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Progress Report for the Chemical and Energy Research Section of the Chemical Technology Division: July–December 1998

R. T. Jubin

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Chemical Technology Division

PROGRESS REPORT FOR THE CHEMICAL AND ENERGY RESEARCH SECTION OF THE CHEMICAL TECHNOLOGY DIVISION: JULY–DECEMBER 1998

R. T. Jubin

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ACRONYMS

ACB	auxiliary charcoal bed
AIChE	American Institute of Chemical Engineers
BES	Basic Energy Sciences (DOE)
CST	crystalline silicotitanate
CTD	Chemical Technology Division
CV	column volumes
DOE	U.S. Department of Energy
DTA	differential thermal analysis
DWPF	Defense Waste Processing Facility
ESP	Environmental Simulation Program
ESW	Enhanced Sludge Washing
ETF	Effluent Treatment Facility
HFIR	High Flux Isotope Reactor
HLW	high-level waste
ITP	In-Tank Precipitation
LED	light-emitting diode
MSRE	Molten Salt Reactor Experiment
NERSC	National Energy Research Supercomputing Center
NSF	National Science Foundation
ORNL	Oak Ridge National Laboratory
PCR	polymerase chain reaction
PNPC	*p*-nitrophenyl cellobioside
SALS	small-angle light scattering
SANS	small-angle neutron scattering
SAXS	small-angle X-ray scattering
SDS	sodium dodecyl sulfate
SRS	Savannah River Site
SRTC	Savannah River Technology Center
TTCF	transient time correlation function
TFA	Tanks Focus Area
TGA	thermogravimetric analysis
WCA	Weeks-Chandler-Andersen

EXECUTIVE SUMMARY

This report summarizes the major activities conducted in the Chemical and Energy Research Section of the Chemical Technology Division at Oak Ridge National Laboratory (ORNL) during the period July–December 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 seven major areas of research: Hot Cell Operations, Process Chemistry and Thermodynamics, Molten Salt Reactor Experiment (MSRE) Remediation Studies, Chemistry Research, Fluid Structure and Properties, Biotechnology Research, and Molecular Studies. The name of a technical contact is included with each task described, and readers are encouraged to contact these individuals if they need additional information.

Activities conducted within the area of *Hot Cell Operations* included completion of the study of Enhanced Sludge Washing of Hanford tank sludge, with publication of the final results, and batch testing of cesium removal using an engineered form of crystalline silicotitanate with a simulant of sludge from the Savannah River Site (SRS). Tests were also conducted to verify that this sorbent can be used to decontaminate an aqueous waste stream generated by the vitrification process at the SRS.

Within the area of *Process Chemistry and Thermodynamics*, a test plan that addresses the problem of solids formation in process solutions from caustic treatment of Hanford sludge was approved, and investigation of solution conditions required to dissolve Hanford saltcake continued. Attempts to interpret chemical thermodynamics in applied technology ceramic systems focused on the phase fields that include the superconducting compounds.

MSRE Remediation Studies focused on recovery of ^{233}U and its transformation into a stable oxide and radiolysis experiments to permit remediation of MSRE fuel salt.

In the area of *Chemistry Research*, activities included studies relative to molecular imprinting for use in areas such as selective sorption, chemical sensing, and catalysis, as well as spectroscopic investigation into the fundamental interaction between ionic solvents and solutes in both low- and high-temperature ionic liquids.

Fluid Structure and Properties included molecular-based studies of systems with supercritical solvents, 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 to assess the thermodynamic limits of renewable photosynthetic hydrogen production were performed, related studies with algae were directed toward optimizing the photoevolution of hydrogen and oxygen and the photoassimilation of CO_2, and voltages generated by a single Photosystem I reaction center have been positively identified. The initiative to produce hydrogen from iron filings and gluconic acid continued, and the role of $NADP^+$ in reversing the decline in the rate of hydrogen production during a reaction was investigated. In other enzyme-related work, studies were made to determine possible inhibitors of cellulase activity in isolates of thermophilic subsurface culture, and experiments were conducted on psychrophiles grown on xylan. Lastly, molecular taxonomic characterization is under way for organisms that make up a commercial culture that affords protection from *Salmonella* contamination.

In the final area—*Molecular Studies*—as part of an effort to enhance our microscopic-level understanding of aqueous electrolyte solutions, molecular simulations were performed using a newly implemented flexible water model, molecular dynamics simulations of supercooled water were performed, and the stability of a new phase of ice was studied. Also in progress were the investigation of simulation algorithms for nonequilibrium systems, work on an integral equation theory for such systems, and preparation of a final report and related publications on mathematical modeling of in situ bioremediation processes. The Chialvo-Cummings solvation formalism was applied to electrolyte solutions, significant progress was made in parallel implementations of the Geocore algorithm, and the key simulation code for the study of reverse miscelles in supercritical water was completed and production runs conducted. In addition to these areas of ongoing work, a new study was initiated, which involves molecular dynamics simulations of alkanes confined to nanoscale gaps.

1. HOT CELL OPERATIONS

E. C. Beahm

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

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Summary: This task has completed its study of the potential of water and caustic solutions [Enhanced Sludge Washing (ESW)] to remove aluminum and other nonradioactive components from Hanford tank sludges so that the volume of the high-level waste (HLW) stream can be reduced. The final report on the results from the FY 1998 tests was issued.

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 HLW for disposal. Other less abundant, inert components, such as chromium and phosphate, can also determine the volume of an 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 waste 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 the simple sludge washing, which is followed by caustic leaching with 2–3 *M* NaOH at an elevated temperature. The leached solids are then washed with the dilute NaOH to remove the dissolved components and the added NaOH. ESW is effective due to the increased solubility of some of these inert components under very caustic conditions, which can be used to partition the radioactive and nonradioactive components. The primary objective of this task was 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 were determined under more realistic processing conditions.

1.1.2 Progress

This task has completed its study of the potential of water and caustic solutions (ESW) to remove aluminum and other nonradioactive components from Hanford tank sludges so that the volume of the HLW stream can be reduced. The final report on the FY 1998 tests was issued. An excerpt from the conclusions and recommendations portion of this report, *Water Washes and Caustic Leaches of Sludge from Hanford Tank S-101 and Water Washes of Sludge from Hanford Tank C-103* (ORNL/TM-13655), follows.

> For the sludge from tank S-101, the initial water washes were quite effective. Only 21% of the initial sludge mass remained after the sludge was washed and dried. While 99% of the ^{99}Tc and 98% of the ^{137}Cs were transferred into the wash solutions, all of the ^{60}Co, ^{90}Sr, ^{154}Eu, ^{155}Eu, ^{241}Am, ^{244}Cm, plutonium, and uranium remained with the solids. After the washes, the only removal goals which had not been met were for aluminum and chromium. While each combination of sodium hydroxide concentration and temperature could exceed the removal goal of 64% for chromium, the 3 *M* sodium hydroxide leach at 70°C failed to meet the aluminum removal goal of 68% by 3%. The leaches at 95°C were clearly more effective at aluminum and chromium removal than the 70°C leaches. Overall, the leaches with 3 *M* sodium hydroxide at 95°C were the most effective, even though the leaches used the smallest number of moles of sodium hydroxide per gram of sludge. Leaching time is another critical processing variable because the aluminum and chromium concentrations increased significantly as the leaching times were increased. It is expected that these results will eventually be used by the full-scale remediation effort to determine the appropriate ESW processing conditions after the feed specifications for the vitrifier have been set. In the future, similar studies should be performed on additional sludge samples if they represent significant quantities of wastes, which require a more aggressive treatment than the inhibited water washes.
>
> The weight changes of the leached solids clearly demonstrated the complex chemistry involved in the ESW process. With 3 of the 16 tests, the dry weight of the leached/washed solids was greater than the dry weight of the initial washed solids. Since the caustic leaches should only affect aluminum, chromium, phosphate, silicon, and cesium, the new precipitant(s) can be expected to be due to combination(s) of these components plus sodium, hydroxide, and oxides. The most likely candidates are sodium aluminosilicates. This speculation is supported by the preliminary results of an ESW study on a sludge sample from Hanford tank BX-112. A key difference between the ESW tests with sludge from tanks S-101 and BX-112 is the ultimate fate of these aluminosilicates. The aluminosilicates in the PNNL tests could not be redissolved, while the aluminosilicates in this study could be dissolved with longer leaching times. This difference should not be surprising since various forms of aluminosilicates were observed in tank waste simulants. A thorough understanding of the aluminum–silicon–sodium hydroxide system is needed before any attempt to model the kinetics of the caustic leaches will be successful.
>
> Another goal of this study was to evaluate the effectiveness of water washes on a sludge sample from Hanford tank C-103. In sharp contrast to the washes with sludge from tank S-101, the inhibited water washes with the sludge from tank C-103 were not effective, so additional water washes after the retrieval process will not be required. After the third water wash with sludge from tank C-103, the weight of the washed solids was still higher than the initial weight of the sludge sample.

Apparently, the heat that was generated from the high concentrations of ^{90}Sr and ^{137}Cs led to a dehydration of the sludge sample from tank C-103. In addition, very little radioactivity was removed from the solids. Finally, further ESW tests with this sludge cannot be recommended. The initial ESW test (Rapko et al., 1995) removed only 48% of the aluminum, 11% of the chromium, and 66% of the phosphorus. The difficulty in aluminum removal could be due to the high concentration of silicon in comparison to the aluminum concentration. The final reason to not pursue further ESW tests is tank C-103 belongs to a SORWT group, which contains only a small fraction of the total sludge at Hanford.

The final objective of this study was to test potential process control monitors during the water washes and caustic leaches with actual waste. The ^{137}Cs activity and conductance were measured for each of the water washes and caustic leaches. The ^{137}Cs activity can be used to monitor the progress of the water washes and caustic leaches if the solids contain appreciable quantities of ^{137}Cs. The ^{137}Cs concentration of the washed solids in the test with tank S-101 sludge was 1.20E+5 Bq/g, and this level of activity was insufficient to monitor the effectiveness of the caustic leaches. Fortunately, the conductance probe encountered fewer difficulties. Nearly all of the changes in conductance values can be directly related to changes in the masses of the solids. Therefore, these results indicate that a conductance probe can serve as a useful process control monitor for the pretreatment of Hanford tank sludges. It should be noted that the aluminum industry currently uses conductance probes to control hot caustic leaches of bauxite. These preliminary results indicated that the conductance probe should be further developed as a process control monitor.

1.2 CESIUM REMOVAL FOR THE SAVANNAH RIVER SITE (K. K. Anderson, J. L. Collins, R. D. Hunt, and D. D. Lee)

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Summary: At the request of the Savannah River Site (SRS), batch tests were performed on the engineered form of crystalline silicotitanate (CST), IONSIV® IE-911, with a simulant of the "average" SRS supernatant. The distribution ratio (D) results from the batch tests clearly indicated that IONSIV® IE-911 can be very effective in the removal of cesium from the simulant of the "average" SRS supernatant. The variability between the different production runs of IONSIV® IE-911 was very small. However, the variability between the different batches of IONSIV® IE-911 increased after the CST was treated with NaOH and H_2O prior to the batch tests. The predicted D results from the equilibrium model were comparable to the 168-h experimental results with the "as-received" samples of CST. Other tests demonstrated that increases in temperature and particle size can significantly decrease the performance of the IONSIV® IE-911. In sharp contrast, the presence of the organics did not impact the D results.

