SUBSTITUTION IN THE U.S. CHEMICAL INDUSTRY	50
9.8	PUBLICATIONS	50
9.8.1	Submitted	50
9.8.2	Accepted	51
9.8.3	Published	51
9.9	PRESENTATIONS	51
9.9.1	Invited Seminars	51
9.9.2	Invited Conferences	52



ACRONYMS

ACB	auxiliary charcoal bed
ACC	Applied CarboChemicals
AMP	ammonium molybdophosphate
CASD	Chemical and Analytical Sciences Division (ORNL)
CMC	carboxymethylcellulose
CRADA	cooperative research and development agreement
CTD	Chemical Technology Division
DOE	U.S. Department of Energy
EM	Environmental Management (DOE)
ESP	Environmental Simulation Program
ESW	Enhanced Sludge Washing
FBR	fluidized-bed reactor
FTIR	Fourier transform infrared
HLW	high-level waste
INEEL	Idaho National Engineering and Environmental Laboratory
LiP	lignin peroxidase
MSRE	Molten Salt Reactor Experiment
ORNL	Oak Ridge National Laboratory
PAN	polyacrylonitrile
PCP	pentachlorophenol
PEG	polyethylene glycol
PNNL	Pacific Northwest National Laboratory
PSI	Photosystem I
SANS	small-angle neutron scattering
SAXS	small-angle X-ray scattering
SERS	surface-enhanced Raman spectroscopy
TPA	tetrapropylammonium hydroxide
UC	University of California
VOC	volatile organic compound
XRD	X-ray diffraction
ZrHP	zirconium monohydrogen phosphate(s)



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

Activities conducted within the area of *Hot Cell Operations* included efforts to optimize the processing conditions for Enhanced Sludge Washing of Hanford tank sludge and attempts to develop a cesium-specific spherical inorganic sorbent for the treatment of acidic high-salt waste solutions.

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. Experimental collaborative efforts with Russian scientists to determine the solidification conditions of yttrium, barium, and copper oxides from their melts were completed.

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, the investigation of mesoporous sorbents for adsorption of uranyl species, and experimental studies of two uranyl carbonate compounds to understand the hydrothermal oxidation processing of hazardous and mixed wastes. Funding was obtained from the Federal Aviation Administration to develop explosive sensors based on technology previously applied to radionuclide analysis.

Biotechnology initiatives included efforts to enhance the production of ethanol through development of advanced bioreactor systems, as well as the production of commercially valuable chemicals from a renewable feedstock (biologically derived succinic acid). Biotechnology research also focused on attempts to improve the design and operation of biofiltration systems for treatment of volatile organic compounds, characterization of chemically modified enzymes for bioremediation, and explorations of ways in which advanced biological processes can improve coal utilization and conversion. Attention was also directed to the use of dry-state enzymes for removal or destruction of chemical warfare agents and volatile organic contaminants and to the removal of organic sulfur from hydrocarbon feedstocks.

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 application of magnetic-seeding filtration to remove solids from waste streams, 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. Areas of possible industrial interaction were also investigated.

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, photovoltages from isolated Photosystem I reaction centers were measured for the first time, and research continued on the production of renewable hydrogen by photosynthetic water splitting. In enzyme-related work, the kinetic characteristics of thermophilic microorganisms were studied, efforts were made to maximize the efficiency of the enzymatic production of hydrogen from glucose, and test fungi were cultivated under a microcycle regime.

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, mathematical modeling of in situ bioremediation processes, and extension of a molecular formalism to reaction kinetics in supercritical fluid solvents. 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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Contact: J. L. Collins
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Summary: A 111-g sludge sample from Hanford tank S-101 was washed four times (16–143 h) with inhibited water at ambient temperature. The sludge sample was also washed twice at 97°C for approximately 1 h. Based on the conductance measurements of the wash solutions after decantation, a conductance meter can adequately determine when water washes will no longer be effective. Then, the washed sludge was slurried to a mixer system. The sludge slurry was transferred into 20 centrifuge tubes. One of the samples was sent for chemical analysis, while another sample was dried in an oven at 104°C until a constant weight was achieved. The water content in the washed sludge was 73%. The density of a composite of the wash solutions was 1.042 g/mL. Based on these results, the original sludge sample contained 33.40 g or 30 wt % of water. Sixteen samples were used to 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 Enhanced Sludge Washing (ESW) procedure. At the conclusion of each leach, the conductance of the caustic solution was measured, and a portion of the filtered leach solution was sent for chemical analysis. A preliminary analysis of the results indicates that a conductivity probe may serve as a useful process control tool for the pretreatment of Hanford tank sludges. It should be noted that the aluminum industry currently uses conductivity probes to control its hot caustic leaches of bauxite.

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 ESW as its baseline technology to separate key inert components from the radionuclides in the HLW sludges. ESW refers to simple sludge washing, 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. This process is effective because of 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 the volume of the high-level waste 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.

A 111-g sludge sample from Hanford tank S-101 was washed four times (16–143 h) with inhibited water at ambient temperature. The sludge sample was also washed twice at 97°C for approximately 1 h. The volume of the combined water washes was approximately 650 mL. After each wash, the sample was centrifuged, the water was decanted, and the remaining wet solids were weighed. Based on the final sample weight, approximately 40% of the initial sludge sample was removed during the six washes. The conductance of each wash solution was measured after the decantation. Based on a preliminary analysis of the results, a conductance meter can adequately determine when water washes will no longer be effective.

After the sixth wash, the washed sludge was then slurried into a mixer system with 191 g of inhibited water. Earlier tests indicate that the mixer can generate uniform sludge samples, which will permit direct comparisons between all of the test results. While the sample was being mixed, the slurry was transferred into 20 preweighed centrifuge tubes with sealing caps. Then, each of the tubes was weighed, centrifuged, decanted, and reweighed. One of the sample aliquots was sent to the Chemical and Analytical Sciences Division (CASD) at Oak Ridge National Laboratory (ORNL) for chemical analysis.

A small sample of the washed sludge, which weighed 0.9245 g, was dried in an oven at 104°C until a constant weight was achieved. The water content in the washed sludge was 73%. A composite of the wash solutions was then prepared and filtered. The density of this filtered composite was 1.042 g/mL. Based on these results, the original sludge sample contained 33.40 g or 30 wt % of water-soluble solids, 23.17 g or 21 wt % of water-insoluble solids, and 54.04 g or 49 wt % of water. An earlier test at Pacific Northwest National Laboratory (PNNL) determined that its sludge sample from Hanford tank S-101 contained 22 wt % of insoluble solids and 36 wt % of water.

Sixteen samples of the washed sludge from tank S-101 were leached at various temperatures, NaOH concentrations, and leaching times, which were described earlier. At the conclusion of each leach, the sample was centrifuged and the caustic solution was decanted. For each of the 1 M solutions, a 2-mL sample was mixed with 8 mL of distilled water. A 1-mL sample was mixed with 9 mL of distilled water for the 3 M solutions. This dilution was necessary because the upper limit for our hot conductivity probe is 200 millimhos. At a particular temperature and NaOH concentration, the conductance of the leach solutions declined as the leaching time was increased from 24 to 168 h. Based on the wet sample weights before and after leaching, it appears that the effectiveness of the leach procedure increased as the leaching time was increased. Therefore, this preliminary analysis of the results indicates that a conductivity probe may serve as a useful process control tool for the pretreatment of Hanford tank sludges. The aluminum industry currently uses conductivity probes to control its hot caustic leaches of bauxite. The usefulness of the conductivity probe for Hanford will be further analyzed as soon as the chemical analyses of the leach solutions are received.

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

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Summary: This program had the task of developing a cesium-specific spherical inorganic sorbent for the treatment of acidic high-salt waste solutions. Acid-side treatment is important at Idaho National Engineering and Environmental Laboratory (INEEL). A composite microsphere of zirconium monohydrogen phosphates (ZrHP) embedded with ammonium molybdophosphate (AMP) was developed and characterized. The amount of AMP that could be embedded in the microspheres for maximum cesium loading from acidic supernatant with high salt concentrations was determined. Sample preparations of air-dried and undried ZrHP microspheres that were embedded with fine particles of AMP were sent to Terry Todd at INEEL for testing.

1.2.1 Purpose and Scope

The general objectives of this task were to develop, prepare, and test new and unique inorganic ion exchangers *made as microspheres* by the internal gelation process to remove fission products, actinides, and other metals (such as the Resource Conservation and Recovery Act metals) from waste streams occurring at the various DOE sites. Inorganic sorbents made in the engineered form as microspheres were much more column usable than the powder or granular forms that were commercially available. The focus of this program was to develop microspheres of materials that

have already been shown to be highly effective as cesium and strontium sorbents. The experimental objectives have been completed.

1.2.2 Progress

The experimental work for the development of a microspherical sorbent of ZrHP embedded with fine particles of AMP was completed. This sorbent has the potential of being very effective in removing cesium from acidic supernatants with high salt concentrations, such as the ones found at INEEL. As a totally inorganic sorbent, it has the advantage of being stable in high radiation fields. ZrHP-AMP microspheres loaded with cesium could be stored for indefinite periods, or the cesium could be desorbed from the sorbent with solutions of ammonium salts.

Sample preparations of air-dried and not-dried ZrHP microspheres that were embedded with fine particles of AMP were sent to Terry Todd at INEEL for testing. The dry-weight percentages of the AMP in the microspheres were about 50, which was optimal. Sample preparations of air-dried titanium monohydrogen phosphate (TiHP) microspheres that were embedded with fine particles of potassium cobalt hexacyanoferrate (KCoCF) and sodium cobalt hexacyanoferrate (NaCoCF) were also sent. The dry-weight percentages of the KCoCF and the NaCoCF were about 18. A special preparation of KCoCF-ZrHP in which the dry-weight percentage of the KCoCF was about 50 was also sent. Cesium-removal batch tests were conducted for samples of these materials with Melton Valley Storage Tank W-27 supernatant that was acidified with nitric acid. In removing the cesium, all of the microspherical sorbents were as (or about as) effective as samples of AMP-polyacrylonitrile (PAN) sorbent that were also tested under the same conditions. The average distribution ratio (D) for the AMP-PAN samples was ~35,600 mL/g. [The AMP-PAN was obtained from F. Sebesta at the Czech Technical University in Prague, Czech Republic.] In these tests, a ratio of volume of supernatant (in milliliters) to mass of dry sorbent (in grams) of 200 was used.

A task-summary paper by J. L. Collins and K. K. Anderson entitled "Development and Testing of Spheroidal Inorganic Sorbents" was published in the *Proceedings of the Efficient Separations and Processing Crosscutting Program 1998 Technical Exchange Meeting, Augusta, Georgia, March 17-19, 1998*.

2. PROCESS CHEMISTRY AND THERMODYNAMICS

E. C. Beahm

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

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Summary: In ESW, lime treatment of the leachate initially had no effect on the formation of gel-like material. However, when the samples were examined 6 months later, the gel was no longer present. We are assessing whether lime in the wash receiving tank would be effective in controlling gel formation in the long term.