1.2.1 Purpose and Scope

DOE is required by law to treat and safely dispose of the radioactive wastes from its nuclear weapon production activities. The primary radionuclide in the DOE liquid wastes or supernatants is ^{137}Cs. At the SRS, the In-Tank Precipitation (ITP) process was selected as the baseline technology to remove ^{137}Cs from the supernatants; however, problems were encountered during the full-scale ITP processing.

These difficulties have led to an evaluation of alternative technologies and/or concepts to the currently configured ITP process. The High-Level Waste Salt Disposition Team at the SRS has chosen CST, an inorganic ion exchanger, as one of the leading alternatives. Since nearly all of the CST tests have been performed on supernatants from Hanford and Oak Ridge, the Salt Disposition Team has requested that ORNL personnel perform batch tests on the engineered form of CST, IONSIV® IE-911, with a simulant of the "average" SRS supernatant.

1.2.2 Progress

Since nearly all the CST tests have been performed on supernatants from other sites, batch tests were conducted to determine the performance of IONSIV® IE-911 with a simulant of the "average" SRS supernatant. The D results from the batch tests clearly indicated that IONSIV® IE-911 can be very effective in the removal of cesium from the simulant of the "average" SRS supernatant. The variability between the different production runs of IONSIV® IE-911 was very small; the 168-h D results for the "as-received" samples were 2149 and 2253 mL/g. However, the variability between the different batches of IONSIV® IE-911 increased after the CST was treated with NaOH and H_2O prior to the batch tests. The 168-h D values for the "treated" samples ranged from 1454 to 2032 mL/g. The predicted D results from the equilibrium model were comparable to the 168-h experimental results with the "as-received" samples of CST. Other tests demonstrated that increases in temperature and particle size can significantly decrease the performance of the IONSIV® IE-911. In particular, the equilibrium model predicted that a temperature increase from 25 to 30°C would decrease the D value from 2340 to 2060 mL/g. Unlike sample preparation, temperature, and sample size, the presence of the organics did not impact the D results.

Finally, the maximum concentration of soluble strontium in the simulant of the "average" SRS supernatant was 0.37 ppm. This low concentration of strontium should not significantly reduce the performance of the CST.

1.2.3 Publications

M. R. Poirier, R. D. Hunt, and C. Carlson, *Identification of Cesium Removal Technologies*, WSRC-TR-98-00181, 1998.

R. D. Hunt, *Water Washes and Caustic Leaches of Sludge from Hanford Tank S-101 and Water Washes of Sludge from Hanford Tank C-103,* ORNL/TM-13655, July 1998.

R. D. Hunt, K. K. Anderson, J. L. Collins, and D. D. Lee, *Batch Tests with IONSIV® IE-911 and a Simulant of the Savannah River Site "Average" Supernatant: Distribution Ratios vs Time*, ORNL/TM-13740, February, 1999; printed after the conclusion of the reporting period.

1.3 ION-EXCHANGE BATCH AND COLUMN TESTS WITH CST (UOP IONSIV® IE-911) USING SRS TANK 22 SIMULANT AND PROJECTED REDUCED-INHIBITOR SIMULANT (D. D. Lee and C. W. Chase)

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Summary: At the SRS, radioactive sludge from the SRS tank farms is vitrified in the SRS Defense Waste Processing Facility (DWPF). The DWPF process generates intermediate-activity aqueous waste that is returned to the tank farm for storage. Because of the lack of additional storage space in the tank farm, sending the DWPF aqueous waste stream to the Effluent Treatment Facility (ETF) after cesium removal would free tank space and ensure continued operation of the DWPF (ref. 1, listed in Sect. 1.3.3).

A cesium-specific inorganic sorbent, CST, has been developed at Sandia National Laboratory and Texas A&M University as a fine powder (refs. 2 and 3, see Sect. 1.3.3). It was developed in an engineered form known as IONSIV® IE-911 by UOP. The cesium-loaded sorbent cannot be easily eluted and can be disposed of as a solid waste form itself or by vitrification in the DWPF. This study examines the feasibility of using the engineered form of CST to decontaminate the DWPF recycle stream and send the decontaminated stream to the ETF (ref. 1, listed in Sect. 1.3.3).

We examined the uptake of cesium on CST (IONSIV® IE-911) from the SRS tank 22 simulant and projected reduced-inhibitor simulant using batch contact tests. The results indicate how well the simulant compares with results for similar tests done on the actual liquid material from tank 22H at the SRS that showed a distribution coefficient (K_d) of 14,850 mL/g. This study resulted in a K_d of 25,000 mL/g under similar conditions for the simulant. The results were also compared with equilibrium model predictions for CST powder that gave 35,000 mL/g, which shows good agreement between the model and experiments when the CST content (70%) of the engineered form is considered.

The second part of the report examines the uptake of cesium on CST (IONSIV® IE-911) using ion-exchange column studies. The results compare the continuous column behavior with results of simulant batch tests conducted earlier on the same simulants. Tests were also done to compare different column bed depths and superficial velocities using the same simulant. The column results at 50% breakthroughs for the tank 22 simulant and the reduced-inhibitor simulant

were both about 5800 column volumes (CV) with columns longer than about 17 cm, but the reduced-inhibitor simulant caused problems with precipitation in the pump head during the column loading and resulted in a premature end to the experiment.

1.3.1 Purpose and Scope

The objective of this set of experiments is to verify that CST can be used to decontaminate the DWPF recycle stream in the SRS High-Level Waste Tank Farm. This is part of the overall program to optimize treatment of the DWPF recycle, test the DWPF vitrification compatibility of CST, and evaluate the in-tank storage of the loaded CST. This task provides information for the design of the CST ion-exchange columns.

1.3.2 Progress

1.3.2.1 Batch Tests

The first series of tests used the data obtained by the Savannah River Technology Center (SRTC), based on sample analysis of the aqueous contents of tank 22. These tests were used to develop a simulant for the Oak Ridge National Laboratory (ORNL) work. The SRTC measurements of the K_d value for the waste stream were compared with the K_d values for the simulant for validation. The validated simulant was used in ORNL tests to optimize the design parameters for the ion-exchange columns. The initial batch contact tests were run using the data from the analyses, but the total cesium concentration was projected from the concentration of ^{137}Cs in the aqueous or soluble layer (supernatant). Additional analytical tests at the SRTC gave results that showed the actual cesium concentration was about 100 times greater than calculated, because of cold cesium that resulted from cold ITP testing in the tank. The simulant formulas for the two tank 22 feeds with the two different cesium concentrations are shown in Table 1 and are based on the analytical results given by McCabe and Oji (ref. 1, see Sect. 1.3.3).

An additional set of tests used the reduced-inhibitor, low-hydroxide projected composition. This feed is projected to result when the recycle stream does not require added inhibitor to protect the evaporator, which is used to reduce feed volume before it is added back to the storage tank. The concentrations are shown in Table 2. Both sets of the ORNL batch K_d tests are done with liquid-to-solid ratios of 200, 500, and 1000 to 1, using 50-mL tubes on a tilting-bed mixer. The tubes are sampled at 3, 24, and 72 h for the cesium and strontium remaining in the supernatant (DWPF recycle), using tracers for cesium and strontium. The tests are done in duplicate. The strontium uptake by CSTs was tested by measuring the K_d using ^{85}Sr tracer with cold strontium in addition to the ^{137}Cs tracer used for cesium uptake testing.

Table 1. Tank 22 simulant[a]

Component	Concentration
KNO_3	20 mg/L potassium
$Al(NO_3)\cdot 9H_2O$	13 mg/L aluminum
$Ca(NO_3)_2\cdot 4H_2O$	2.7 mg/L calcium
Sodium formate	230. mg/L formate
$Na_2B_4O_7\cdot 10H_2O$	13 mg/L boron
$Na_2SiO_3\cdot 5H_2O$	
$Hg(NO_2)_2\cdot H_2O$	52. mg/L silicon
Na_2HPO_4	11. mg/L mercury
$NaNO_2$	7.5 mg/L phosphorus
$NaNO_3$	0.127 *M* nitrite
$NaHCO_3$	0.034 *M* nitrate
Na_2CO_3	0.005 *M* carbon
NaOH	0.095 *M* carbon
$UO_2(NO_3)_2\cdot 6H_2O$	0.52 *M* free hydroxide
$CsNO_3$	28.4 mg/L uranium
$CsNO_3$	3.3×10^{-8} *M* Cs (first batch test)
	3.7×10^{-6} *M* Cs (second batch test and column tests)

[a] Prepare with distilled/deionized water, and adjust free hydroxide to 0.515 *M* with caustic as measured by titration. Filter using 0.45-μm filter.

Table 2. Reduced-inhibitor simulant[a]

Component	Concentration
KNO_3	20 mg/L potassium
$Al(NO_3)\cdot 9H_2O$	13 mg/L aluminum
$Ca(NO_3)_2\cdot 4H_2O$	2.7 mg/L calcium
Sodium formate	230. mg/L formate
$Na_2B_4O_7\cdot 10H_2O$	13 mg/L boron
$Na_2SiO_3\cdot 5H_2O$	52. mg/L silicon
Na_2HPO_4	7.5 mg/L phosphorus
$NaNO_2$	0.120 *M* nitrite
$NaNO_3$	0.0655 *M* nitrate
$NaHCO_3$	0.005 *M* carbon
Na_2CO_3	0.095 *M* carbon
NaOH	0.01 *M* free hydroxide
$UO_2(NO_3)_2\cdot 6H_2O$	28.4 mg/L uranium
$CsNO_3$	3.31×10^{-8} *M* Cs
$Sr(NO_3)_2$	1–2 mg/L strontium [both cold Sr and ^{85}Sr (~40 μCi/L)]

[a] Prepare with distilled/deionized water, and adjust pH with caustic to 0.01 *M* free hydroxide as measured by titration. Filter using 0.45-μm filter.

1.3.2.2 Column Tests

The series of ORNL ion-exchange column tests used the previously described simulants for tank 22 with high cesium content. These simulants also included strontium (with ^{85}Sr tracer) to evaluate strontium uptake by the CST when used in column ion exchange. An additional column test used the reduced-inhibitor, low-hydroxide composition. The feed was made up in 40-L batches and pumped into the cell feed tank, which held 10 L. The pH of each batch was checked before use, and a gamma count of the batch was made to check the added quantity of ^{137}Cs and ^{85}Sr.

1.3.2.3 Batch Results

It is apparent that the equilibrium between solution and sorbent is not reached in 24 h, because the K_d values continued to increase for all the feeds and liquid-to-sorbent ratios. It is possible that the values may increase even more after the 3-d measurement, but no samples were obtained after that time. Compared with the predictions generated by the Texas A&M model (ref. 4, listed in Sect. 1.3.3) of CST equilibrium behavior with the high-cesium tank 22 simulant (K_d = 25,000) and reduced-inhibitor simulant formulas (K_d = 56,000), the K_d values obtained in these experiments are somewhat lower but follow the same trends. The lower values are expected because the Texas A&M model is based on the CST powder, and the tests were done with the engineered form. The engineered form is generally about 60–70% CST, with the remainder being binder, so the experimental values are very reasonable. A comparison of the model predictions and the experimental results at the different contact times and liquid-to-solid ratios is shown in Table 3.

Also shown in Table 3 are the experimental and predicted values of the loading on the CST, Q, in millimoles of cesium per kilogram of CST. The experimental value of Q is calculated from the amount of cesium removed from solution and the volume of liquid and mass of CST at the start of the contact. These values agree closely and vary as expected, based on the starting cesium concentration. If these values are known, then the total cesium and radioactive cesium loading on a column of CST can be estimated, as well as the radiation levels resulting from that loading.

1.3.2.4 Results of Ion-Exchange Column Tests

Ion-exchange column tests were conducted in the hot cell in Building 4501 that has been previously used for these tests. The system was set up for unattended operation (possibly due to the low level of radioactivity present with the tracer quantities used) with automatic shutdown in case of excessive pressure resulting from line blockage or leaks from the system. However, the testing was conducted in the hot cell because the total loading of radioactive cesium on the column would create a very radioactive point source.

Table 3. Comparison of experimental results and model predictions

Simulant/sorbent ratio (mL/g)	Avg. Cs K_d[a] (mL/g)	Predicted Cs K_d (mL/g)	Experiment/prediction for the K_d's	Predicted Q (mmol Cs/kg CST)	Experimental Q (mmol Cs/kg CST)
Tank 22 – low Cs, no Sr					
200	33,650	35,100	0.96	0.00656	0.0065
500	22,000	34,900	0.63	0.0163	0.0155
1000	27,190	34,800	0.78	0.0321	0.0315
Tank 22 – high Cs					
200	24,860	35,000	0.71	0.736	0.721
1000	25,160	34,200	0.74	3.59	3.50
Low inhibitor					
200	56,400	71,600	0.79	0.00658	0.00641
500	37,400	70,100	0.53	0.0164	0.0158
1000	36,020	69,000	0.52	0.0325	0.0319

[a] Values of K_d are not corrected for the engineered form. The difference between the model prediction and the experimental value is a measure of the correction factor for powder versus the engineered form.

Two tests were run using the tank 22 simulant with the same superficial velocity but different column lengths. This resulted in two different residence times in the columns and two different volumetric flow rates (column volumes per hour). The first flow rate was about 17.8 CV/h, and the second was about 32 CV/h, with an average superficial velocity of 9.5 cm/min for both tests. The reduced-inhibitor test used the same superficial velocity and an intermediate column length in order to further define the mass transfer zone.

The reduced-inhibitor simulant feed was made up according to the formula shown in Table 2. The pH of the feed was 11.3–11.5 when checked by titration and 11.6–11.8 when tested by pH strips. After problems with the pump freezing, several samples of the column effluent were tested for the pH by titration, and the pH was found to be about 12.4–12.5 for all samples checked. This is about a pH unit higher than the feed and matches what the calculations showed should be the equilibrium pH of the feed.

Calculations on the thermodynamics of the reduced-inhibitor simulant system showed that under test conditions at the low pH (11–11.5) to which the simulant was made up, some of the chemicals in solution, particularly the aluminum compounds, could precipitate in the presence of a seed material. The piston and cylinder of the pump head were made from a ceramic material and could have provided the seed for crystallization on the surfaces as the piston moved inside of the cylinder and simulant constantly flowed through the head.

A test was also done to determine whether increasing the pH of the simulant would prevent precipitation. The thermodynamic analysis predicted that increasing the pH of the simulant to above 12.7 would prevent the precipitation that would cause pump stoppage. A batch of simulant was prepared and adjusted to pH 12.87 (as measured by titration) and pumped through the pump head, as had occurred in the hot cell test of the ion-exchange column system. The pumping lasted for over 1 week, and no pump stoppages occurred and no crystallization was seen in the system. Samples of effluent from the pump showed that the pH did not change after passing through the pump.

The loading results for the column test showed an estimate for the 50% breakthrough of about 5650 CV for cesium and about 5625 CV for strontium, when the tailing at the end of the run was disregarded. Based on these estimates, the calculated length of the mass transfer zone for cesium for this column was 4833 CV for the column volumes between 5 and 63.2% breakthrough, indicating that the mass transfer zone was contained in the column.

1.3.3 References for Sect. 1.3

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2. PROCESS CHEMISTRY AND THERMODYNAMICS

E. C. Beahm

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

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Summary: The management of the Tanks Focus Area (TFA) has approved the FY 1999 test plan. Four types of tests will be performed:

1. an evaluation of the formation of aluminosilicates during caustic leaching;
2. viscosity measurements of actual process waste solutions as a function of temperature;
3. tests with selected components to link their concentrations, temperatures, and viscosities (initial experimental design based on a two-level seven-factor partial factorial); and
4. tests in support of other TFA and user programs (primarily pipeline plugs).

A sludge sample from Hanford tank S-104 was washed three times with inhibited water in an effort to remove water-soluble salt. However, the sample actually gained weight because the initial sample was very dehydrated. After the water washes are completed, the portions of the washed solids will be leached with 1–4 *M* sodium hydroxide. The weights of the sludge residues will be closely followed to determine if aluminosilicates form during the leaching process.

With respect to the tests on viscosity and pipeline plugs, several pieces of equipment were ordered. It is expected that both experimental systems will be fully functional early next quarter.

2.1.1 Purpose and Scope

Nuclear waste remediation efforts at Hanford and Savannah River have been adversely affected by unwanted or unintentional solids formation. Transfer pipes at Hanford and Savannah River have become plugged with the nuclear waste, leading to schedule delays and to higher remediation costs. Fortunately, operating windows where solids can form during tank operations such as pretreatment, transfers, and storage can be predicted. These windows are based on thermodynamic calculations that use ionic strengths and the concentrations of phosphate, fluoride, silica, alumina, and hydroxide. To improve process control, it will also be necessary to correlate chemical effects and solid formation with physical properties, which can be continuously monitored if necessary. The properties of interest in many operations are viscosity and specific gravity. The ultimate aim is to provide relationships between the chemistry and physical properties so the tank farm operators can avoid unwanted or unintentional solids formation.

2.1.2 Progress

At the request of the TFA, a test plan for the FY 1999 research effort was submitted to the Pretreatment Technical Integration Manager. The approved test plan consists of the following research activities:

1. an evaluation of the formation of aluminosilicates during the caustic leaching of an actual sludge sample from a Hanford storage tank;
2. viscosity measurements of actual process waste solutions as a function of temperature;
3. tests with selected components to link their concentrations, temperatures, and viscosities (initial experimental design based on a two-level seven-factor partial factorial); and
4. tests in support of other TFA and user programs (primarily pipeline plugs).

With respect to the formation of aluminosilicates, a sludge sample from Hanford tank S-104 was washed three times with inhibited water at room temperature. The initial weight of the sludge was 40.34 g, and approximately 170 mL of inhibited water, which consists of 0.01 *M* sodium hydroxide and 0.01 *M* sodium nitrite, was used in each of the washes. At the end of each wash, the sample was centrifuged, and the wash solution was decanted. The weights of the washed solids after the first and third washes were 49.79 and 56.16 g, respectively. It is apparent that the initial sludge sample was very dehydrated and that the rehydration process in a tank with dehydrated sludge and limited mixing capabilities can be very slow. At the end of the water washes, the washed solids will be divided into aliquots and leached with 1–4 *M* sodium hydroxide. The weights of the sludge residues will be closely followed to determine if aluminosilicates form during the leaching process.

With respect to the tests on viscosity and pipeline plugs, several pieces of equipment were ordered. A rheometer from Brookfield will be used to make the viscosity measurements. The rheometer will be remotely controlled with the assistance of the RHEOCALC software package, which will also be used in data analysis. Since temperature is expected to play a critical role in the viscosity measurements, a jacketed beaker will be added to the rheometer so the temperature of the samples can be controlled. The output from the data analysis will include shear rate and shear stress. For the pipeline plugs, pressure transducers, temperature probes, solenoid valves, and a computer card for process control and data analysis were ordered. It is expected that both systems will be fully functional early next quarter.

2.1.3 Publication

H. A. Mook, P. Dai, R. D. Hunt, and F. Dogan, "Neutron Scattering Studies of the Magnetic Fluctuations in $YBa_2Cu_3O_n$," *J. Phys. Chem. Solids* **59**(10–12), 2140–44 (1998).

2.2 SALTCAKE DISSOLUTION (E. C. Beahm)

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

2.2.1 Purpose and Scope

This effort provides coordination and thermochemical evaluations for a team effort on Hanford saltcake dissolution. Tests on Hanford saltcake are run at Numatec Hanford, and calculations using the ESP are run at Mississippi State University. 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

The uncertainties in standard free energies of formation for trisodium phosphate, sodium fluoride, and sodium phosphate fluoride double salt were evaluated. These uncertainties were then used to calculate ranges of uncertainty in the solubility of these solids. This information was plotted to show the range of uncertainty in the formation of solids in the Na-F-PO_4-HPO_4-OH system. A comparison of the ranges where solid formation may occur with experimental tests showed that solids were observed generally within the range of uncertainty.

Data from this evaluation was sent to Mississippi State so that coworkers on the Saltcake Dissolution Program could insert values calculated using the ESP to see where its results occurred in comparison with the uncertainty evaluation.

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

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Summary: Our experimental facilities were used in support of our collaborations with Basic Energy Sciences (BES) projects, which are led by Herb Mook and Mariappan Paranthaman. A new collaboration with Nanopowder Enterprises, Inc., was established.

2.3.1 Purpose and Scope

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

2.3.2 Progress

This task maintained its support of the BES project, which is directed by Herb Mook. Single crystals of $YBa_2Cu_3O_n$ were treated in our high-temperature furnace to set the oxygen content at a particular level. It is important to remember that the oxygen content in $YBa_2Cu_3O_n$ determines its superconducting properties. After the heat treatment in a controlled atmosphere, the samples are studied with neutron scattering. The results from previous neutron-scattering experiments were incorporated into a manuscript which will be submitted to *Science* after the internal review process is completed.

This project has also continued its collaborative effort with a second BES task, which is led by Mariappan Paranthaman. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on gadolinium methoxy oxide. The results indicated that the initial preparation of gadolinium methoxy oxide contained an impurity.

Finally, a new collaboration with Nanopowder Enterprises, Inc., was established. Several samples of titanium oxide powders and microspheres were prepared and examined with DTA/TGA. Preparation of additional microspheres is currently under way.

3. MSRE REMEDIATION STUDIES

D. F. Williams

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

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Summary: Fissile ^{233}U is presently being recovered, trapped, and removed as an essential part of the remediation and decommissioning activities presently under way at the Molten Salt Reactor Experiment (MSRE). Uranium hexafluoride trapped in NaF, along with uranium-laden activated charcoal, represents the bulk of the inventory. For permanent storage, all of the ^{233}U needs to be recovered and transformed into a stable oxide. Efforts focused on prototypical conversion of the UF_6 sorbed on NaF, preparation of uranium-laden passivated charcoal [auxiliary charcoal bed (ACB) simulant] for future conversion trials, preparation of the facility in Building 4501 for conversion operations, and assembly and identification of the cold-test mock apparatus. The conversion facility is scheduled to start the actual conversion operation in August 2000.