Two acid treatment tests were conducted on residue from caustic leaching of S-101 sludge. Leaching with 3 M nitric acid and limited hydrofluoric acid was not effective in dissolving the residue or in preventing solids in the leachates.

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

2.1.2.1 Control of Solids in Enhanced Sludge Washing

Lime can react with phosphate to produce a calcium phosphate and calcium fluoride. Success with lime treatment of sludge leachates and wash solutions will depend on the outcome of the competition between sodium and calcium ions to form either sodium phosphate–sodium phosphate fluoride or a calcium phosphate–calcium fluoride.

Two samples of Hanford T-104 sludge were treated simultaneously to evaluate the effectiveness of lime in preventing the formation of sodium phosphate fluoride. Both samples were leached at 75°C for 24 h with 3.9 g of 3.8 M NaOH solution per gram of sludge. The sludge residues were washed at 75°C three times. Lime was added to the filtered leachate and wash solutions of one of the samples.

Sticky solids formed in both the lime-treated and untreated leachates within an hour after they were removed from heat and allowed to approach ambient temperature. The leachates were examined periodically for several weeks, and the sticky solids persisted. However, when the

leachates were examined 6 months later, the sample that had the lime no longer had the sticky solids, but the one without lime retained a mass of gel-like material. This indicates that the initial gel formation in the limed leachate was due to the rapid formation of sodium phosphate fluoride, and, over time, this converted to calcium phosphate-calcium fluoride.

In Phase I pretreatment flow sheets, leachate and wash solutions are directed to a wash receiving tank. The entire process for one tank will take 9 to 12 months. If a concentration of lime sufficient to react with all of the phosphate, fluoride, and other materials that may react with calcium ions is maintained, the formation of gel-like phosphates would most likely be prevented. Additional tests with sludge and simulants are being run to evaluate precipitation and flocculation to control solids.

2.1.2.2 Acid Treatment

Sludge solids contain silica, aluminum, and a variety of metal ions that may participate in gels if they enter the solution during processing. In acid solutions, silica is present as silicic acid. At concentrations greater than 50–100 ppm, silicic acid polymerizes to form silica gel. The formation of silica gel may be prevented by acid treatment with a combination of nitric acid and hydrofluoric acid. Hydrofluoric acid will convert silica to the silicon hexafluoride ion, which is soluble.

One pretreatment proposal involves ESW followed by acid treatment. ESW would remove aluminum and some of the silicon and could potentially result in more effective acid treatment.

Two portions of residue from ESW of material from Hanford underground storage tank S-101 were obtained from the Sludge-Partitioning Chemistry Program (Sect. 1.1) managed by Rodney Hunt. The sludge had been leached at 70°C with 3 M sodium hydroxide solution and washed with inhibited water.

The S-101 sludge residue was treated with a combination of nitric acid and hydrofluoric acid at 75°C. One sample was treated with 10 mL per gram of residue of a solution of 3 M nitric acid and 0.6 M hydrofluoric acid. The other sample had the same leachate-to-residue ratio and nitric acid concentration but only half as much fluoride. The first sample contained enough fluoride to react with the silica in the residue and form silicon hexafluoride if no other material consumed fluoride. The second sample had half as much fluoride. These acid leaches were not effective in dissolving the residue. A significant amount of solids remained. Small solid particles formed in filtered leachates from both of the samples when they cooled to ambient temperature. In the present tests, the hydrofluoric acid concentration was kept low to see if material dissolution and prevention of solid formation could still be attained; it could not. Previous tests with sludge from SX-113 that had

not been leached with caustic found that an excess of fluoride was required for effective dissolution and solid control.

2.2 SALTCAKE DISSOLUTION (E. C. Beahm)

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Summary: A chemical species that should be included in calculations of alumina behavior in pretreatment was identified. After an assessment of thermochemical data for this compound is completed, we will transmit it to the users at Hanford.

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 Environmental Simulation Program (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

An examination of the data used in the ESP for sodium aluminate found that an additional species was needed to represent the system. This species, sodium oxide–aluminum oxide–2.5 water, is recognized in the aluminum industry, and it appears in phase diagrams associated with the Bayer process. We are assessing the thermochemical data for this compound. When this assessment is completed, we will use it in calculations of saltcake dissolution and transmit the thermochemical data to the users for possible use in ESP calculations.

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

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Summary: Experimental work on the collaboration with Dr. Gennady Voronin of Moscow State University has been completed as directed by DOE. The goal of this effort was to determine the solidification conditions of yttrium, barium, and copper oxides from their melts. These conditions include temperature, partial oxygen pressure, chemical composition of the melt, and chemical composition of the growing solids. A manuscript, which describes phase transitions and

oxygen content in the melts of $\text{YBa}_2\text{Cu}_3\text{O}_n$ (1:2:3:n) and 1:2:3:n + BaCuO_2 (1:3:4:n), has been accepted for publication by *Physica C*.

Several attempts to determine the oxidation state of copper in superconducting 1:2:3:n have been made. However, a comprehensive evaluation of all potential oxidation states at different oxygen stoichiometries has not been made. While 1:2:3:n is usually expressed in terms of the formula $\text{YBa}_2\text{Cu}^{+2}_{2+2x}\text{Cu}^{+3}_{1-2x}\text{O}_{7-x}$ ($0 \leq x \leq 0.5$), it is possible that all of the copper in 1:2:3:n is Cu^{+2} or a combination of Cu^+ and Cu^{+2} and that some oxygen is present in the form of peroxide. Our study used both oxidizers and reductants to determine the proper representation of 1:2:3:n at its different oxygen stoichiometries. Samples of $\text{YBa}_2\text{Cu}_3\text{O}_6$, $\text{YBa}_2\text{Cu}_3\text{O}_{6.36}$, $\text{YBa}_2\text{Cu}_3\text{O}_{6.64}$, and $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ have been dissolved in hydrochloric acid solutions with potassium permanganate (strong oxidizer) or sodium thiosulfate (strong reductant). An analysis of the results indicates that the best representations for $\text{YBa}_2\text{Cu}_3\text{O}_6$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6.36}$ are $\text{YBa}_2\text{Cu}_2^{+2}\text{Cu}^+\text{O}_6^{-2}$ and $\text{YBa}_2\text{Cu}_{2.72}^{+2}\text{Cu}_{0.28}^+\text{O}_{6.36}^{-2}$, respectively. The results with $\text{YBa}_2\text{Cu}_3\text{O}_{6.64}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ imply the presence of Cu^{+3} . A manuscript entitled "Oxidation States of Copper and Oxygen in Superconducting and Nonsuperconducting $\text{YBa}_2\text{Cu}_3\text{O}_n$ " will be submitted to *Superconductor Science and Technology*.

2.3.1 Purpose and Scope

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

2.3.2 Progress

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

Experimental work in collaboration with Dr. Gennady Voronin of Moscow State University has been completed as directed by DOE. The goal of this joint effort was to determine the solidification conditions of yttrium, barium, and copper oxides from their melts. These conditions included temperature, partial oxygen pressure, chemical composition of the melt, and phase and chemical composition of the growing solids. The liquidus and solidus surfaces in the Y-Ba-Cu-O system can be determined in terms of temperature, composition, and oxygen chemical potential.

The phase transitions and oxygen content in the melts of 1:2:3:n and 1:3:4:n at partial oxygen pressures of 0.1, 0.01, 0.001, 0.0001, and 0.00006 MPa have been determined experimentally. A manuscript entitled "Partial Oxygen Pressure and Temperature Effects on the Oxygen Content of the Y-Ba-Cu-O Melts" has been accepted for publication by *Physica C*.

2.3.2.2 Oxidation States of Copper and Oxygen in 1:2:3:n

With the discovery of 1:2:3:n, several attempts to determine the oxidation state of copper in superconducting 1:2:3:n have been made. However, a comprehensive evaluation of all potential

oxidation states at different oxygen stoichiometries has not been made. While 1:2:3: n is usually expressed by the formula $\text{YBa}_2\text{Cu}^{2+}_{2+2x}\text{Cu}^{3+}_{1-2x}\text{O}_{7-x}$ ($0 \leq x \leq 0.5$), it is possible that all of the copper in 1:2:3: n is Cu^{+2} or a combination of Cu^{+} and Cu^{+2} and that some oxygen is present in the form of peroxide. Our study used both oxidizers and reductants to determine the proper representation of 1:2:3: n at its different oxygen stoichiometries.

Samples of $\text{YBa}_2\text{Cu}_3\text{O}_6$, $\text{YBa}_2\text{Cu}_3\text{O}_{6.36}$, $\text{YBa}_2\text{Cu}_3\text{O}_{6.64}$, and $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ have been dissolved in hydrochloric acid solutions with potassium permanganate (strong oxidizer) or sodium thiosulfate (strong reductant). Key components from each possible formulation, with the exception of the formulas with Cu^{+3} , were treated in the same manner as the 1:2:3: n samples. The results indicate that the best representations for $\text{YBa}_2\text{Cu}_3\text{O}_6$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6.36}$ are $\text{YBa}_2\text{Cu}_2^{+2}\text{Cu}^{+}\text{O}_6^{-2}$ and $\text{YBa}_2\text{Cu}_{2.72}^{+2}\text{Cu}_{0.28}^{+}\text{O}_{6.36}^{-2}$, respectively. The results with $\text{YBa}_2\text{Cu}_3\text{O}_{6.64}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ imply the presence of Cu^{+3} . A manuscript entitled "Oxidation States of Copper and Oxygen in Superconducting and Nonsuperconducting $\text{YBa}_2\text{Cu}_3\text{O}_n$ " will be submitted to *Superconductor Science and Technology*.

2.3.2.3 Collaboration

This project has continued its collaborative effort with the Basic Energy Sciences project, which is led by Mariappan Paranthaman. After the 1:2:3: n has been prepared through the sol-gel technique, the sample was analyzed with our differential thermal analysis/thermogravimetric analysis apparatus. Since our task has performed the same experiments on 1:2:3: n samples that were prepared by conventional means, a direct comparison of the different sample preparations can be made. The results were included in a manuscript entitled "Solution Processing of $\text{YBa}_2\text{Cu}_3\text{O}_x$ Thin Films." This paper has been accepted for publication in the Materials Research Society proceedings entitled *Chemical Aspects in Electronic Ceramics Processing*.

3. MSRE REMEDIATION STUDIES

L. M. Toth

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

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Summary: The second test run of the full-scale conversion prototype using a NaF trap loaded with 1.7 kg of UF_6 is complete. During the test run, design changes were identified, and

modifications in the prototype are being implemented. The facility selection process was completed, and hot cell D in Building 4501 was chosen. A task plan tailored to the 4501 facility is being drafted. Work has started on the design of facility modifications, safety analyses, nuclear criticality safety evaluation, and a transportation plan.