3.1.1 Purpose and Scope

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

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

3.1.2 Progress

The material prepared to simulate the behavior of the charcoal deposit at MSRE was successfully burned in oxygen (to remove the carbon and other impurities) before fluorination of the uranium content and conversion to a stable oxide (as occurs for the UF_6 unloaded from the NaF traps). The trial was successful; however, a simpler, faster integrated fluorine combustion of the charcoal has been proposed for future investigation.

The milestone for the 60% design of the conversion process was completed on schedule, and the full-scale conversion prototype was constructed in Laboratory 123 of Building 4501. The prototype layout and construction were based as closely as possible on the 60% design for the installation of the actual process in hot cell D of Building 4501. Two full-scale conversion prototype operations were successfully completed. Uranium hexafluoride, initially chemisorbed on NaF pellets, was converted to uranium oxide. An operational procedure was developed for routine conversion and processing of NaF traps. These tests were also used for formal on-the-job training of operations personnel. All of the equipment performed well, and samples of the converted material will be analyzed. Uranium-laden charcoal was prepared for use in future tests.

Preparation of hot cell D in Building 4501 is continuing. Material was procured to fabricate the frame that will hold the conversion equipment in the hot cell. The frame and conversion equipment will be assembled in the 4501 High Bay area, cold tested, and then installed in hot cell D for operation. The draft safety analysis report and technical safety requirements document for the upgrade of a portion of Building 4501 to Category 2 nuclear facility were completed. The safety analysis report was reviewed by Chemical Technology Division (CTD) personnel, and comments were forwarded to the safety engineer.

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

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Summary: Efforts to establish a fluoride standard for conversion of the oxide product and to address issues of interim storage continued. Radiolysis data from previous gamma irradiation experiments were analyzed, and preparations were made for upcoming experiments. Additional attention was given to the measurement of ammonium fluoride radiolysis. Significant fluorine pressure has accumulated in the large batch (~ 800 g) of MSRE simulant salt being irradiated in the High Flux Isotope Reactor (HFIR) cooling pool. Significant progress was made in the search for a suitable fluorine trapping agent that does not generate any additional gas pressure.

3.2.1 Purpose and Scope

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

3.2.2 Progress

Currently, one of the major uncertainties is the maximum acceptable fluoride content for the long-term storage of the converted oxide. There are two bases for a fluoride limitation: (1) pressure buildup due to radiolysis and (2) corrosion due to HF if H_2O is also present. Investigations with the goal of establishing the fluoride limit for long-term storage of $^{233}U_3O_8$ are being conducted. Experimental irradiation of (1) the converted oxide and (2) surrogate samples of known fluoride and water content are being used to simulate long-term storage conditions. A variety of metal coupons (e.g., SS304, SS304L, SS316, SS316L, carbon steel, and aluminum) placed in contact with uranium oxide samples are being irradiated under very high radiation fields (i.e., using a ^{60}Co source). During the period, samples of UO_2F_2, $UO_2F_2 \cdot 3H_2O$, and partially denatured (ammonia-treated) carbon fluoride were irradiated in CTD's ^{60}Co irradiator. Gas and solid samples were taken and analyzed for radiolytic products, data were evaluated, and plans were made for further irradiations. Additional concerns regarding the radiolysis of water sorbed on uranium oxides (in the absence of fluorine) have provided another focus for our experiments. Uranium oxides containing different amounts of sorbed water were prepared. Both uranium oxyfluorides and uranium oxides with sorbed water will be irradiated during the next quarter.

Irradiation of the largest possible batch size (~800 g) of MSRE simulant fuel salt in the HFIR cooling pool was started, and significant radiolytic damage was produced. A rather long induction period before a fluorine pressure rise was observed. Some of this delay may have been due to inadequate heat transfer between the sample holder and the containment vessel. Before this issue was addressed, extensive irradiation produced no pressure rise; however, afterwards, the typical induction period was observed. The observed radiolytic yield (G-value) for this large monolithic cylindrical block is slightly less than that observed for smaller granular samples, but a more complete transport analysis will be required to get a truly accurate estimate of the absorbed dose. This sample will accumulate the radiolytic damage necessary to support the hydrofluorination test early in the next quarter.

Gas sampling was carried out in the ACB with the intention of detecting NH_4F radiolysis products. Two samples taken early in the reporting period revealed levels of N_2 and H_2 consistent with the values seen in the literature for radiolysis of NH_4F studies and related compounds. The NH_4F was formed during the stabilization of C_xF with anhydrous ammonia earlier this year. As a result of this observation in the ACB, modifications were recommended and made to current operations and to plans for removal and interim storage of the ACB's uranium-laden charcoal. These relate primarily to eliminating the possibility of accumulating explosive mixtures containing H_2 and to the radiolytic pressure buildup in the material during interim storage.

A concentrated effort to identify suitable fluorine trapping agents for interim and long-term storage was conducted. The goal is to identify a material that traps fluorine efficiently, even at low fluxes (no reactive heating), but does not generate any additional pressure or give off any gas. Of all the systems tested, only a high-surface-area nickel catalyst and sodium iodide continued to trap fluorine rapidly and efficiently without becoming passivated. Both reacted to a high degree of their stoichiometric capacity. The only other material known to possess these qualities is charcoal. The fluorine capacity and behavior of this material have already been established, and the relative instability of the carbon fluoride reaction product prompted the search for other candidates.

4. CHEMISTRY RESEARCH

D. F. Williams

4.1 MOLECULAR IMPRINTING ON SOL-GEL MATRICES (S. Dai, Y. S. Shin, M. C. Burleigh, Y. H. Ju, and C. C. Morrow)

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Summary: We have successfully synthesized highly selective functionalized ordered mesoporous sorbents through surface molecular imprinting. The selectivity coefficient of our sorbents is much greater than those of conventional sorbents.

4.1.1 Purpose and Scope

The purpose of this research is to incorporate molecular recognition in advanced sorbent development. The design principles illustrated by these results highlight opportunities for application of imprint-coated mesoporous materials in areas such as selective sorption, chemical sensing, and catalysis.

4.1.2 Progress

A novel method for introducing template-selective recognition sites in mesoporous sorbents through surface molecular imprinting was developed. This method makes use of the unique surface environment of hexagonally packed mesopore surfaces of selected pore size and coats these surfaces by binding functional ligands to a target metal-ion template. The procedure produces ideal uniform imprints that exhibit the necessary size and sterochemical requirements for binding target metal ions and has led to the preparation of sorbents that are much more selective than those prepared by conventional coating methods. This development has resulted in a new class of ordered mesoporous sorbents with molecular recognition capabilities. We view these sorbents as an adsorbed-phase analog to crown-ether ligands that can be tailored for a specific target ion. The simplicity of this technique should lead to a wide variety of new, highly selective sorbents, the properties of which can be optimized for many metal ions. The present method requires only that the sorbate form stable coordination complexes with a suitable bifunctional ligand containing a silane group. Furthermore, this surface-imprinting methodology should not be limited to the binding of metal ions. If complexes of molecules can be formed between targeted organic molecules and functional groups containing a silane group, application of the previously described methodology should lead to the synthesis of sorbents that exhibit molecular recognition of organic molecules. The design principles illustrated by these results highlight opportunities for application of imprint-coated mesoporous materials in areas such as selective sorption, chemical sensing, and catalysis. Our most recent results in this area have been accepted for publication in *Angewandte Chemie International Edition.*

4.2 IONIC LIQUIDS RESEARCH (S. Dai, Y. H. Ju, and Y. S. Shin)

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Summary: The preliminary results described here show that much larger distribution coefficients can be achieved if ionic liquids are used as the extraction solvent during the separation

of metal ions by crown ethers. This work highlights the significant opportunity for improving separations by using ionic liquids in conjunction with crown ethers.

4.2.1 Purpose and Scope

The purpose of this research is to conduct a spectroscopic investigation into the fundamental interaction between ionic solvents and solutes in both low- and high-temperature ionic liquids (e.g., molten salts). The fundamental knowledge gained in these studies will be used to design novel separation systems involving ionic liquids. These systems utilize organic phases containing crown ethers to extract target metal ions from aqueous solutions through the complexation of the targeted radionuclides and the specific crown ethers.

4.2.2 Progress

The discovery of crown ethers has led to a new class of ligands for alkaline and alkaline earth metal cations. Crown ethers and related macrocycles have found wide application in the design of novel solvent extraction systems that are selective for fission products, such as Cs^+ and Sr^{2+}, based on the sizes of the crown-ether rings. These systems utilize organic phases containing crown ethers to extract target metal ions from the aqueous phase because of a highly selective complexation of the metal ion by the extractant. The distribution ratios for the extraction process depend on two major factors: (1) the thermodynamic driving force for cation complexation by a crown ether and (2) the solvation of the cation and counteranion by the organic solvent. The former factor is usually thermodynamically favored. For example, the stability constant (K) of Li^+ with 15-crown-5 is greater than 10^4. The difficulty in increasing the solvent extraction efficiency with conventional solvents lies in the unfavorable transport of the cation and counteranions from the aqueous phase to the organic phase. The limited solubility of ionic species in nonionic organic solvents is the main barrier to improvement in conventional solvent extraction systems. Accordingly, this generally leads to a very small distribution ratio for the total extraction process. For example, the distribution ratio for the extraction of strontium nitrate into nonpolar organic phases by crown ethers is generally less than one, even though the thermodynamic driving force for the complexation of Sr^{2+} with a number of crown ethers is very favorable. This distribution ratio is low because the solvation free energy for simple inorganic anions such as nitrate by organic solvents is extremely unfavorable. A number of strategies have been proposed to address this problem, including the addition of hydrophobic anions to the aqueous solution or the addition of hydrophilic solvents to the organic phase. For example, McDowell et al. made use of lipophilic carboxylic acids to enhance the distribution ratio of Sr^{2+}. The carboxylic anion is more readily solvated in the organic phase than simple inorganic anions. The obvious drawback to this approach is that more chemicals would have to be added to the system, thereby increasing the complexity and cost of the original aqueous solution. Another drawback is the loss of some selectivity due to the nonselective ion exchange of the carboxylate anion.

These key deficiencies associated with current extraction processes based on conventional solvents suggested to us that molten salts may offer a better way to solvate the ionic species in the nonaqueous phase. Ionic systems consisting of salts that are liquid at ambient temperatures can act as solvents for a broad spectrum of chemical species. These ionic liquids are attracting increased attention worldwide because they promise significant environmental benefits. Unlike the conventional solvents currently in use, they are nonvolatile and, therefore, do not emit noxious vapors that can contribute to air pollution and health problems for workers. A very unusual property of these melts is that they consist only of ions and can be made hydrophobic. The novel properties of these new ionic liquids make them efficient solvents for the extraction of ionic species from aqueous solutions. From a thermodynamic perspective, the solvation of ionic species, such as crown-ether complexes, NO_3^-, and SO_4^{2-}, in ionic liquids should be strongly favored when compared with the situation in conventional solvents. This is the key advantage ionic liquids possess in separations. These salts typically exist as liquids at temperatures as low as $-100°C$ and are thermally stable up to 200°C. Some room-temperature ionic liquids, such as 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, are reported to be stable up to 4000°C. A solvent with a liquid range of over 3000°C without measurable vapor pressure is amazing. These properties should greatly simplify the chemical engineering of processes utilizing these solvents. Therefore, these room-temperature ionic liquids (molten salts) have been recently described as "neoteric," or "groundbreaking," solvents. Our preliminary demonstrations found that ionic liquids containing crown ethers and other macrocycles exhibit unusually large distribution ratios (D) for the selective extraction of Sr^{2+} and Cs^+ from aqueous solutions. Whereas conventional solvents utilizing crown ethers and related extractants can deliver practical D values of up to 10^2 for the extraction of Sr^{2+} and Cs^+, preliminary tests with ionic liquids as extraction solvents revealed D values on the order of 10^4. These results clearly show the potential of ionic liquids for increasing the extractive strength of ionophores such as crown ethers in fission-product separation applications. To our knowledge, no solvent extraction system based on mixtures of ionic liquids and crown ethers has been previously reported in the literature. Our preliminary results have been accepted for publication as a communication in the *Journal of the Chemical Society, Dalton Transactions*.

4.3 PUBLICATIONS

S. Dai, M. C. Burleigh, Y. S. Shin, C. C. Morrow, C. E. Barnes, and Z. L. Xue, "Imprint Coating: Novel Synthesis of Selective Functionalized Ordered Mesoporous Sorbents," *Angewandte Chemie International Edition*, in press.

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5. FLUID STRUCTURE AND PROPERTIES

H. D. Cochran

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

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

5.1.1 Objective

This program focuses on our fundamental interest in understanding the practical behavior of separation processes in terms of the underlying molecular interactions. Currently, the work focuses on systems with supercritical solvents and systems with surfactants that form micelles.

5.1.2 Progress

K. D. Heath has begun measurement of the density of binary solutions of isopropanol, styrene, and methyl methacrylate in supercritical CO_2 with the vibrating-tube apparatus in the ORNL Chemical and Analytical Sciences Division. These data will allow us to complete quantitative analysis of some previous small-angle X-ray scattering (SAXS) and small-angle neutron-scattering (SANS) data. H. J. Dai will complete this work.

Heath has resumed work with the apparatus for electrodispersion of aqueous media in supercritical CO_2. He plans to complete the characterization of the effect of independent variables on mean droplet diameter. He then plans mass transfer studies on the extraction of ethanol from ethanol-water mixtures to complete the research for his dissertation.

Working in collaboration with S. Dai and Y. H. Ju, H.-C. Li and H. J. Dai completed some exploratory experiments aimed at determining whether a surfactant will form micelles in a room-temperature molten salt. SAXS experiments indicate a structure of about the expected size, ~ 2.9-nm diameter. The liquid is optically clear. We plan to try to swell the putative micelles by addition of *n*-decane, which we determined to have a solubility of less than 0.1 wt %. Codes to be modified for molecular dynamics simulation of reverse micelles in room-temperature molten salts have been acquired from former student J. Slusher.

The manuscript "SANS Studies of Polymers in Organic Solvents and Supercritical Fluids in Poor, Theta, and Good Solvent Domains" has been accepted by the American Chemical Society Symposium Series. At the American Institute of Chemical Engineers (AIChE) Annual Meeting in Miami Beach, K. D. Heath, H.-C. Li, and H. D. Cochran presented papers on their work.

5.2 MOLECULAR-BASED STUDY OF REVERSE MICELLES IN SUPERCRITICAL CO_2 (P. T. Cummings, H. D. Cochran, G. D. Wignall, J. M. DeSimone, E. J. Beckman, Yu. B. Melnichenko, S. T. Cui, S. Salaniwal, and K. D. Heath)

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

5.2.1 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.

5.2.2 Progress

S. Salaniwal has completed pioneering molecular dynamics simulations of reverse micelles with aqueous cores in supercritical CO_2, with two significant accomplishments: more rapid equilibration of large simulations by occasional "temperature spikes" (brief excursions to temperatures 25 or 50 K higher) and stabilization of a second simulation (started from an independent initial configuration) to the same three-micelle state as a previous one, giving reassurance that an equilibrium state has been reached. An even larger simulation is currently in progress that will accurately reproduce experimental conditions for the study of this system.

Codes for interpreting SAXS and SANS data from systems containing spherical micelles were acquired from R. Triolo of the University of Palermo.

S. Salaniwal and K. E. Heath's work with Y. B. Melnichenko on SANS studies of polydimethylsiloxane in supercritical CO_2 has been submitted to *Science*, and S. T. Cui has submitted an article on vapor-liquid phase coexistence of alkane-CO_2 and perfluoroalkane-CO_2 mixtures to the *Journal of Physical Chemistry*. Salaniwal, Cui, and Cochran also presented papers related to this work at the AIChE meeting in Miami Beach.

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

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

5.3.1 Objective

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

5.3.2 Progress

Calculations with the nonequilibrium Ornstein-Zernike equation with a nonequilibrium potential (Y. V. Kalyuzhnyi) have been compared with nonequilibrium and equilibrium molecular dynamics calculations (S. T. Cui). Although the nonequilibrium integral equation theory was quite accurate with a given nonequilibrium potential, that used in the initial calculations was not very accurate. This theoretical work is continuing with other nonequilibrium potentials that may be better suited to high-shear-rate conditions.

J. D. Moore has analyzed transient and steady-state results from molecular dynamics simulations of linear C_{100} chains at equilibrium and under shear flow, and new molecular insights have been gained into the phenomenon of stress overshoot.

Using nonequilibrium molecular dynamics simulation, we have studied the response of a C_{100} model polymer melt to a step change from equilibrium to a constant, high shear rate. Both the transient shear stress and first normal stress of the model polymer melt exhibit pronounced overshoot at the strain values predicted by reptation models, in striking similarity to melts of longer, entangled polymers governed by reptation motion. At the maximum of shear stress overshoot, the molecular orientational order and the alignment angle are found to be midway between those characteristic of Newtonian flow and full alignment with the flow. We further analyzed the molecular origins of such behavior in short polymer chains by decomposing the total stress into the contributions from various molecular interactions. The result is a new insight into how theory should be applied to such systems.

H. J. Dai has begun some measurements of viscosity of polymer solutions as a function of temperature and concentration in the vicinity of the liquid-liquid critical point. These data will complement some earlier SANS experiments. Dai has also been assembling an apparatus for SALS, including a cell capable of scattering studies with fluids at ultrahigh shear rates.

The manuscript "Distribution Functions of a Simple Fluid under Shear" has been submitted to *Physical Review E*, and J. D. Moore and S. T. Cui presented papers at the AIChE meeting held in November.

5.4 PUBLICATIONS

5.4.1 Submitted

Y. B. Melnichenko, E. Kiran, G. D. Wignall, K. D. Heath, S. Salaniwal, H. C. Cochran, and M. Stamm, "Pressure and Temperature-Induced Transitions in Polymer Solutions in Supercritical Fluids," *Science* (1998).

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5.4.2 Published

S. A. Gupta, H. D. Cochran, and P. T. Cummings, "Nanorheology of Liquid Alkanes," *Fluid Phase Equilib.* **151**, 125–31 (1998).

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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.* **19**, 449–59 (1998).

5.5 PRESENTATIONS

S. T. Cui, P. T. Cummings, and H. D. Cochran, "Dynamical Properties of Linear and Branched Alkanes in Confinement," American Institute of Chemical Engineers Annual Meeting, Miami Beach, Florida, November 15–20, 1998.

H. D. Cochran, J. D. Londono, and G. D. Wignall, "Neutron Scattering Characterization of Polymerization Mechanisms in Supercritical Carbon Dioxide," American Institute of Chemical Engineers Annual Meeting, Miami Beach, Florida, November 15–20, 1998.

S. Salaniwal, S. T. Cui, P. T. Cummings, and H. D. Cochran, "Molecular Dynamics Simulation of Hybrid Surfactants in Supercritical Carbon Dioxide," American Institute of Chemical Engineers Annual Meeting, Miami Beach, Florida, November 15–20, 1998.

J. D. Moore, S. T. Cui, P. T. Cummings, and H. D. Cochran, "Molecular Dynamics Simulation of a Polyethylene Melt," American Institute of Chemical Engineers Annual Meeting, Miami, Beach, Florida, November 15–20, 1998.

R. G. Alamo, L. Mandelkern, M. M. Agamalian, G. D. Wignall, and H. D. Cochran, "Phase Behavior of Blends of Linear and Branched Polyethylenes via SANS and USANS," American Institute of Chemical Engineers Annual Meeting, Miami Beach, Florida, November 15–20, 1998.

H.-C. Li, V. M. Shah, and H. D. Cochran, "A Generalized Quartic Equation of State: Simplification and Extension to Mixtures," American Institute of Chemical Engineers Annual Meeting, Miami Beach, Florida, November 15–20, 1998.

S. T. Cui, P. T. Cummings, and H. D. Cochran, "Gibbs Ensemble Molecular Simulation Study of Solubility of Alkanes and Perfluoroalkanes in Supercritical CO_2," American Institute of Chemical Engineers Annual Meeting, Miami Beach, Florida, November 15–20, 1998.

K. D. Heath and H. D. Cochran, "Producing Aqueous Microdispersions in Supercritical CO_2 Using High-Intensity Electric Fields," American Institute of Chemical Engineers Annual Meeting, Miami Beach, Florida, November 15–20, 1998.

6. BIOTECHNOLOGY RESEARCH

E. Greenbaum

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

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Summary: Experiments were conducted to assess the thermodynamic limits of renewable hydrogen production by photosynthesis. An enzymatic mixture was used to maximize the yield of hydrogen from renewable sugars.

We have performed measurements of the thermodynamic limits of renewable hydrogen production by photosynthesis. Working with anaerobic hydrogenase-adapted *Scenedesmus* D_3, we have shown that the rate of photosynthetically evolved oxygen proceeds undiminished in atmospheres of either pure helium or pure hydrogen. This is an indirect method of assessing the thermodynamic driving force of the photosynthetic hydrogen-evolving reaction in *Scenedesmus* D_3. The significance of these results is that for *Scenedesmus* D_3 the reaction appears to be occurring relatively far from equilibrium with a strong forward-driving force.

The maximum molar yield of hydrogen that can be obtained from a renewable sugar such as glucose is 12 mol H_2 per mole of glucose. However, the production of hydrogen by the fermentation of glucose is inefficient because less than 40% of the theoretical maximum amount of hydrogen possible is usually obtained. In this work, it has been shown that a mixture of enzymes of the pentose phosphate pathway coupled to hydrogenase, using $NADP^+$ as the electron carrier, is capable of generating 11.6 mol H_2 per mole of glucose-6-phosphate. These results provide the first evidence to suggest that the maximum molar yield of hydrogen from renewable sugars such as glucose is possible enzymatically.