3.1.1 Purpose and Scope

The Molten Salt Reactor Experiment (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 , as well as its transport from the fuel salt, was unexpected. These samples proved that these gaseous products had moved through the piping to a charcoal bed since the reactor was shut down. After this finding, a multiyear project was launched to remediate the potentially hazardous conditions generated by the movement of fissile material and reactive gases.

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

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

3.1.2 Progress

Samples from the second test run of the full-scale conversion prototype are being analyzed. Modifications identified during the second test run are complete. A surrogate batch of uranium-bearing charcoal is being prepared by reacting activated charcoal with a 5:1 F_2/UF_6 gas mixture. The uranium-laden fluorinated charcoal will be denatured with ammonia to simulate the filter media that will be removed from the charcoal bed. A process of sequential oxidation using oxygen followed by fluorine is being tested at laboratory scale, with the goal of recovering the uranium from the charcoal in a closed subatmospheric system. Radiolysis experiments have been initiated to evaluate the radiolytic yields from uranium oxides that contain fluoride impurities. Results from these experiments will be used to establish a residual fluoride limit for the converted uranium removed from the MSRE. For the initial experiments, two samples of uranyl fluoride (one dry and one loaded with water) were placed in the Chemical Technology Division's (CTD's) ^{60}Co

irradiator. Pressure transducers are being used to monitor the pressure in the sample containers and, after removal from the irradiator, gas samples will be analyzed.

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

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Summary: Throughout February and March, operations took place resulting in the denaturing of potentially explosive carbon-fluoride compounds in the MSRE activated charcoal bed. The denaturing process reacted ammonia with low-temperature fluorinated charcoal, partially laden with trapped $^{233}\text{UF}_6$ to yield stable compounds. This stabilization of the potentially explosive carbon-fluoride compounds greatly increased the safety associated with the MSRE and will allow the removal of the uranium to proceed. This proprietary process was invented, developed, and demonstrated by CTD personnel, who also participated in guiding and carrying out the actual operations as part of a program team involving participants from many other organizations.

3.2.1 Purpose and Scope

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

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

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

3.2.2 Progress

Chemical operations to denature the fluorinated charcoal in the ACB were completed. The "soak" period, in which the ACB was isolated and pure ammonia was periodically added to ensure

complete reaction with the fluorinated charcoal, was initiated on March 6, 1998. This period was completed on March 24, and removal of ammonia was initiated, completing the DOE milestone. After removal of ammonia, the ACB will be backfilled with inert gas. DOE approved the unresolved safety question to suspend the Technical Safety Requirements and Basic for Interim Operations controls on the charcoal bed cell atmosphere as a result of the successful denaturing of the ACB. The manipulator shield plate and ventilated enclosure crane have been received on-site, and the crane has been installed over the ACB mockup. The crane will be used in the mockup to remotely test the installation and operation of the pneumatic vacuum system. The crane and associated remote tools will also be used in the training of the operators who will perform the actual uranium deposit removal.

3.3 SALT DISPOSITION STUDIES (D. F. Williams, A. S. Icenhour, and L. M. Toth)

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Summary: New radiolysis experiments were initiated to establish the radiolytic stability of various forms of uranium oxyfluoride solids. This work is being pursued in parallel to the ongoing radiolysis studies on MSRE simulant salts.

3.3.1 Purpose and Scope

Understanding the radiolysis of MSRE fuel salt and uranium oxides that are derived from conversion of the recovered UF_6 is necessary in order to proceed with remediation and permitted storage of the radioactive MSRE materials. 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.

3.3.2 Progress

Radiolysis experiments have been initiated to evaluate the radiolytic yields from uranium oxides that contain fluoride impurities. Results from these experiments will be used to establish a residual fluoride limit for the converted uranium removed from the MSRE. For the initial experiments, two samples of uranyl fluoride (one dry and one loaded with water) were placed in the CTD's ^{60}Co irradiator. Pressure transducers are being used to monitor the pressure in the sample containers, and, after removal from the irradiator, gas samples will be analyzed by Fourier transform infrared (FTIR) and mass spectrometry.

The present focus for the salt radiolysis task is an irradiation of the largest possible plug of simulant salt (~1 kg) in order to support the most realistic simulation of melting and treating the fuel salt. Previous work has been restricted to 30-g granular batches. All of the materials for the preparation and irradiation of a large plug of MSRE fuel salt simulant have been assembled except for the new, larger irradiation vessel.

4. CHEMISTRY RESEARCH

L. M. Toth

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

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

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 in mixed waste characterization, treatment, and disposal.

4.1.2 Progress

Templating synthesis using metal ions is a well-known technique to assemble small molecules into macrocyclic ligands. These macrocyclic ligands are expected to have strong affinities toward the templating metal ions. The functionalized silicon alkoxide monomers thus synthesized form hybrid polymers upon hydrolysis with tertamethyl orthosilicate. Hybrid silica sorbents templated by UO_2^{2+} and Ni^{2+} have been prepared. New glasses have been prepared with diethylphosphatoethyltriethoxysilane and diethyl(trimethylsilylmethyl)malonate as monomers. The protonation method used previously was adopted to efficiently remove Cu^{2+} , UO_2^{2+} , and Ni^{2+} template ions from our sol-gel glasses. Copper-, nickel-, and uranyl-free imprinted glasses were obtained by soaking the doped glasses with nitric acid overnight. Tests of adsorption capacities of these glasses are under way.

4.2 URANYL ADSORPTION CAPACITY ON MESOPOROUS SORBENTS (S. Dai, Y. Shin, and M. Burleigh)

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Summary: The difference in uranyl adsorption between mesoporous and microporous silica sorbents has been observed and rationalized. The new mesoporous silica sorbents of TiO_2 and ZrO_2 have been demonstrated to be very effective in weakly acidic solutions.

4.2.1 Purpose and Scope

Two classes of porous materials that are used extensively as heterogeneous catalysts and adsorption media are microporous (20-Å pore diameter) and mesoporous (20- to 500-Å) inorganic solids. The mesoporous materials have chemical structures that allow molecules to access large internal surfaces and cavities, thereby greatly enhancing catalytic activity and adsorption capacity. Considerable synthetic effort has been devoted to developing frameworks with pore diameters within the monodispersed mesoporous range. The discovery of new silica-based mesoporous materials (MCM41) by Mobil researchers has attracted great interest because these materials expand typical molecular sieves into the large-pore range, which generates the potential for applications in catalysis,

separation, and adsorption of bulky materials. In this quarter, we studied adsorption kinetics and adsorption capacity of mesoporous sorbents (TiO_2 and ZrO_2) for binding uranyl (UO_2^{2+}) ions.

4.2.2 Progress

Mesoporous ZrO_2 and TiO_2 were prepared by a neutral (SOIO) templating route based on hydrogen bonding and self-assembly between neutral primary amine surfactants (SO) and neutral inorganic precursors (IO). In a typical preparation, $\text{Si}(\text{OEt})_4$, ZrCl_4 , or $\text{Ti}(\text{O}i\text{Bu})_4$ was slowly added to a stirred solution of amine in ethanol and distilled water. Proper molar composition was 1.0 $\text{Si}(\text{OEt})_4$, ZrCl_4 , or $\text{Ti}(\text{O}i\text{Bu})_4$:0.27 dodecylamine:9.0 EtOH:30.5 H_2O . The final reaction mixture was aged at room temperature for 18 h, filtered, washed with distilled water, and dried in air. The template was removed by calcination at 590°C for 4 h or EtOH extraction (reflux). Solvent extraction was repeated three times. The N_2 adsorption-desorption isotherms were measured at 77 K. Arsenazo III (2,2'-[1,8-dihydroxy-3,6-disulfonaphthylene-2,7-bisazo] bisbenzenearsonic acid) was used to determine uranyl concentration adsorbed on the sol-gels. The photometric determination of uranyl concentration was carried out at pH 1.5–3.3 using a 1.0 Cm quartz cell.

4.3 FAA PROJECT ON EXPLOSIVE DETECTION (S. Dai and C. C. Morrow)

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Summary: We have successfully attracted funding from the Federal Aviation Administration to develop explosive sensors based on surface-enhanced Raman spectroscopy (SERS) sensors developed by us and our colleagues in CASD for radionuclide analysis. Mr. C. C. Morrow, who has an M.S. degree in chemistry, has been hired to work on this project through the Oak Ridge Institute for Science and Education.

A Gilson robotic system for combinatorial chemical synthesis of sol-gel sensors has been purchased and successfully installed. A functionalized SERS sol-gel film has been developed. The unique property of this new film is that its response sensitivity toward anions and cations can be switched on and off by pH.

4.4 SOLUBILITIES OF UO_3 IN CARBONATE BUFFER SOLUTIONS AT HIGH TEMPERATURE ($>1000^\circ\text{C}$) (S. Dai and C. C. Morrow)

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Summary: Experiments conducted in the last year indicated that the UO_3 solid phase is not stable at temperatures $>1000^\circ\text{C}$. This has been tentatively attributed to the conversion of UO_3 to carbonate species, thereby changing the total carbonate concentration and generating uranyl carbonate precipitation. This prompted us to investigate solubilities of two uranyl carbonate compounds— UO_2CO_3 and $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$. These compounds are known to be solid phases in equilibrium with uranyl carbonate solutions at room temperature. We have synthesized and characterized the compounds during this period. The solubility of $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ has been measured as function of time at 1200°C through the spectrophotometric measurement technique developed last year.

4.4.1 Purpose and Scope

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

4.4.2 Progress

The experiment lasted for about 1.5 months and was characterized by two regimes. During the first 2 d, the concentration of the uranyl carbonate complex in the buffer solution ($0.1\text{ M NaHCO}_3/\text{Na}_2\text{CO}_3$) increased with time; afterwards, the uranyl carbonate concentration in the buffer solution decreased steadily. Finally, no detectable uranyl complexes were observed in the solution. Infrared measurements of the reagent solids and the solids from the experiment reveal two different uranyl solid phases. This indicates that the $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ solid phase is not stable at 1200°C in this system.

4.5 PUBLICATIONS

S. Dai, M. Burleigh, J. M. Simonson, R. E. Mesmer, and Z.-L. Xue, "Application of Chemometric Methods in UV-Vis Absorption Spectroscopic Studies of Uranyl Ion Dimerization Reaction in Aqueous Solutions," *Radiochimica Acta*, in press.

5. BIOTECHNOLOGY

B. H. Davison

5.1 ADVANCED BIOREACTOR SYSTEMS FOR ALCOHOL FUEL PRODUCTION (N. P. Nghiem, B. H. Davison, M. S. Krishnan, and M. M. Blanco-Rivera)

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Summary: Experiments have been completed on the development of a process using separate saccharification and fermentation of solubilized cornstarch. Immobilized glucoamylase and immobilized *Zymomonas mobilis* were used in a packed- and a fluidized-bed reactor, respectively. Almost complete (greater than 95%) conversion was achieved, which resulted in an effluent ethanol concentration of 70 g/L. The overall productivity was 28 g/(L·h), which was ten times higher than that normally obtained in a typical ethanol fermentation process [~ 3 g/(L·h)].