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

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Summary: Positive identification of the voltages generated by a single Photosystem I reaction center has been made.

During this period, we have positively identified the voltages generated by a single Photosystem I reaction center immobilized and oriented on a gold surface. We have measured the potential differences between the substrate and the Photosystem I in the dark and upon light emission. We have also assessed the real-time potential changes generated by a single Photosystem I upon light emission when it was in the dark. These results indicate that Photosystem I can be used not only as a diode element but also as a voltage source. We are currently preparing a manuscript for publication. Also, we have filed a patent application in the U.S. Patent and Trademark Office for our invention, "Method of Orienting Molecular Electronic Components" (U.S. Patent Application ERID 0550).

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

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Summary: Experimental results have indicated that reduction of photosynthetic antenna size in green algae increased production of H_2 and O_2 and fixation of CO_2.

During this reporting period, significant research progress on photosynthetic hydrogen production has been made. Antenna-deficient mutants of *Chlamydomonas* DSP521 and wild-type DES15 were comparatively assayed for photoevolution of H_2 and O_2 and photoassimilation of CO_2 under various actinic intensities using our unique dual-reactor-flow detection system. These algal strains were obtained from our collaborator Professor Laurie Mets of the University of Chicago and grown under a light intensity of about 20 $\mu E \cdot m^{-2} \cdot s^{-1}$ in minimal-plus-acetate medium. The rationale for growing these strains photoheterotrophically is that the selection pressure for algal cells to make antenna would be minimal under such a condition. When the cultures grew to a cell density of about 10^6 cells/mL, the algal cells were harvested by gentle centrifugation (3000 rpm). They then were washed and resuspensed in fresh minimal medium for the assays. The H_2 and O_2 photoevolution was assayed under a helium atmosphere. The CO_2 fixation assays were performed with 700 ppm CO_2 in helium. The actinic illumination was provided by a red (peak wavelength at 670 nm) light-emitting diode (LED) light source that was controlled with a computerized step motor. Because of the automatic control of the LED light source by the computerized step motor, precise and reproducible step functions of actinic intensity were generated. The actinic intensity was monitored and recorded by a computer simultaneously with the rates of H_2 and O_2 evolution and CO_2

fixation. Preliminary analysis of the data has shown that the maximal rates of H_2 and O_2 photo-evolution and CO_2 fixation were about two times higher than those of the wild type. This is an important result since it demonstrates that reduction of photosynthetic antenna size in green algae can indeed improve the overall efficiency in H_2 and O_2 production and CO_2 fixation. Based on the measured rates of photosynthesis, the antenna size in DSP521 was estimated to be about half of that of the wild type, DES15. More experimental studies are under way to verify these findings.

6.4 CELLULASES WITH ENHANCED ACTIVITY (B. R. Evans and J. Woodward)

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Summary: Investigations were conducted to determine possible inhibitors of cellulase activity in isolates of thermophilic ORNL subsurface culture. Experiments were also conducted on psychrophiles grown on xylan.

6.4.1 Thermophilic Cellulases from ORNL Subsurface Culture

Cell extracts of X1-10 and X1-11S isolates grown on 1% xylose were found to have glucose isomerase activity. To determine why yields of cellulase activity from purified X-isolates were low, the pellet from the xylan culture of the C1 isolate from the original mixed culture was examined for activities. Resuspension of the pellet in 50 m*M* Tris-HCl buffer, pH 7.0, followed by centrifugation yielded substantial protein in the supernatant. Three main protein bands were detected on sodium dodecyl sulfate (SDS)–polyacrylamide gel electrophoresis with molecular weights of 65,000, 50,000, and 40,000 g/mol. Activities detected in this solution included xylanase, β-xylosidase, a small amount of endoglucanase, and small amounts of β-galactosidase and invertase activities. No β-glucosidase could be detected. The endoglucanase hydrolyzed *p*-nitrophenyl cellobioside (PNPC) and carboxymethylcellulose but not microcrystalline cellulose. The effect of divalent metal ions on the endoglucanase was investigated. At 5 m*M* concentration, activity on PNPC was inhibited 71% by calcium, 52% by magnesium, and 100% by ferrous ion.

Since the medium used for growing the thermophiles contains magnesium, calcium, and ferrous cations, there may be inhibition of cellulase production or assays.

6.4.2 Psychrophiles from the ORNL Permafrost Collection

Culture supernatants from psychrophiles 16-2, 39-2A, 45-9, and 46-9 grown on xylan had xylanase activity but no cellulase activity on microcrystalline cellulose or PNPC. The cell extract from 16-2 hydrolyzed sucrose but not cellobiose or lactose.

6.5 DEVELOPMENT OF A FUEL CELL (H. O'Neill and J. Woodward)

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Summary: The role of $NADP^+$ in reversing the decline in the rate of H_2 production in the course of a reaction was investigated.

Enzymatic Production of Hydrogen from Sugar—In a typical reaction profile, there is an initial rapid rise in the rate of H_2 production followed by a steady decline until no more H_2 is produced. It was noted that during the course of a reaction, the decline in the rate of H_2 production could be reversed by the addition of $NADP^+$. However, it is not possible to restore the rate of H_2 production to its initial levels. In these experiments, a partially purified hydrogenase preparation was used. The possibility that $NADP^+$-degrading enzymes were present in the hydrogenase preparation was examined. Two reactions were carried out: one contained purified hydrogenase, and the other contained the partially purified enzyme. Comparable yields of H_2 were obtained in both reactions. This implies that an $NADP^+$-degrading enzyme is not responsible for the breakdown of $NADP^+$.

It has been reported that $NADP^+$ is less stable at high temperatures and that the breakdown products of this cofactor can inhibit $NADP^+$-dependent enzymes. This may account for the observation that additional $NADP^+$ will not restore the rate of H_2 production to its initial level.

Experiments were carried out with NAD^+ as the cofactor. The values of K_m for NAD^+ for the glucose dehydrogenase and hydrogenase are >30 and 3.0 m*M*, respectively. The K_m for $NADP^+$ for both glucose dehydrogenase and hydrogenase is 0.04 m*M*. The values for NAD^+ are much higher than the corresponding values for $NADP^+$. However, immobilized NAD^+ is readily available, so it would be useful to substitute this in our reaction. A high concentration of NAD^+ (80 μmol) replaced $NADP^+$ (usually 1 μmol) in the reaction. Unfortunately, the rate of H_2 production was very low. This precludes the use of NAD^+ as a coenzyme in this system.

During the next month, we will attempt to generate an immobilized $NADP^+$ moiety and examine its effect on the production of H_2. The first method to be examined will be immobilization of the $NADP^+$ onto the soluble polymer dextran.

6.6 HYDROGEN PRODUCTION FROM RENEWABLES (J. P. Getty and J. Woodward)

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Summary: Attempts to better understand and optimize the mechanism of hydrogen production from iron fillings and gluconic acid have continued.

The mechanism of hydrogen gas generation by placing iron filings in contact with gluconic acid is becoming clearer as our investigation continues. We have employed several different techniques in order to understand and identify the changes that are taking place in the overall chemical reactions. Numerous time-dependent experiments have isolated possible oxidation-reduction reactions.

TGA identified magnetite as a reaction product. The utilization of fuel cells has shown that the hydrogen production can be used to power electrical devices.

Mechanism of Hydrogen Production from Iron Powder and Gluconic Acid—The proposed mechanism responsible for hydrogen generation is the oxidation of iron with deionized water. The chemical reaction, $3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$, describes the process by which iron is oxidized to produce magnetite and hydrogen gas. Theoretical calculation based on 100% oxidation states that 25 mg of iron (0.45 mmol Fe) produces 0.599 mmol of hydrogen gas (H_2). However, in our system, complete iron oxidation does not occur.

What does take place is the formation of a iron oxide layer that coats the surface of the iron filings. This passive oxide layer limits the amount of hydrogen gas that can be generated. Actual experiments conducted with 25 mg of iron (0.45 mmol) in 15 mL of H_2O, pH 5.75, ceased to produce hydrogen within 10 h of mixing. The average yield obtained from the experiment was 1.8×10^{-3} mmol. This yield is a direct representation of the effects caused by the formation of the passive oxide layer on the surface of the iron filings.

Hydrogen production yields are different when experiments are conducted with iron filings in gluconic acid solution rather than in water alone. The process of iron oxidation appears to be the same as that observed in experiments using deionized water. The difference is noted in the time interval for which the reaction takes place. From the theoretical calculations, 100% oxidation of

11.2 mg of iron (0.201 mmol Fe) produces 0.267 mmol of H_2. The actual reaction of iron filings (11.2 mg) in 15 mL 0.5 *M* gluconic acid, pH 7.4, extended the hydrogen production process beyond 100 h and produced 0.355 mmol of H_2. This level of hydrogen production indicated to us that, in addition to the iron oxidation process, some sort of iron reduction must be taking place as well.

The hydrogen production process by iron oxidation is coupled with iron reduction, and we postulated that when gluconic acid is present in the reaction solution, the following reaction occurs:

$$Fe_3O_4 + 8 \text{ gluconic acid(red)} = 3Fe + 4H_2O + 8 \text{ gluconic acid(ox)} .$$

6.7 DEVELOPMENT OF NOVEL FERMENTATION PRODUCTS FOR THE PREVENTION OF FOOD CONTAMINATION (T. L. Poole and J. Woodward)

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Summary: Molecular taxonomic characterization is under way for organisms that make up PREEMPT, a commercial product that affords protection from *Salmonella* contamination.

Molecular taxonomic characterization is currently being done on the 29 organisms that compose PREEMPT. This is done by isolating the genomic DNA from these organisms. The 16S RNA region of the genome is next amplified using the polymerase chain reaction (PCR). The DNA generated from this process is then sequenced, and the sequences are compared with those in the rRNA database at Michigan State University.

At present, 9 of the 15 aerobic cultures have been received from MS BioScience and cultured on Brain Heart Infusion Agar. Culture 2.2 did not grow. Cultures 2.1 and 3.4 were not pure and were streaked for isolation on Brain Heart Infusion Agar. DNA has been isolated from the six initial cultures that were pure, and the 16S rRNA genes were amplified. The products are being analyzed. The next step is to sequence the DNA representing the 16S rRNA sequence and to isolate genomic DNA from the remaining PREEMPT organisms.

Additionally, equipment is being put in place to grow the 14 anaerobic cultures contained in PREEMPT.

6.8 PATENTS

J. Woodward, "Method for Separating Non-Inked Cellulose Fibers from Inked Cellulose Fibers in Newsprint," U.S. Patent 5843764, Dec. 1, 1998.

J. Woodward, "Structurally Stable Gel Bead Containing Entrapped Enzyme and Method for Manufacture Thereof," U.S. Patent 5846762, Dec. 8, 1998.

J. Woodward and S. M. Mattingly, "Method for the Enzymatic Production of Hydrogen," patent allowed.

I. Lee, J. W. Lee, and E. Greenbaum, "Method of Orienting Molecular Electronic Components," U.S. Patent Application ERID 0550.

6.9 PUBLICATIONS

E. Greenbaum and J. W. Lee, "Photosynthetic Hydrogen and Oxygen Production by Green Algae: An Overview," pp. 235–42 in *BioHydrogen*, ed. O. Zaborsky, Plenum Publishing, New York, 1998.

J. W. Lee, R. T. Collins, and E. Greenbaum, "Molecular Ionic Probes: A New Class of Hill Reagents and Their Potential for Nanofabrication and Biometallocatalysis," *J. Phys. Chem. B.* **102**, 2095–2100 (1998).

J. Woodward and M. Orr, "Enzymatic Conversion of Sucrose to Hydrogen," *Biotechnol. Prog.* **14**, 897–902 (1998).

N. Hershlag, I. Hurley, and J. Woodward, "A Simple Method to Demonstrate the Enzymatic Production of Hydrogen from Sugar," *J. Chem. Ed.* **75**, 1270–74 (1998).

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

6.10 PRESENTATIONS

E. Greenbaum, "Green Logic: The Application of Photosynthesis to Renewable Fuels Production and Molecular Electronic Devices," presented at the Physics Colloquium, Syracuse University, Syracuse, New York, October 8, 1998.

E. Greenbaum, "Fluorometric Tissue-Based Biosensors," invited lecture presented at the DARPA Workshop on Tissue-Based Biosensors, Bethesda, Maryland, October 13–14, 1998.

E. Greenbaum, "Photosynthesis, Carbon Dioxide Sequestration, and Renewable Hydrogen Production," presented to the delegation from the Research Institute for Innovative Technology for the Earth (RITE), Oak Ridge, Tennessee, November 4, 1998.

E. Greenbaum, "Photosynthesis, Carbon Dioxide Sequestration, and Renewable Hydrogen Production," presented at the Los Alamos National Laboratory Innovation in CO_2 Management and Sequestration Workshop, Santa Fe, New Mexico, November 9–12, 1998.

E. Greenbaum, I. Lee, and J. W. Lee, "Biomolecular Optoelectronic Devices," poster presentation at the Sixth Foresight Conference on Nanotechnology, Santa Clara, California, November 12–15, 1998.

E. Greenbaum, "Photosynthesis and the Sequestration of Carbon Dioxide," presented to RITE program managers, Kyoto, Japan, November 19, 1998.

E. Greenbaum, "Photosynthesis and the Production of Renewable Hydrogen," research seminar presented to the Department of Biotechnology, Tokyo University of Agriculture and Technology, Tokyo, Japan, November 20, 1998.

7. MOLECULAR STUDIES

P. T. Cummings

7.1 AQUEOUS ELECTROLYTE SOLUTIONS AT AMBIENT AND SUPERCRITICAL CONDITIONS (P. T. Cummings, A. A. Chialvo, and T. Driesner)

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Summary: Molecular simulations of $SrCl_2$ solutions using a flexible water model were completed, and a new simulation code was written. New evaluations of the Chialvo-Cummings water model showed it to be (unexpectedly) very accurate at the dimer level. Molecular dynamics simulations of supercooled water were performed, and the stability of a new phase of ice was studied.

7.1.1 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).

7.1.2 Progress

Thomas Driesner completed molecular dynamics simulations of aqueous $SrCl_2$ solutions using a flexible water model to complement earlier simulations using rigid water molecules. As part of this initiative, he programmed a molecular dynamics simulation code for flexible water molecules to allow interpretation of Raman/infrared spectra of water under a wide range of conditions. A manuscript describing the work was written and submitted.

Ariel Chialvo analyzed the behavior of the induced dipole moment of a water molecule in a dimer—ab initio and according to the corresponding prediction from the Chialvo-Cummings polarizable smeared charge model. Excellent agreement was found. Chialvo also studied the effects of charge distribution, polarizability, anisotropy, and molecular geometry on the resulting total dipole moment of the Chialvo-Cummings water model.

Chialvo continued using molecular dynamics to explore the supercooled water behavior for the TIP4P water model as part of an ongoing collaboration with P. G. Kusalik at Dalhousie University (Canada), and István Borzsák used this model to study the melting behavior of the recently discovered phase of ice (ice XII).

7.2 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: Computational prediction of the viscosity and viscosity index of various linear and branched alkanes, including a large-scale simulation of C_{100}, was continued. A molecular simulation algorithm for elongational viscosity was completed. The transient time correlation function (TTCF) formalism was also under development.

7.2.1 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.

7.2.2 Progress

We continued production calculations on the ORNL Intel Paragons of the viscosity of various linear and branched alkanes.

Jonathan Moore continued simulations of liquid C_{100} using the massively parallel Cray T3E supercomputer located at the National Energy Research Supercomputing Center (NERSC) at Lawrence Berkeley National Laboratory, as well as Cray T3E's located at Cray headquarters in Minnesota. The goal of the C_{100} simulation is to understand how a C_{100} polyethylene melt behaves at high strain rate compared with the predictions of reptation theory. Moore began preparing a manuscript on this work and also began preparing a technical report on MDVIZ, a molecular dynamics visualization package originally developed by Peter Cummings while at the University of

Virginia. Recently, in collaboration with Bob Ward (faculty) and Wael El Wasif (graduate student) in Computer Science, the capabilities have been enhanced considerably, with the goal of eventually providing a method for steering molecular dynamics computations.

As part of a cooperative research grant [National Science Foundation (NSF)] between the United States and Hungary, Cummings and Moore visited Eötvös University in Hungary to work with Andras Baranyai. This collaboration has resulted in a new algorithm for elongational flow, which will be applied in the future to alkane liquids and polymers.

Shengting Cui continued nonequilibrium molecular dynamics calculations of the pair-correlation functions of the soft sphere fluid under shear for comparison with a newly developed integral equation theory being performed by Yurij Kalyzhnyi.

Borzsák continued development of a computer code to incorporate the TTCF formalism into nonequilibrium molecular dynamics simulations and has ported the serial version of this code to parallel supercomputers. This program calculates the viscosity for fluids composed of particles interacting with the Weeks-Chandler-Andersen (WCA) potential using the TTCF formalism. Borzsák made production runs using both serial and parallel computers for the WCA fluids using this program. He also started implementing the TTCF formalism for fluids of greater industrial importance, namely, alkane chains. The first model for these studies is *n*-decane.

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

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

Summary: Study of an integral equation theory for nonequilibrium systems was continued.

7.3.1 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.

7.3.2 Progress

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

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

Contact: P. T. Cummings
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Internet: u53@ornl.gov

Summary: Preparation of a final report to the sponsors was completed, and several papers from this completed project appeared.

7.4.1 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 with in situ bioremediation and to subsequently develop mathematical models for these processes. The project funding ended on December 31, 1997.

7.4.2 Progress

This project is no longer funded and is being concluded. A final report to the sponsors (IBM) was completed and submitted in October 1998.

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

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

Summary: The Chialvo-Cummings solvation formalism was applied to electrolyte solutions. Molecular simulation of HCl solutions was conducted.

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*University of Virginia.

7.5.1 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).

7.5.2 Progress

Ariel Chialvo applied the Chialvo-Cummings solvation formalism to model electrolyte solutions and compared these results with experimental results for alkali halides.

Chialvo also applied molecular dynamics simulations for calculating the potential of mean-force calculations for aqueous HCl solutions, based on the SPC/E model of water and variations of Fornili's or Kusaka's model for hydronium, to the calculation of the association constant of HCl at near-critical conditions. The Ewald sum method for handling long-range forces was implemented to complement earlier reaction field codes.

7.6 DEVELOPMENT AND APPLICATION OF FAST COMPUTATIONAL PROTEIN-FOLDING ALGORITHMS USING MASSIVELY PARALLEL SUPERCOMPUTERS

(P. T. Cummings, P. H. LoCascio, K. Dill,* and Kai Yue)

Contact: P. T. Cummings
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Internet: u53@ornl.gov

Summary: Progress continued to be made in the parallelization of the Geocore algorithm.

7.6.1 Purpose and Scope

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.

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*University of California–San Francisco.

7.6.2 Progress

During this reporting period, Kai Yue and Phil LoCascio continued development of the Geocore ab initio protein-folding algorithm.

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

Summary: The key simulation code to study reverse micelles in supercritical water was completed, and production runs were conducted.

7.7.1 Purpose and Scope

The aim of this project is to use SAXS and SANS plus complementary molecular dynamics and Monte Carlo simulations to develop a molecular-level understanding of the formation and stability of reverse micelles in supercritical carbon dioxide. The fundamental knowledge resulting from this project will enable the U.S. chemical industry to substitute supercritical CO_2 for many of the toxic or hazardous solvents presently used in most industrial chemical reaction and separation processes. The project is funded by the NSF and the U.S. Environmental Protection Agency.

7.7.2 Progress

During the period, Sumeet Salaniwal calculated the diffusivity of *n*-perfluroheptane in supercritical CO_2 for comparison with the experiments. Salaniwal also completed a parallel molecular dynamics code for simulation of a reverse micelle composed of di-chain surfactant molecules with an aqueous core in supercritical CO_2. In addition, he performed molecular dynamics simulations of reverse micelles in supercritical CO_2 to study the structural features of the aggregates formed for a smaller system compromised of 132 water, 30 surfactant, and 2452 CO_2 molecules. The code was modified for the large system (duplicating the experimental work of Eastoe et al.) for two different starting configurations. The programs were run on the T3E at the NERSC, and results were obtained for about 200 ps with each. Sumeet parallelized these codes for implementation on the T3E.

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*University of Pittsburgh.

†University of North Carolina.

7.8 NANOTECHNOLOGY WITH EMPHASIS ON TRIBOLOGY: A COMBINED EXPERIMENTAL AND SIMULATION STUDY (P. T. Cummings, H. D. Cochran, S. T. Cui, S. Granick,* and G. Grest†)

Contact: P. T. Cummings
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Internet: u53@ornl.gov

Summary: The primary focus was initiating the project and recruiting a postdoctoral researcher. Molecular dynamics simulations of alkanes confined to nanoscale gaps were performed.

7.8.1 Purpose and Scope

This 3-year project, supported by the NSF through the interdisciplinary nanotechnology program, began July 15, 1998. The aim of the project is to undertake a fundamental study of lubrication at nanometer scale, including experiments with surface rheometry and nonequilibrium molecular dynamics simulation. The goals of the research are to achieve overlap in shear rate between experiments and simulations with the same systems, to extend both the experimental and computational efforts to more complicated systems and surface characteristics (including surfaces with chemical and topographical heterogeneity), and to study not only the steady-state shear response of nanotribology systems but also their transient behavior, including the technologically important issues related to adhesion.

7.8.2 Progress

During this reporting period, the emphasis was on setting up the project and recruiting a postdoctoral researcher. Shengting Cui continued molecular dynamics simulations of alkanes confined between walls separated by nanoscale gaps. Clare McCabe, a recent Ph.D. recipient from the University of Sheffield, was recruited as a postdoctoral researcher and will arrive after January 1, 1999.

7.9 OTHER IMPORTANT ACTIVITIES

Cummings officially presented to the NSF the report arising from an NSF workshop he chaired in November 1997. The official presentation included an invited seminar—"Outcomes of the Workshop on Future Directions in Molecular Simulation and Computational Chemistry:

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*University of Illinois.

†Sandia National Laboratory.