5.1.1 Purpose and Scope

The objective of this project is to develop and demonstrate advanced fermentation and separation systems for enhanced biofuel ethanol production that operate continuously and have high productivity, high yield, and good operability with reduced energy requirements. The feedstocks examined in this project include cornstarch, lignocellulosic hydrolysates, and gasified biomass.

5.1.2 Progress

A fermentation process for ethanol production by immobilized *Zymomonas mobilis* in a fluidized-bed reactor (FBR) was proposed and approved for development by the industrial partner (Morris Ag-Energy). In the proposed process, centrifugation or filtration will remove the solids in the cooked cornstarch. The solid-free liquid then will be used for ethanol production in the FBR. The water recycled from the distillation operation will be used to wash the solids to recover the residual starch. The solids will then again be removed by centrifugation or filtration and the wash water recycled to the cooker for use in the hydrolysis of the dry-milled corn flour.

Experiments have been completed on the development of a process using separate saccharification and fermentation. In the first step, saccharification of soluble starch was performed in a packed-bed reactor containing immobilized glucoamylase (from Genencor International). Complete hydrolysis to glucose was achieved at 0.5-h residence time. In the second step, fermentation of the glucose solution was performed in an FBR containing immobilized *Z. mobilis*. At a residence time of 2 h, greater than 95% conversion of the glucose solution was achieved, which gave an ethanol concentration in the effluent of 70 g/L. The overall productivity, therefore, was

28 g/(L·h), which was one order of magnitude higher than that typically obtained in the ethanol industry with the batch process [~ 3 g/(L·h)]. Discussion of the results with Morris Ag-Energy is being continued.

5.1.3 Publication

M. Y. Sun, N. P. Nghiem, B. H. Davison, O. F. Webb, and P. R. Bienkowski, "Production of Ethanol from Starch by Co-immobilized *Zymomonas mobilis*-Glucoamylase in a Fluidized-Bed Reactor," *Appl. Biochem. Biotechnol.* **70-72**, 429-39 (1998).

5.2 ALTERNATIVE FEEDSTOCKS FOR CHEMICALS AND PETROLEUM REFINING INDUSTRIES: PLASTICS, FIBERS, AND SOLVENTS FROM BIOLOGICALLY DERIVED SUCCINIC ACID (B. H. Davison, N. P. Nghiem, C. K. McKeown, and M. Rodriguez, Jr.)

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Summary: Scaleup of the fermentation process for succinic acid production was completed. Results obtained in 75- and 500-L fermenters showed very good reproducibility. An effort to commercialize succinic acid production by the industrial partner Applied CarboChemicals (ACC) has continued with discussion between ACC and several chemical manufacturers.

5.2.1 Purpose and Scope

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

5.2.2 Progress

5.2.2.1 Programmatic and Industrial Partnering

The work of the cooperative research and development agreement (CRADA) between the four laboratories (Argonne National Laboratory, National Renewable Energy Laboratory, ORNL, and PNNL) and ACC on the "Production of Chemicals from Renewable Feedstocks" continued on schedule. The team held regular teleconference calls that included the industrial partner. ACC is

continuing its efforts to commercialize the process. Discussion was held between ACC and several companies that manufacture industrial chemicals.

5.2.2.2 Biocatalyst and Fermentation Development

For the successful scaleup of the fermentation process at the 500-L scale (reported last quarter), the team received a Special Event Award in January 1998. The letter of approval for the patent application for the fermentation process has been received. Issuance of the patent is expected within the next 3 months. The development of a semicontinuous cell recycle process aimed at doubling the productivity by using higher cell concentration has begun. The system, consisting of a 2-L fermenter and a microfiltration unit for cell concentration and recycle, has been set up and tested. To prepare for the cell recycle experiments, two baseline experiments have been performed.

5.3 BIOFILTRATION OF VOLATILE POLLUTANTS: FUNDAMENTAL MECHANISMS FOR IMPROVED DESIGN, LONG-TERM OPERATION, PREDICTION, AND IMPLEMENTATION (B. H. Davison, K. T. Klasson, and J. W. Barton)

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Summary: Biofiltration systems can be used for treatment of volatile organic compounds (VOCs); however, the systems are poorly understood and are currently operated as "black boxes." Common operational problems associated with biofilters include fouling, deactivation, and overgrowth, all of which make them ineffective for continuous, long-term use. The objective of this investigation is to develop generic methods for long-term stable operation, in particular by using selective limitation of supplemental nutrients while maintaining high activity. As part of this effort, we will provide deeper fundamental understanding of the important biological and transport mechanisms in biodestruction of sparingly soluble VOCs and extend this approach and mathematical models to additional systems of high priority to Environmental Management (EM)—direct degradation and cometabolic degradation of priority pollutants such as BTEX (benzene, toluene, ethylbenzene, and xylene) and chlorinated organics.

5.3.1 Progress

A comprehensive two-dimensional predictive model was developed to elucidate mass transfer and kinetic limitations in biofiltration systems and will be extended to a variety of columnar biofiltration systems by changing appropriate parameters. This user-friendly model/program can also be installed and run independently on any IBM-compatible personal computer using Microsoft Windows 95/98. Fundamental measurements of Henry's law coefficients for a variety of sparingly soluble alkanes in biomass were made; results indicated that these compounds have substantially higher solubilities in aqueous biomass than in pure water. Since predictive calculations for bioprocesses are strongly affected by the magnitude of the Henry's law parameters, new

correlations/measurements are needed to compensate for this effect. Isolation of the VOC-degrading microorganism present in the trickle-bed consortium was accomplished. Identification is pending.

5.3.2 Publications

A. F. Francisco, J. W. Barton, K. T. Klasson, and B. H. Davison, "Nutrient Limitation Effects on a Microbial Consortium in Trickle-Bed Bioreactors," submitted for publication.

J. W. Barton, B. H. Davison, K. T. Klasson, and C. C. Gable III, "Estimation of Mass Transfer and Kinetics in Operating Trickle-Bed Bioreactors for Removal of VOCs," accepted for publication in *Environmental Progress*.

K. T. Klasson, B. H. Davison, J. W. Barton, and J. E. Jacobs, "Removal of Chlorinated and Non-chlorinated Alkanes in a Trickle-Bed Reactor," accepted for publication in the proceedings of the Air & Waste Management Association 91st Annual Meeting & Exhibition.

J. W. Barton, X. S. Zhang, K. T. Klasson, and B. H. Davison, "Predictive Mathematical Modeling of Trickling Bed Biofilters for Elucidating Mass Transfer and Kinetic Effects," accepted for publication in the proceedings of the Air & Waste Management Association 91st Annual Meeting & Exhibition.

J. W. Barton, S. M. Hartz, K. T. Klasson, and B. H. Davison, "Microbial Removal of Alkanes from Dilute Gaseous Waste Streams: Mathematical Modeling of Advanced Bioreactor Systems," accepted for publication in *Journal of Chemical Technology and Biotechnology*.

5.4 CHARACTERIZATION OF CHEMICALLY MODIFIED ENZYMES FOR BIOREMEDIATION REACTIONS (E. N. Kaufman, P. Wang, and C. A. Woodward)

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Summary: Ligninperoxidase (LiP) was modified by polyethylene glycol (PEG) and examined for the degradation of pentachlorophenol (PCP) in water-solvent mixtures. The catalytic efficiency of PEG-LiP for PCP degradation in the presence of 15 vol % acetonitrile was 11-fold higher than that of the native enzyme in pure aqueous buffer, as tested in an unoptimized continuous reactor system.

5.4.1 Purpose and Scope

Remediation processes frequently involve species possessing limited solubility in water. We are interested in novel strategies that use molecularly engineered enzymes with enhanced activity and stability for the remediation of recalcitrant compounds in organic media. It is expected that continued studies using the demonstrated strategy will lead to a wide array of large-scale,

environmentally benign, and cost-effective processes for the biodegradation of recalcitrant organic pollutants.

5.4.2 Progress

PCP is only slightly soluble in water, with a solubility of 14 mg/L (or 0.052 mM) at 20°C. In the current work, PCP solubility in pH 4.2 (an optimized pH for the degradation of PCP catalyzed by LiP, as determined in this study) buffer solutions containing various amounts of MeCN was measured at room temperature (22°C). The solubility of PCP increases exponentially with MeCN content, and the addition of 15% MeCN enhances the solubility of PCP by over one order of magnitude (from 0.06 to 0.65 mM).

The chemical modification of LiP was examined in terms of the titratable free amine groups of the enzyme molecules. Titration tests of these groups showed that 46% of the $-NH_2$ groups of native LiP disappeared after the modification reaction. As a result, about 12 PEG molecules, on average, were attached to each LiP. The modification did not result in any loss of enzyme activity, as expected for most other chemical modification procedures, and the PEG-LiP activity was the same as that of native LiP as tested with veratryl alcohol. The PEG-LiP was partially soluble in pure MeCN, while no native LiP was found dissolved in MeCN.

The effect of MeCN content (1–30 vol %) was examined for the PCP degradation catalyzed by LiP. Overall, the activity (as measured by initial reaction rate) of PEG-LiP was higher than that of native LiP. PEG-LiP also showed a better solvent tolerance, but both enzymes lost activity at 30% MeCN. As the concentration of MeCN increased from 1 to 10%, the initial reaction rate with native LiP decreased by ~50%, while over 90% of the PEG-LiP activity was retained. Intrinsic activities in solutions containing 1 and 10% MeCN were determined. Interestingly, the activity of PEG-LiP in the presence of 10% MeCN is about 2.5-fold higher than that of native LiP.

Experiments with PCP concentrations close to saturation with different amounts of MeCN (up to 15 vol %) were performed. Enzyme and peroxide were added into the reactor continuously by a syringe pump to reduce the enzyme inactivation effect by peroxide. In pure buffer, the native and modified enzyme gave similar results, with an overall degradation rate of 44 mol PCP·mol LiP⁻¹·h⁻¹. If one compares the data of native LiP in pure buffer with those of PEG-LiP with 15% MeCN, the overall enhancement is 11-fold (from 44 to 480 mol PCP·mol LiP⁻¹·h⁻¹) as a result of the augmentation in both PCP solubility and enzyme activity.

5.4.3 Publications

- P. Wang, C. A. Woodward, and E. N. Kaufman, "Poly(ethylene glycol) Modified Ligninase Enhances Pentachlorophenol Biodegradation in Water-Solvent Mixtures," *Biotechnology Progress*, submitted (1998).
- M. D. Bredwell, P. T. Selvaraj, M. H. Little, R. M. Worden, and E. N. Kaufman, "Biological Reduction of Sulfur Dioxide with Coal Synthesis Gas as a Feedstock: Improving Reactor Productivity Through Enhanced Mass Transport," *Biotechnology Progress*, submitted (1998).
- C. Tsouris, A. P. Borole, and E. N. Kaufman, "Hydrodynamic Behavior of an Electrically Driven Bioreactor for Oil Desulfurization," *Industrial and Engineering Chemistry Research*, submitted (1998).
- E. N. Kaufman, A. P. Borole, R. Shong, J. L. Sides, and C. Juengst, "Sulfur Specificity in the Bench Scale Biological Desulfurization of Crude Oil by *Rhodococcus* IGTS8," *Applied Microbiology and Biotechnology*, submitted (1998).
- E. N. Kaufman and A. P. Borole, "Comparison of Stirred Batch and Electro-Spray Reactors for the Biodesulfurization of Dibenzothiophene in Crude Oil and Hydrocarbon Feedstocks," *Applied Biochemistry and Biotechnology*, in press (1998).