Fundamentals and Applications," presented to the Chemical and Transport Systems Division, NSF, Arlington, Virginia, July 8, 1998,—and transfer to NSF of several hundred copies of the report and trifold summary brochure.

Cummings continued his work on educational initiatives related to molecular modeling and simulation. He presented an invited talk on his work with the Molecular Modeling Task Force. Cummings also participated in a National Academy of Sciences workshop on computational chemistry, October 31–November 2, 1998. Finally, on November 16, 1998, Cummings was presented with the Alpha Chi Sigma award at the AIChE Annual Meeting, Miami Beach, Florida.

7.10 PUBLICATIONS

7.10.1 Submitted

S. T. Cui, H. D. Cochran, and P. T. Cummings, "Vapor-Liquid Phase Coexistence of Alkane-CO_2 and Perfluoroalkane-CO_2 Mixtures," *J. Am. Chem. Soc.* (1998).

T. Driesner and P. T. Cummings, "Molecular Simulation of the Temperature- and Density-Dependence of Ionic Hydration in Aqueous $SrCl_2$ Solutions Using Rigid and Flexible Water Models," *J. Chem. Phys.* (1998).

A. A. Chialvo, P. T. Cummings, J. M. Simonson, and R. E. Mesmer, "Solvation in High-Temperature Electrolyte Solutions," *J. Mol. Liq.* (1998).

7.10.2 Accepted

A. Baranyai and P. T. Cummings, "Steady State Simulation of Planar Elongation Flow by Nonequilibrium Molecular Dynamics," *J. Chem. Phys.* (1998).

I. Borzsák and P. T. Cummings, "Molecular Dynamics Simulation of Ice XII," *Chem. Phys. Letts.* (1998).

A. A. Chialvo and P. T. Cummings, "Molecular Simulation and Modeling of Supercritical Water and Aqueous Solutions," in *NATO Advanced Study Institute on Supercritical Fluids, July 12–24, 1998, Kemer, Antalya, Turkey*, ed. E. Kiran, Kluwer, Dordrecht, The Netherlands, 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.* **110**, 1064–74 (1999); published after the conclusion of the reporting period.

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.* **110**, 1075–86 (1999); published after the conclusion of the reporting period.

7.10.3 Published

S. A. Gupta, H. D. Cochran, and P. T. Cummings, "Nanorheology of Liquid Alkanes," *Fluid Phase Equilib.* **150–151**, 125–31 (1998).

A. A. Chialvo, P. T. Cummings, J. M. Simonson, and R. E. Mesmer, "Thermodynamics and Kinetics of Ion Speciation in Supercritical Aqueous Solutions: A Molecular-Based Study," *Fluid Phase Equilib.* **150–151**, 107-15 (1998).

A. A. Chialvo and P. T. Cummings, "Simple Transferable Intermolecular Potential for the Molecular Simulation of Water over Wide Ranges of State Conditions," *Fluid Phase Equilib.* **150–151**, 73–81 (1998).

D. A. Kofke and P. T. Cummings, "Precision and Accuracy of Staged Free-Energy Perturbation Methods for Computing the Chemical Potential by Molecular Simulation," *Fluid Phase Equilib.* **150–151**, 41–49 (1998).

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. Letts.* **293**, 289–94 (1998).

I. Borzsák and P. T. Cummings, "Effect of Oscillatory Shear on the Fluid-Solid Transition of Supercooled Water," *Fluid Phase Equilib.* **150–151**, 141–49 (1998).

P. T. Cummings and A. Baranyai, "Classical Dynamics of Nonequilibrium Processes in Fluids," in *Encyclopedia of Computational Chemistry*, ed. P. von Rague Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, and H. F. Schaefer III, John Wiley & Sons, New York, 1998.

A. A. Chialvo and P. T. Cummings, "Molecular Simulation of Supercritical Water and Aqueous Solutions," in *Encyclopedia of Computational Chemistry*, ed. P. von Rague Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, and H. F. Schaefer III, John Wiley & Sons, New York, 1998.

K. C. Chen, R. M. Ford, and P. T. Cummings, "Mathematical Models for Motile Bacterial Transport in Cylindrical Tubes,," *J. Theor. Biol.* **195**, 481–504 (1998).

K. C. Chen, R. M. Ford, and P. T. Cummings, "The Global Turning Probability Density Function for Motile Bacteria and Its Applications," *J. Theor. Biol.* **195**, 139–155 (1998).

7.11 PRESENTATIONS

7.11.1 Invited Seminars

P. T. Cummings, "Outcomes of the Workshop on Future Directions in Molecular Simulation and Computational Chemistry: Fundamentals and Applications," Chemical and Transport Systems Division, National Science Foundation, Arlington, Virginia, July 8, 1998.

P. T. Cummings, "Molecular Simulation of Supercritical Water and of Ionic Association in Supercritical Aqueous Solutions," Department of Chemistry, University of Nevada–Reno, Reno, Nevada, October 9, 1998.

P. T. Cummings, "Molecular Modeling of Real Systems Using Massively Parallel Supercomputers," Department of Chemical Engineering, University of Nevada–Reno, Reno, Nevada, October 12, 1998.

P. T. Cummings, "Molecular Simulation of Supercritical Water and of Ionic Association in Supercritical Aqueous Solutions," Department of Chemistry, University of California–Davis, Davis, California, October 13, 1998.

P. T. Cummings, "Molecular Modeling and Simulation: Present and Future Tools for Physical Properties Prediction," Department of Chemical Engineering, Brigham Young University, Provo, Utah, October 15, 1998.

P. T. Cummings, "Molecular Modeling on Massively Parallel Supercomputers," Center for Computational Sciences, University of Kentucky, Lexington, Kentucky, October 21, 1998.

7.11.2 Invited Conferences

P. T. Cummings, "Molecular Simulation of Supercritical Water and Aqueous Solutions," NATO Advanced Study Institute on Supercritical Fluids, Kemer, Antalya, Turkey, July 12–24, 1998.

P. T. Cummings, "Molecular Thermodynamics of Dilute Supercritical Mixtures," NATO Advanced Study Institute on Supercritical Fluids, Kemer, Antalya, Turkey, July 12–24, 1998.

P. T. Cummings, "Molecular Simulation of Supercritical Water and Aqueous Solutions," Gordon Conference on the Physics and Physical Chemistry of Water and Aqueous Solutions, Plymouth, New Hampshire, August 2–7, 1998.

P. T. Cummings, "Computational Protein Folding," Supercomputing '98, Orlando, Florida, November 8–13, 1998.

P. T. Cummings, "Molecular Simulation of Lubricant Components," American Institute of Chemical Engineers Annual Meeting, Miami Beach, Florida, November 15–20, 1998.

P. T. Cummings, "Molecular Simulation Methods for Phase Equilibrium and Transport Properties," American Institute of Chemical Engineers Annual Meeting, Miami Beach, Florida, November 15–20, 1998.

P. T. Cummings, "Case Studies: Molecular Simulation Methods for Phase Equilibrium and Transport Properties," American Institute of Chemical Engineers Annual Meeting, Miami Beach, Florida, November 15–20, 1998.

P. T. Cummings, "Molecular Simulation: A Present and Future Tool for Physical Properties Prediction," American Institute of Chemical Engineers Annual Meeting, DIPPR Liaison Forum, Miami Beach, Florida, November 15–20, 1998.

P. T. Cummings and D. A. Kofke, "CACHE Molecular Modeling Task Force: Bringing Molecular Modeling into the Undergraduate Classroom," American Institute of Chemical Engineers Annual Meeting, CACHE Trustees Reception, Miami Beach, Florida, November 15–20, 1998.

7.11.3 Contributed Conferences

T. Driesner and P. T. Cummings, "Molecular Dynamics Simulation of Ionic Hydration and Ion Association in Aqueous $SrCl_2$ Solutions from Ambient to Supercritical Conditions," NATO Advanced Study Institute on Supercritical Fluids, Kemer, Turkey, July 12–24, 1998.

A. A. Chialvo, P. T. Cummings, J. M. Simonson, and R. E. Mesmer, "Solvation in High-Temperature Electrolyte Solutions," Gordon Conference on the Physics and Physical Chemistry of Water and Aqueous Solutions, Plymouth New Hampshire, August 2–7, 1998.

I. Borsák and P. T. Cummings, "Computer Simulation of a New Phase of Ice (Ice XII)," Gordon Conference on the Physics and Physical Chemistry of Water and Aqueous Solutions, Plymouth, New Hampshire, August 2–7, 1998.

P. LoCascio, K. Yue, K. A. Dill, and P. T. Cummings, "The Large Scale Parallelization of a Conformational 3D Protein Structure Prediction Application," Supercomputing '98, Orlando, Florida, November 8–13, 1998.

A. A. Chialvo, P. T. Cummings, and P. B. Kusalik, "Solvation Phenomena in Supercritical Aqueous Electrolyte Solutions: Formal, Integral Equation, and Experimental Results," American Institute of Chemical Engineers Annual Meeting, Miami Beach, Florida, November 15–20, 1998.

S. Salaniwal, S. Cui, H. D. Cochran, and P. T. Cummings, "Molecular Dynamics Simulation of Hybrid Surfactants in Supercritical Carbon Dioxide," American Institute of Chemical Engineers Annual Meeting, Miami Beach, Florida, November 15–20, 1998.

S. Cui, H. D. Cochran, and P. T. Cummings, "Dynamical Properties of Linear and Branched Alkanes in Confinement," American Institute of Chemical Engineers Annual Meeting, Miami Beach, Florida, November 15–20, 1998.

A. A. Chialvo and P. T. Cummings, "Modeling of Water: On How Polarizability and Repulsive Interactions Affect the Model's Transferability," American Institute of Chemical Engineers Annual Meeting, Miami Beach, Florida, November 15–20, 1998.

A. A. Chialvo, P. T. Cummings, J. M. Simonson, and R. E. Mesmer, "Ion Association Reaction in Supercritical Aqueous Hydrochloric Acid Solutions: A Molecular Simulation Study," American Institute of Chemical Engineers Annual Meeting, Miami Beach, Florida, November 15–20, 1998.

S. Cui, P. T. Cummings, and H. D. Cochran, "Gibbs Ensemble Molecular Simulation Study of Solubility of Alkanes, Perfluoroalkanes, and Partially Fluorinated Alkanes in Supercritical Carbon Dioxide," American Institute of Chemical Engineers Annual Meeting, Miami Beach, Florida, November 15–20, 1998.

I. Borzsák and P. T. Cummings, "Molecular Simulation Study and Comparison of Various Phases of Ice," American Institute of Chemical Engineers Annual Meeting, Miami Beach, Florida, November 15–20, 1998.

P. T. Cummings, P. LoCascio, K. Yue, and K. Dill, "Computational Protein Structure Prediction Using Geocore Implemented on Massively Parallel Supercomputers," American Institute of Chemical Engineers Annual Meeting, Miami Beach, Florida, November 15–20, 1998.

J. D. Moore, S. Cui, H. D. Cochran, and P. T. Cummings, "Molecular Dynamics Simulation of a Polyethylene Melt," American Institute of Chemical Engineers Annual Meeting, Miami Beach, Florida, November 15–20, 1998.

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