5.5 FUNDAMENTAL BIOPROCESSING RESEARCH FOR COAL APPLICATIONS (E. N. Kaufman, P. T. Selvaraj, J. R. Parrott, and M. Rodriguez)

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Summary: Bioreactor design for the conversion of coal synthesis gas to ethanol has been investigated with efforts focusing upon the augmentation of sparingly soluble syn-gas components. The use of immobilized-cell trickle-bed reactors increased the mass transport coefficient of CO to the reactor by twofold, resulting in a syn-gas utilization of $47 \text{ mmol}\cdot\text{h}^{-1}\cdot\text{L}^{-1}$. Solvent systems have also been investigated to increase syn-gas bioavailability.

5.5.1 Purpose and Scope

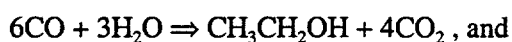
The purpose of this program is to gain a fundamental understanding and sound technical basis for evaluating the potential roles of innovative bioprocessing concepts for the utilization and conversion of coal. The aim is to explore the numerous ways in which advanced biological processes and techniques can create new opportunities for coal utilization or replace more conventional techniques by using milder conditions with less energy consumption or loss.

Biotechnology is likely to be important in coal utilization and conversion in several ways. These include potential bioprocessing systems such as conversion of coal synthesis gas to liquid fuels and chemicals, biocatalytic removal of SO_x and NO_x from coal combustion off-gas,

environmental control technology for the removal or destruction of hazardous materials in process effluents and/or solid residues, and removal and utilization of CO₂ from combustion off-gas. Effective bioprocesses for such applications will require detailed knowledge of the biological process mechanisms and advanced bioreactor technology that can be optimized for high productivity, as well as supporting upstream and downstream processes that will allow an effective integrated bioprocess.

5.5.2 Progress

Continuous stirred-tank reactors and trickle-bed reactors were operated using *Clostridia ljungdahlii* to convert synthesis gas (36% H₂, 47% CO, 10% CO₂) into ethanol via these reactions:



Mass transport coefficients, gas- and liquid-residence times, and gas utilization were assessed in each reactor. The trickle-bed reactor was seen to increase the rate of mass transport of CO and achieved a higher productivity with much reduced gas- and liquid-residence times.

Reactor configuration ^a	LRT ^a (h)	GRT ^a (h)	CO utilization (mmol·h ⁻¹ ·L ⁻¹) ^b	H ₂ utilization (mmol·h ⁻¹ ·L ⁻¹) ^b	K _L a ^{CO} (h ⁻¹)
CSTR with microfiltration	83	1.23	9.2 (65)	5.7 (50)	58
TBR with Bio-Sep beads	3.4	0.14	46.5 (80)	17.8 (40)	130

^aLRT = liquid-residence time; GRT = gas residence time; CSTR = continuous stirred-tank reactor; TBR = trickle-bed reactor.

^bParenthetical values indicate percent utilization.

Initial work utilizing solvent systems to further enhance the mass transport of synthesis gas to the biocatalyst has indicated that hexadecane may serve to increase gas utilization with no impact upon biocatalyst viability.

5.6 NOVEL DRY-STATE BIOCATALYSIS FOR AIRBORNE HYDROCARBONS (B. H. Davison, K. T. Klasson, and J. W. Barton)

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Summary: We have hypothesized that enzymes that are capable of degrading certain volatile organic contaminants would be able to degrade these compounds more effectively by direct contact with the gaseous vapors. These "dry" enzymes, which exist in the absence of free water, should have reduced mass transfer resistance. In addition, immobilized dry-state systems should possess additional thermostability and durability in comparison with their aqueous counterparts. We have begun examinations of three model systems to test our theories, as well as to identify, quantify, and qualify the parameters necessary for turning these theories into viable processes. In particular, we are testing dry-state enzymes for removal/destruction of chemical warfare agents and volatile organic contaminants, with some effort made to investigate this technique as an alternative means of producing commodity chemicals. Substantial effort has been directed toward developing safe protocols for experiments with these compounds.

5.6.1 Progress

Tanya Kuritz (of the ORNL Life Sciences Division) has successfully expressed methyl parathion hydrolase in *Escherichia coli* bacteria. We have obtained a variety of chemical warfare agent simulants, including methyl parathion, to examine the potential for removing these compounds using dry-state catalysis; in addition, we have updated our analytical techniques to test for organo-phosphate compounds using flame photometric detection. A necessary petition made to DOE slowed work on the simulants themselves; the petition, which was granted near the end of March, allows subcontractors working in the laboratory near or on this project to receive proper medical monitoring.

We have also begun examination of whole-cell enzyme catalysis in dry (no free-flowing liquid) batch systems and have found that degradation of volatile organics by one model organism is strongly dependent on humidity and, we hypothesize, pH. Experiments were conducted in sealed test vials with whole cells immobilized on filter paper and suspended above a saturated salt solution. We are continuing to examine this system to determine the important operating parameters, including longevity and pH control. The whole cell being used for these studies was first isolated in January 1998 and is capable of removing a wide range of organic and chloroorganic gases.

In another model system (lipase), we have found that dry-enzyme activity is strongly dependent on both temperature and humidity. At very low humidity (water activity), the enzyme has been found to be active with enhanced thermostability. At higher humidities, the enzyme becomes

more active but is less stable at higher-temperature regimes. These facts suggest that the system could be optimized to take advantage of competing effects.

5.6.2 Publications and Outside Contacts

These and other results from this phase of the project are to be presented at the 20th Symposium on Biotechnology for Fuels and Chemicals, to be held May 3–7, 1998, in Gatlinburg, Tennessee. We are submitting a manuscript for peer-reviewed journal publication to accompany this presentation. We have made two academic contacts who have shown strong interest in collaborating with us on future projects. Dr. Michael Adams of the University of Georgia–Athens has agreed to provide us with crude enzymes isolated from plants that can degrade a variety of organophosphates (in the aqueous phase). Dr. Ashok Mulchandani of the University of California at Riverside, who has worked extensively with aqueous biological destruction of chemical warfare agent simulants in various reactor systems, has also expressed interest in collaboration.

5.7 REMOVAL OF HETEROATOMS FROM CRUDE OIL (E. N. Kaufman, A. P. Borole, and J. R. Parrott)

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Summary: Biocatalysts with widely differing hydrophobicities were characterized in terms of the quality and persistency of the emulsions they formed with both crude oil and model organic systems. Crude oil of varying viscosity was also tested in the emulsion-phase contactor to determine the ranges of oil properties where spraying is feasible. Due to the proprietary nature of this project, research progress is not reported in detail.

To reduce its sulfur content, petroleum is currently treated thermochemically, a process that is energy intensive. Our goal is to develop a cost-effective and environmentally acceptable biological process for the removal of organic sulfur from hydrocarbon feedstocks. With our five CRADA partners—Baker Petrolite, Chevron, Energy Biosystems, Exxon, and Texaco—we are developing both biocatalysts and bioreactors for crude oil desulfurization.

6. SEPARATIONS AND MATERIALS SYNTHESIS

D. W. DePaoli

6.1 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. Progress has been made in several areas, including (1) drop deformation and breakup from a capillary tube in liquid-air and liquid-liquid systems, (2) wetting and stability of drops on solid surfaces, (3) electric field simulations, (4) spraying and mixing in electrohydrodynamic flows, and (5) aggregation of colloidal particles in reactive solutions and under magnetic fields.

6.1.1 Purpose and Scope

This program is composed 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.

6.1.2 Progress

6.1.2.1 Drop Deformation and Breakup

Work has continued on simulating the dynamics of drop formation and breakup from a capillary tube into air or another immiscible liquid using the volume-of-fluid and continuous-surface-force methods. The results are presented in two manuscripts that have been submitted to the *Journal of Fluid Mechanics* and *Chemical Engineering Science*.

6.1.2.2 Wetting and Stability of Drops on Solid Surfaces

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

6.1.2.3 Spraying and Mixing in Electrohydrodynamic Flows

Discussions were conducted with C. S. Daw of the ORNL Engineering Technology Division and K. Nguyen and D. Bruns of The University of Tennessee regarding potential collaborations on inverse electrostatic spraying. This topic provides an interesting extension to their previous studies of nonlinear bubble formation, since the applied electric field is an additional control variable.

6.1.2.4 Particle Interactions Under Magnetic Fields

The aggregation of colloidal magnetic particles has been investigated in collaboration with Professors S. Grant of the University of California (UC) at Irvine and S. Yiacoumi of the Georgia Institute of Technology. Scarlet Relle, Ph.D., a student at UC-Irvine, visited ORNL to study the formation of chains by colloidal superparamagnetic particles under magnetic fields. Her objective was to obtain experimental data in order to test whether scaling theory applies to the chain-length distribution. Experimental data were successfully obtained and are currently being analyzed by S. Relle. In parallel, experiments were conducted to observe the transition from three-dimensional aggregates to one-dimensional chains as the magnetic field was increased. These experiments are still in progress. Diffusion- and reaction-limited models being developed at Georgia Tech are used to simulate particle aggregation and calculate the fractal dimension of the aggregates. Breakup of chains by removing the magnetic field is also investigated for various conditions of pH, ionic strength, magnetic field strength, and the presence of surfactants. These studies are relevant to wastewater treatment techniques and the behavior of magnetorheological fluids.

6.1.2.5 Particle Interactions in Reactive Systems

The behavior of sorbent alumina particles in copper solutions has been experimentally investigated. In these experiments, the objective is to observe surface-charge modification during sorption and its effect on aggregation kinetics of the sorbent particles. Results were similar to those previously obtained for ferric oxide particles. The sorption process is pH dependent, with the uptake

increasing as the initial pH is increased. The equilibrium pH was higher than the initial pH in the acidic range and lower than the initial pH in the basic range. A large increase in the zeta potential of the particles was also observed during sorption. This increase is due to surface-charge neutralization due to metal ion uptake. Particle destabilization occurred as a result of metal ion sorption. The objective of future work is to determine conditions under which sorption of metal ions destabilizes the particles and develop unified models to predict kinetics of metal ion sorption and aggregation of sorbent particles.

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

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Summary: We have received several of industrial requests for our newly developed methods in ultrafine monodispersed particle synthesis, and various samples were prepared for industrial evaluation. Concerning aspects of fundamental research, we have demonstrated the feasibility of sol-gel processing using inorganic precursor salts. In addition to investigations involving zirconia, careful studies were conducted on hydrous titania formation. The high-temperature X-ray diffraction (HRD) studies of nanocrystalline strontium titanate were completed. A study of supported zeolite membrane was initiated via collaboration with the Chemical Engineering Department of the University of Cincinnati.

6.2.1 Purpose and Scope

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

Our current emphasis lies with the chemistry, reaction engineering, colloidal/interfacial sciences, and materials sciences in three major wet-chemical systems: (1) homogeneous precipitation in inorganic salt solutions of mixed solvent; (2) forced hydrolysis via hydrothermal processing of inorganic salt aqueous solutions; and (3) acid- or base-catalyzed hydrolysis and condensation of organometallic compounds (such as alkoxides) in water-alcohol solutions. Experiments utilize several specially developed techniques, including real-time dynamic light scattering (DLS), rapid-mixing flow cell coupled with FTIR and small-angle X-ray scattering (SAXS), as well as high-temperature XRD, electron microscopy, Raman spectroscopy, and electrostatic spraying.

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

6.2.2 Progress

Studies on nucleation and growth of particles in mixed-solvent solutions were extended to the formation of hydrous titania from titanium tetrachloride precursor. Nearly perfect submicron microspheres were obtained. Scanning electron microscopy photographs show that the microspheres are aggregates of smaller primary particles, indicating that the forced hydrolysis reactions and physical properties of the solvent played equally important roles in the formation of titania microspheres. Chemical conversion of hydrous titania to barium titanate proved to be possible and did not change the size and morphology of the submicron-sized microspheres. The effect of reaction conditions on the conversion kinetics is under investigation. We have responded to many industrial requests for the particle synthesis methods we have developed. Various titania particles were synthesized for DuPont's evaluation for potential pigment applications.

In situ growth of zeolite membrane on a substrate and related high-temperature XRD characterizations (such as phase transformation and residual stress during calcination) were conducted through collaboration with Professor J. S. Lin at the University of Cincinnati. Silicalite or ZSM-5 zeolite are usually synthesized by using the template tetrapropylammonium hydroxide (TPA): $(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{NOH}$. This template blocks the channels in the as-synthesized zeolite crystal and thus needs to be removed (become activated). Heat treatment (calcination at 400–450°C) is the common method of activating the silicalite/ZSM-5 zeolites. During calcination, TPA decomposes at temperatures of ~380–400°C and the crystalline framework contracts. In the case of the supported silicalite membrane, the support (α -alumina or yttria-stabilized zirconia) expands in the process of calcination. Consequently, the mechanical stress imposed on the zeolite layer (which shrinks on calcination) by the support phase (which expands during the calcination according to its thermal expansion coefficient) will increase. This mechanical stress can cause crack formation in the zeolite layer and therefore damage the membrane. This results in the low success rate of synthesis of high-quality zeolite membranes. In this study, we investigated variation in the silicalite lattice parameter during calcination and the development and evolution of mechanical stress in the zeolite layer during heat treatment. No work of this type has previously been reported.

We continued the research on nanocrystalline (Ba,Sr)TiO₃ synthesis by the autoignition method via collaboration with Professor Bhaduri at the University of Idaho. The process uses a redox reaction between suitably chosen oxidizers and fuels. This study addressed the issue of formation of intermediate products leading to the final product. Metallic nitrates were used as oxidizers, and urea was used as the fuel. We completed the high-temperature XRD data analysis to understand how the synthesis conditions affect the crystallization and phase transformations of these ceramics. The results show how the reactants can be optimized.

6.3 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-equilibrium, liquid-liquid-equilibrium, 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.

6.3.1 Purpose and Scope

The primary objective of this project is to enhance separations of mixtures by applying an electric field across an interface between two phases. Enhancement in separation may be 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.

6.3.2 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

decreased when the electrical current was increased. An interesting result, however, was that the field strength did not play a significant role. It was found that the applied voltage, rather than the ratio of voltage to distance (or field strength), controlled the effect. By solving Maxwell's equations, Jim Hylton of the ORNL Instrumentation and Controls Division showed that, at short electrode separation 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 order to prevent liquid masses at the interface from reaching the electrode in the vapor phase, we did not place the electrodes very close to the interface; therefore, all our experiments were conducted under 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. In order to further investigate this hypothesis, spectroscopic studies are planned for the next quarter.

6.4 MAGNETIC-SEEDING FILTRATION (D. W. DePaoli and C. Tsouris)

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Summary: Efforts continued to distribute the results of this project in a timely manner through peer-reviewed publications. One manuscript was submitted for publication this quarter.

6.4.1 Purpose and Scope

This project is focused on the development of magnetic-seeding filtration for the enhanced removal of magnetic and nonmagnetic particulates from DOE waste liquids. The technology involves the addition of a small amount of magnetic seed particles (such as naturally occurring iron oxide) to a waste suspension, followed by magnetic filtration. This technology is applicable to a wide range of liquid wastes, including groundwater, process waters, and tank supernatants.

6.4.2 Progress

With the carryover funding remaining in this EM-50 project, efforts were focused on distributing the results in a timely manner through peer-reviewed publications. One manuscript was prepared and submitted to the *Journal of Colloid and Interface Science*. The magnetic-seeding-filtration task ended this quarter.

6.5 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.

6.5.1 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, which 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 rise at a lower 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.

6.5.2 Progress

Three types of experiments were conducted during this quarter: (1) mass-transfer experiments of ozone from the bubbles to deionized water, (2) oxidation of a colored compound dissolved into water (indigo), and (3) oxidation of phenol. In the first set of experiments, the off-gas ozone concentration was continuously monitored by a spectrophotometer. In the second set of experiments, liquid samples were taken and the concentration of indigo was measured using the spectrophotometer. In the third set of experiments, liquid samples were taken and used for the extraction of phenol by a solid-phase microextraction technique. A gas chromatograph was then used to measure the concentration of phenol. These experiments showed that microbubbles formed

by inverse electrostatic spraying significantly enhance ozone transfer rates to aqueous solutions as well as ozonation rates.

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

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

6.6.1 Purpose and Scope

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

6.6.2 Progress

Experiments were conducted using a three-stage distillation column under electric fields. The results showed a small effect of the electric fields on the separation of isopropanol-water mixtures. Efforts are currently concentrated on improving the electrode geometry, with the objective of increasing the electric-field effect. These efforts are guided by experimental data obtained by using simpler electrode geometries, which showed that the mechanism of electric-field effects on phase equilibria is probably related to interfacial effects. A different distillation column allowing a higher interfacial area, across which an electric field may be applied, is currently under construction to be used for further experiments.

6.7 INDUSTRIAL INTERACTION (D. W. DePaoli)

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Summary: D. W. DePaoli was one of four ORNL employees who spent 3 weeks in 1997 in an off-site assignment at the R&D centers of a major industrial firm. Efforts have continued to develop contacts and to host visitors from the company. Several potential collaborative efforts have been identified.

6.7.1 Purpose and Scope

PPG Industries and ORNL have been working to develop opportunities for technology transfer and collaborative research. PPG has four major business units—glass, fiberglass, coatings and resins, and specialty chemicals. Four ORNL staff members were assigned to cover these business units in the technical areas of chemistry, analytical chemistry, metallurgy, and instrumentation and controls. These staff members continue to serve as points of contact to develop links between ORNL capabilities and the needs of PPG.

6.7.2 Results

During this quarter, one group of PPG personnel visited with CTD researchers who were identified as working on topics pertinent to the guests' needs. Another PPG group is scheduled to meet with several CTD staff in April 1998. In addition, the statement of work authored by X. Zhang and D. W. DePaoli for a potential CRADA was approved by PPG management; contract negotiations are under way.

6.8 PUBLICATIONS

- M. A. Norato, C. Tsouris, and L. L. Tavlarides, "Phase Inversion Studies in Liquid-Liquid Dispersions," accepted for publication in *Canadian Journal of Chemical Engineering* (June 1998).
- C. Tsouris, W.-T. Shin, and S. Yiacoymi, "Spraying, Pumping, and Mixing of Fluids by Electric Fields," accepted for publication in *Canadian Journal of Chemical Engineers* (June 1998).
- C. J. Chin, S. Yiacoymi, and C. Tsouris, "Shear-Induced Flocculation of Colloidal Particles in Stirred Tanks," submitted for publication in *Journal of Colloid and Interface Science* (February 1998).
- X. Zhang, "Dynamics of Growth and Breakup of Viscous Pendant Drops in Air," submitted to *Journal of Fluid Mechanics*.

X. Zhang, "Dynamics of Drop Formation in Viscous Flows," submitted to *Chemical Engineering Science*.

7. FLUID STRUCTURE AND PROPERTIES

H. D. Cochran

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

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

7.1.1 Objective

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

7.1.2 Progress

The apparatus for studying the electrodispersion of aqueous systems in supercritical carbon dioxide has been used successfully to extract ethanol from water-ethanol solution. We plan to use this well-characterized system to test the mass-transfer performance of the electrodispersion cell during the next quarter. Despite some industrial interest and plans to publish this work in November, the Office of Technology Transfer has not yet filed a patent application.

Yu. B. Melnichenko (with assistance from S. Salaniwal and K. D. Heath) has performed a series of small-angle neutron-scattering (SANS) experiments of polydimethylsiloxane of two molecular weights in supercritical carbon dioxide as a function of temperature and pressure. The results show that the theta point of a polymer solution is a function of density (or pressure) as well as the usual temperature dependency when the solvent is a compressible fluid.

H.-C. Li has tested the simplified, generalized quartic equation of state with about 50 binary mixtures and will begin testing with some ternary mixtures during the next quarter. So far, the

performance of the equation with mixtures is little different from the performance of the Peng-Robinson equation of state.

7.2 MOLECULAR-BASED STUDY OF REVERSE MICELLES IN SUPERCRITICAL CO₂ (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.

7.2.1 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.

7.2.2 Progress

Using molecular dynamics simulations, S. Salaniwal has studied the relative tendency of alkane chains versus perfluoroalkane chains to aggregate in supercritical carbon dioxide. Current efforts aim to export these calculations to parallel computers. S.-T. Cui has found from Gibbs ensemble Monte Carlo calculations that the relatively higher solubility of perfluoroalkanes (compared with alkanes) in supercritical carbon dioxide can be predicted simply on the basis of different size and energy parameters for the Lennard-Jones chain sites, requiring no special chemical interaction as had been postulated by others. However, the predicted solubilities are not quantitative, and a small chemical effect may be present.

There have been no scattering experiments with surfactant systems this quarter. However, Johnston at Texas is developing surfactants based on polydimethylsiloxane; therefore, the experiments reported in Sect. 7.1 may become relevant to this project.

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

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

7.3.1 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, SAXS, and SANS experiments on sheared systems.

7.3.2 Progress

We have found and corrected some errors in the papers describing the theory by Eu and Gan of the nonequilibrium pair distribution functions; the errors were found in the high-strain-rate, non-Newtonian version of the theory. Calculations are in progress by Yu. V. Kalyuzhnyi to attempt to reproduce Eu and Gan's published results. S.-T. Cui has initiated nonequilibrium molecular dynamics simulations of the same system to test the theory. J. D. Moore has performed both equilibrium and nonequilibrium molecular dynamics simulations with a realistic model of n-C100H202.

Horng-Ji Dai from Brooklyn Polytechnic Institute has accepted the postdoc position to develop and use the ultrahigh-strain-rate shear cell for scattering experiments and will begin work in June 1998.

7.4 PUBLICATIONS

7.4.1 Submitted

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

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

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

7.4.2 Accepted

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

L. L. Lee and H. D. Cochran, "Molecular Adsorption: Repulsive and Attractive Supercritical Fluid Mixtures," *J. Supercrit. Fluids*, in press (1998).

7.4.3 Published

H. D. Cochran, P. T. Cummings, S. T. Cui, S. A. Gupta, R. K. Bhupathiraju, and P. F. LoCascio, "Classical Molecular Simulations of Complex, Industrially-Important Systems on the Intel Paragon," *Comp. Math. Appl.* **35**, 73-84 (1998).

S. T. Cui, P. T. Cummings, and H. D. Cochran, "The Calculation of Viscosity of Liquid n-Decane and n-Hexadecane by the Green-Kubo Method," *Mol. Phys.* **93**, 117-21 (1998).

8. BIOTECHNOLOGY RESEARCH

E. Greenbaum

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

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Summary: Preliminary measurements using a reconstituted system composed of photosynthetic membranes from K. Redding's B4 deletion mutant, ferredoxin, and hydrogenase indicated the simultaneous photoevolution of hydrogen and oxygen. This represents the first photoactivity measured with a deletion mutant.

8.1.1 Purpose and Scope

The purpose of this research program is a study of the fundamental reactions of photosynthesis and conversion of light energy into chemical energy. Sustained simultaneous photoevolution of molecular hydrogen and oxygen is studied as a model photosynthetic reaction in which the energy-rich product is molecular hydrogen rather than a carbon dioxide fixation compound. Basic questions such as the molecular mechanisms of gas evolution, thermodynamic limits of photosynthesis, and minimum number of light reactions that are required to split water to

hydrogen and oxygen are studied. Fundamental studies on the enzymology of cellulase are also performed.

8.1.2 Progress

During the current reporting period, experiments on the simultaneous photoevolution of hydrogen and oxygen were performed with a reconstituted system composed of photosynthetic membranes, ferredoxin, and hydrogenase. The interesting aspect of this work is that the photosynthetic membranes were derived from Kevin Reddings B4 deletion mutant. In this mutant, the genes that code for the Photosystem I (PSI) reaction center were genetically deleted. There should be no trace of PSI in these membranes. In one experiment, simultaneous photoevolution of hydrogen and oxygen was observed, and in a second, hydrogen was observed. This is the first example of photoactivity from a source utilizing material derived from PSI deletion mutants. We have sent the membranes back to Redding's laboratory for confirmation of the absence of PSI. If the membranes check out, this will represent the first in vitro system for the simultaneous photoevolution of hydrogen and oxygen.

We have studied the kinetics of a thermophilic cellulase from *Thermotoga maritima*. The main findings are summarized as follows. It has the highest activity on barley β -glucan, compared with other cellulases (80°C, optimal temperature; optimal pH, 5.0). It is stable for at least 4 h at 80°C. The main product of its reaction on Avicel is cellobiose. However, in order to determine whether the enzyme is an exoglucanase or endoglucanase, we conducted the following experiments. First, we measured the rate of carboxymethylcellulose (CMC) and barley β -glucan hydrolysis by *T. maritima* cellulase compared with the rates of EG II, a known endoglucanase, and CBH I, a known exoglucanase from the mesophilic fungus *Trichoderma reesei* using viscosity-reduction measurements. Whereas CBH I had little effect on the viscosity of CMC or β -glucan, EG II and *T. maritima* cellulase possessed the ability to reduce the viscosity of these substrates similarly. It was concluded that the *T. maritima* cellulase is an endoglucanase. It is a novel enzyme in that it has only 38% identity with sequences of known cellulases and does not possess an inherent cellulose-binding domain. It possesses a high degree of synergy with CBH I.

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

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Summary: Photovoltages from isolated PSI reaction centers were measured for the first time.

8.2.1 Purpose and Scope

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

8.2.2 Progress

During this report period, electric-potential measurements of PSI oriented and immobilized on a gold substrate have been performed using a scanning probe microscope. The voltage generated by a single PSI reaction center was measured for the first time. In our setup, topography and potential are measured sequentially with minimal cross talk using the lifting-mode technique. Upon the light incident, a clear negative potential was measured on PSI oriented in an "up" position. We did not observe any voltage contrast on PSI oriented parallel to the gold surface. When the light is off, a slightly positive potential (compared with gold substrate at ground) was observed on PSI in the "up" position. A calibration device is under construction to quantitate the voltage measurements.

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

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Summary: Oxygen evolution in a pure hydrogen atmosphere was measured for the first time. These data can be used to set an upper limit for the thermodynamic potential of the hydrogen evolution reaction.

8.3.1 Purpose and Scope

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

8.3.2 Progress

An important issue concerning the practical development of photobiological reactors for hydrogen and oxygen production is the question of the thermodynamic potential of the light reaction that drives hydrogen production. During the current reporting period, we have addressed this problem indirectly by measuring oxygen production in a *hydrogen* atmosphere. The important aspect of this result is that the rates of oxygen production in helium and hydrogen were the same. This implies that the thermodynamic driving force of the light-activated hydrogen reaction was sufficient to overcome a back-pressure of hydrogen of 1 atm.

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

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Summary: Isolation of ORNL thermophilic microorganisms was carried out. Three isolates from a subsurface mixed culture were grown on xylan, revealing cellulase and xylanase activity on the supernatants.

8.4.1 Progress

Isolation of ORNL thermophilic microorganisms was carried out by Ji-Zhong Zhou and Heshu Huang of the ORNL Environmental Sciences Division. A mixed culture had been obtained from a 2.7-km drill hole as described previously. The mixed culture had been found to produce both xylanase and cellulase activities when grown on xylan. In order to isolate the cellulolytic thermophiles, the mixed culture was streaked on xylan plates. Single colonies that grew on the plates were used to inoculate 150 mL of media containing xylan as the carbon source. The cultures were grown at 65°C for 2 d and then centrifuged. Cell pellets and supernatants were stored at -70°C. The culture supernatants were thawed and assayed for activity on birchwood xylan and microcrystalline cellulose at 70°C in 50 mM potassium phosphate, pH 6.0.

The culture supernatants were dialyzed at 4°C for 18 h against 50 mM Tris-HCl, pH 7.0. The dialyzed supernatants were then applied to 1.5 × 8.0 cm columns of Pharmacia DEAE Sepharose equilibrated in 50 mM Tris-HCl, pH 7.0. Protein fractions were eluted with 50 mM Tris-HCl, 1.0 M NaCl, pH 7.0. The eluted protein was assayed for cellulase and xylanase activity.

Examination of the proteins eluted from the DEAE chromatography on sodium dodecyl sulfate and isoelectric focusing polyacrylamide gels indicated that at least six proteins were present in the peaks eluted with 1.0 M NaCl. Gel filtration was used to separate the components. Concentrated protein from the X-1 supernatant that had been eluted from the DEAE column with 1 M NaCl (1 mL, 0.233 mg/mL) was loaded on a Pharmacia 10/30 Superdex-75 column equilibrated in 20 mM Tris-HCl, pH 8.0. Fractions (1 mL) were eluted and assayed for protein concentration and activity on birchwood xylan, Avicel, and CMC. Activity assays were carried out by following reducing sugar production at 70°C in 50 mM potassium phosphate buffer, pH 6.0, with 1% substrate. The brown color eluted in fractions 13-19, necessitating the use of the Coomassie blue protein assay to determine the protein concentration of the fractions. Superdex-75 has a fractionation range of 70,000-3,000 g/mol for globular proteins.

Three isolates from a thermophilic, subsurface mixed culture were grown on xylan. The culture supernatants were found to contain cellulase and xylanase activity. The cellulase and xylanase activities were found to bind to DEAE Sepharose at pH 7.0. Isoelectric focusing gels and fractionation by molecular weight were used to analyze the composition of the supernatant of one of the isolates, X-1. The enzymes appear to be acidic and to vary in size from 70,000 to 20,000 g/mol. Variation of the relative activities on xylan, Avicel, and CMC between the Superdex-75 pools indicates that a typical array of exoglucanases, endoglucanases, and xylanases is probably present. The lower specific activity on Avicel after Superdex-75 fractionation may

indicate that there is synergy between the enzyme components that are separated by this chromatography.

8.4.2 Publications

S.V. Liu, J. Zhou, C. Zhang, D. R. Cole, and M. Gajdarziska-Josifovksa, "Thermophilic Fe(III)-Reducing Bacteria from the Deep Subsurface: The Evolutionary Implications," *Science* **277**, 1106-109 (1997).

C. Zhang, S. Liu, J. Logan, R. Mazumder, and T. J. Phelps, "Enhancement of Fe(III), Co(III), and Cr(IV) Reduction at Elevated Temperatures and by a Thermophilic Bacterium," *Appl. Biochem. Biotechnol.* **57/58**, 923-32 (1996).

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

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Summary: Research continued to focus on improving the molar yields of hydrogen from glucose. Experimentation was also initiated to convert environmental sources of sugar (biomass) to hydrogen.

During this reporting period, the research emphasis has been on improving the molar yields of hydrogen from glucose, utilizing enzymes of the pentose phosphate pathway. It has also been determined that for long-term experiments on hydrogen production, it is necessary to incorporate microbial growth inhibitors into the reaction vessel. Initiation of experiments on the conversion of biomass (environmental sources of sugar) to hydrogen has also commenced. Progress includes the development of a method for the extraction of maple tree sap from tree branches and the setup and operation of a high-performance liquid chromatograph for the determination of the type and concentration of sugar in sap. It was determined that the major sugar in maple tree sap is sucrose. Utilizing the enzymes invertase, glucose isomerase, glucose dehydrogenase, and hydrogenase, it has been established that sucrose can be enzymatically hydrolyzed to glucose and fructose (the latter being isomerized to glucose) and hydrogen generated by the oxidation of glucose. Depending on the sucrose concentration, a range of power output of 0.3-1.18 mW was obtained. Some of the problems still to be overcome include improving the rate at which fructose is isomerized to glucose and stabilization of glucose dehydrogenase. A major research proposal to the Defense Advanced

Research Projects Agency is being prepared. If successful, this will allow continuation of this work in collaboration with U.S. industry that specializes in biofuel cell production.

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

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Summary: As part of attempts to maximize enzymatic yield, test fungi were cultivated on a variety of carbon substrates under a microcycle regime.

8.6.1 Purpose and Scope

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

8.6.2 Progress

Test organisms for this work—*Phanerochaete chrysosporium* strains ME-446, VKM-1761, and SC-26—have been grown on a variety of carbon substrates (glucose, microcrystalline cellulose, CMC, sorbose, glycerol) under nitrogen-limiting conditions with the goal of inducing microcycle growth. Preliminary results indicate that sorbose and CMC support more luxuriant growth than does glucose, the traditional carbon source. Cultures grown on sorbose exhibited a compact morphology that may be suitable for submerged culture, while those grown on CMC would be preferred for surface culture work. Growth on glycerol promoted spore clumping and yielded a more synchronous spore germination. This finding suggests that spore germination occurs more rapidly in dense spore preparations, suggesting the existence of an endogenous spore-borne regulator of germination. That regulator appears to be veratryl alcohol, a secondary metabolite produced by *P. chrysosporium* that triggers rapid spore germination. Planned experiments will integrate these observations to yield

rapid spore germination, extensive (but rapid) growth, and rapid sporulation—the three critical elements of the desired microcycle regime.

8.7 PUBLICATIONS

8.7.1 Published

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

8.7.2 In Press

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

N. Hershlag, I. Hurley, and J. Woodward, "A Simple Method to Demonstrate the Enzymatic Production of Hydrogen from Sugar," accepted for publication in the *Journal of Chemical Education*.

8.8 PRESENTATIONS

E. Greenbaum, J. W. Lee, C. V. Tevault, and S. L. Blankinship, "A Study of Photosynthetic Reactions in PSI-Deficient Mutants of *C. reinhardtii*," presented at the 42nd Annual Meeting of the Biophysical Society, Kansas City, Missouri, February 22–26, 1998.

I. Lee, J. W. Lee, and E. Greenbaum, "Biomolecular Electronics: Vectorial Arrays of Photosynthetic Reaction Centers," presented at the 42nd Annual Meeting of the Biophysical Society, Kansas City, Missouri, February 22–26, 1998.

J. W. Lee, X. Zhang, R. Collins, I. Lee, and E. Greenbaum, "Electro-Energized Photon Emission from Photosynthetic Membranes," presented at the 42nd Annual Meeting of the Biophysical Society, Kansas City, Missouri, February 22–26, 1998.

E. Greenbaum, "BioHydrogen Production," poster presentation at the Annual Meeting of the National Hydrogen Association, Vienna, Austria, March 3–5, 1998.

E. Greenbaum, J. W. Lee, and S. L. Blankinship, "A New Photosynthetic Pathway and Its Evolutionary Significance," presented at the 15th Eastern Regional Photosynthesis Conference, Woods Hole, Massachusetts, March 13–15, 1998.

I. Lee, J. W. Lee, and E. Greenbaum, "Biomolecular Electronics: Vectorial Arrays of Photosynthetic Reaction Centers," presented at the meeting of the American Physical Society, Los Angeles, California, March 16–20, 1998.

- E. Greenbaum, "New Photosynthetic Pathways: Renewable Fuels Production and Biomolecular Electronics," research seminar presented to the Department of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, March 26, 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, "Hydrogen Production by Photosynthetic Water Splitting," presented at the 1998 DOE Hydrogen Program Technical Peer Review," Alexandria, Virginia, April 28-30, 1998.

9. MOLECULAR STUDIES

P. T. Cummings

9.1 AQUEOUS ELECTROLYTE SOLUTIONS AT AMBIENT AND SUPERCRITICAL CONDITIONS (P. T. Cummings, A. A. Chialvo, S. H. Lee, and 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 largely completed. Simulations of limiting conductance in supercritical aqueous electrolyte solutions were continued.

9.1.1 Purpose and Scope

This project is aimed at developing microscopic-level understanding of aqueous electrolyte solutions using a combination of molecular simulation, statistical mechanical theory, and experimental measurement of vapor-liquid equilibrium and solution densities. The 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).

9.1.2 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, a substantial portion of the review article was written.

Visiting Professor Song Hi Lee continued molecular dynamics simulations of sodium, chlorine, and other 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.

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

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Summary: The viscosity and viscosity index of various linear and branched alkanes were in the process of being predicted computationally. A large-scale simulation of C_{100} was continued. A presentation to Mobil Research was well received and will likely result in funding for the molecular design of lubricants.

9.2.1 Purpose and Scope

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

9.2.2 Progress

We continued production calculations on the Intel Paragons at ORNL of the viscosity of various linear and branched alkanes and, in particular, focused on the viscosity index of octyldocosane, another branched C_{30} alkane, to complement our earlier work on squalane (also a branched C_{30} alkane, for which excellent agreement with experiment was found).

During the quarter, we initiated 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.

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

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Summary: No progress was made this quarter.

9.3.1 Purpose and Scope

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

9.3.2 Progress

Noe Herrera, a faculty member from Mexico, who worked on this project during 1997, returned to his home institution at the end of December. No new researcher has been recruited for this project.

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

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

9.4.1 Purpose and Scope

This project is part of a broad effort at the University of Virginia funded by the IBM Environmental Research Program with Roseanne Ford and Peter Cummings as coprincipal investigators. The goal of the project is to perform experimental studies and computer simulations of bacterial motion in bulk aqueous phases and in porous media to develop an understanding of the transport processes involved in in situ bioremediation and to subsequently develop mathematical models for these processes. The project funding ended on December 31, 1997.

*University of Virginia.

9.4.2 Progress

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

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

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

Summary: Progress was made on extending the Chialvo-Cummings molecular formalism for studying solvation and partial molar thermodynamic properties in supercritical fluid mixtures to reaction kinetics in supercritical fluid solvents.

9.5.1 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).

9.5.2 Progress

During the current quarter, the Chialvo-Cummings molecular formalism for studying solvation and partial molar thermodynamic properties in supercritical fluid mixtures was extended to reaction kinetics in supercritical fluid solvents and used to provide an alternate explanation of recent experimental data published by Brenneke and Roberts. Two papers describing this work were submitted for publication.

9.6 DEVELOPMENT AND APPLICATION OF FAST COMPUTATIONAL PROTEIN-FOLDING ALGORITHMS USING MASSIVELY PARALLEL SUPERCOMPUTERS (P. T. Cummings and P. H. LoCascio)

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

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

9.6.1 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.

9.6.2 Progress

During this quarter, Kai Yue, who, along with Ken Dill, developed the Geocore ab initio protein-folding algorithm visited ORNL to work with Phil LoCascio from the Center for Computational Sciences on the parallelization of Geocore. Excellent progress was made. A strategy for the parallelization of Geocore was developed, in addition to a mechanism whereby Yue and Dill could continue to make enhancements to the Geocore algorithm simultaneously with parallelization.

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

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

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

9.8 PUBLICATIONS

9.8.1. Submitted

S. H. Lee, P. T. Cummings, J. M. Simonson, and R. E. Mesmer, "Molecular Dynamics Simulation of the Limiting Conductance of NaCl in Supercritical Water," *Chem. Phys. Lett.* (1998).

A. A. Chialvo, P. T. Cummings, J. M. Simonson, and R. E. Mesmer, "Solvation in High-Temperature Electrolyte Solutions. I. Hydration Shell Behavior from Molecular Simulation," *J. Chem. Phys.* (1998).

*University of Pittsburgh.

†University of North Carolina.

- A. A. Chialvo, P. T. Cummings, J. M. Simonson, and R. E. Mesmer, "Solvation in High-Temperature Electrolyte Solutions. II. Some Formal Results," *J. Chem. Phys.* (1998).

9.8.2 Accepted

- A. A. Chialvo, P. T. Cummings, J. M. Simonson, R. E. Mesmer, and H. D. Cochran, "The Importance of the Interplay Between Molecular Simulation and Neutron Scattering in Developing New Insights into the Structure of Water," *Ind. Eng. Chem. Res.* (1997).
- S. A. Gupta, H. D. Cochran, and P. T. Cummings, "Nanorheology of Liquid Alkanes," *Fluid Phase Equilib.* (1997).
- S. H. Lee and P. T. Cummings, "Molecular Dynamics Simulation of the Rheology of n-Decane and 4-Propyl-heptane," *Mol. Simul.* (1998).

9.8.3 Published

- S. T. Cui, P. T. Cummings, and H. D. Cochran, "The Calculation of Viscosity of Liquid n-Decane and n-Hexadecane by the Green-Kubo Method," *Mol. Phys.* **93**, 117-21 (1998).
- A. A. Chialvo, Yu. V. Kalyuzhnyi, and P. T. Cummings, "Molecular-Based Interpretation of Solvation Effects on the Reaction Kinetics of Dilute Reactants in Supercritical Solvents," *AIChE J.* **44**, 667-680 (1998).

9.9 PRESENTATIONS

9.9.1 Invited Seminars

- P. T. Cummings, "Molecular Simulation of Supercritical Water and of Ionic Association in Supercritical Aqueous Solutions," Department of Chemistry, University of Nebraska, Lincoln, Nebraska, January 23, 1997.
- P. T. Cummings, "Molecular Modeling and Simulation: Present and Future Tools for Physical Properties Prediction," Department of Mechanical and Aerospace Engineering, University of Tennessee, Knoxville, Tennessee, February 5, 1998.
- P. T. Cummings, "Molecular Modeling and Simulation: Present and Future Tools for Physical Properties Prediction," Mobil Technical Center, Paulsboro, New Jersey, February 11, 1998.
- P. T. Cummings, "Molecular Modeling and Simulation: Present and Future Tools for Physical Properties Prediction," Department of Chemical and Petroleum Engineering, Colorado School of Mines, Golden, Colorado, February 20, 1998.
- P. T. Cummings, "Molecular Modeling and Simulation: Present and Future Tools for Physical Properties Prediction," Department of Chemical Engineering, SUNY-Buffalo, Buffalo, New York, March 3, 1997.

- P. T. Cummings, "Modeling of Bacterial Migration: Application of Concepts from Molecular Theory," Departments of Chemical Engineering and Civil Engineering, Michigan State University, Lansing, Michigan, March 19, 1997.
- P. T. Cummings, "Molecular Modeling and Simulation: Present and Future Tools for Physical Properties Prediction," Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, March 31, 1997.

9.9.2 Invited Conferences

- P. T. Cummings, "Nonequilibrium Molecular Dynamics Simulations of the Rheology of Confined and Bulk Alkane Liquids," NSF Workshop on Particulate/Multiphase Flows, Santa Barbara, California, February 23–25, 1998.
- P. T. Cummings, "NSF Workshop Report—Future Directions in Molecular Modeling and Simulation: Fundamentals and Applications," Department of Energy Office of Industrial Technology Computational Chemistry Roadmap Workshop, College Park, Maryland, March 16–17, 1998.
- A. A. Chialvo, P. T. Cummings, M. J. Simonson, and R. E. Mesmer, "Solvation in Supercritical Electrolyte Solutions: Formal and Experimental Results," 215th ACS National Meeting, Dallas, Texas, March 29–April 2, 1998.

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