Partnership Progress

Natural Gas & Oil Technology Partnership

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U.S. Department of Energy ■ National Laboratories ■ U.S. Petroleum Industry

Changes

The Bush administration has entered the White House and under the direction of Vice President Cheney is reevaluating the nation's energy policy. Results of the reevaluation are expected later this spring. The Partnership eagerly awaits the declaration of the new energy policy and looks forward to addressing the technology needs that may be identified.

Changes have occurred within the roster of Partnership representatives. Earl Whitney of LANL, who has served as Partnership co-chair for the past three years, is leaving the Partnership to assume greater

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The Partnership on the World Wide Web
http://www.sandia.gov/ngotp/

Featured Partnership Project

Predictive Model of Indoor Concentrations of Outdoor $PM_{2.5}$ in Homes

Model Will Accurately Apportion Health Risks for $PM_{2.5}$

National Ambient Air Quality Standards for airborne particulate matter smaller than 2.5 μm in diameter ($PM_{2.5}$), were established largely on epidemiological studies that found relatively consistent associations between outdoor particulate-matter concentrations and various adverse health effects. However, because individuals are indoors 80%–90% of the time (70% in homes), determining indoor concentrations of outdoor particles is key to learning and accurately apportioning the health risks associated with specific $PM_{2.5}$ components.

Predictive Model

At two California sites—the San Joaquin Valley (Fresno Field) (see Figure 1) and the San Francisco Bay area (Richmond Field)—project researchers are measuring indoor concentrations of outdoor particles under a variety of experimental conditions to develop a physically based, semi-empirical predictive model of transport and transformation processes. This model will be used to estimate distributions of indoor $PM_{2.5}$ concentrations of specific chemical constituents based on outdoor measurements. Researchers are developing a predictive mass balance model—one based on the principle that treats a residential building as a single well-mixed zone.

Current regulatory standards have focused on the mass of suspended particles, because there is no scientific evidence to implicate any particular component(s) of the mass. For example, several petroleum refineries along the California coast are thought to be responsible for particle loading in downwind areas. As a result, San Fran-

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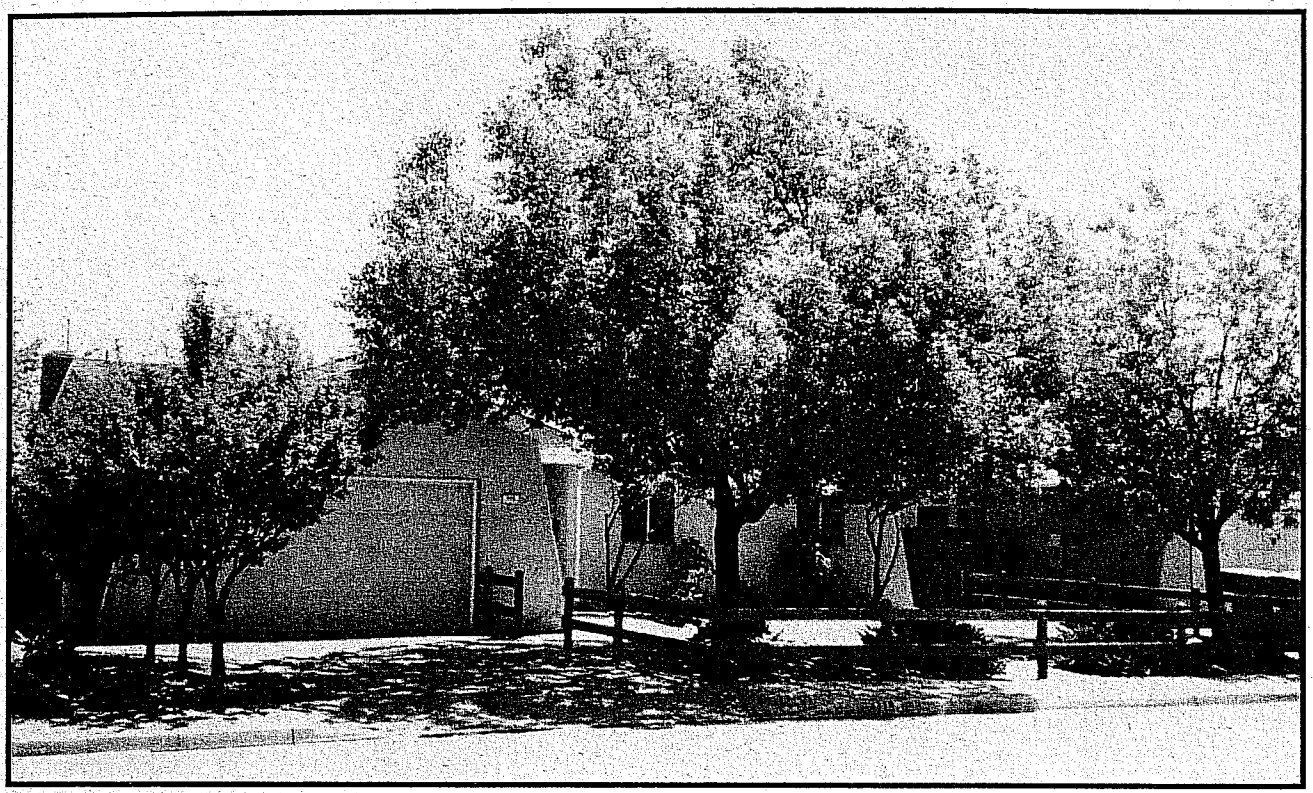

Figure 1. San Joaquin Valley (Fresno Field) site.

Determining Exposure

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cisco Bay area refineries have been subjected to strict NOx rules because they are thought to contribute substantially to particle loading in the San Joaquin Valley. Exposure to various kinds of $PM_{2.5}$ must be determined and quantified for accurate apportionment of their associated health effects. Only then can controls be designed that actually will reduce risk.

Field Measurements

Particle characteristics and size/composition relationships change as they cross a building shell (Figure 2). Complex interactions of particles with a building shell are further complicated by the effects of residential contents (e.g., furnishings, carpets, wall coverings, appliances, pets) on the transport process. For example, the gas-to-particle partitioning of ammonium nitrate—often the largest chemical mass constituent of $PM_{2.5}$ in many areas of the Western United States—is highly dependent on factors such as temperature, relative humidity, and ammonia concentrations that change as outdoor air is transported indoors. Phase changes depend on chemical composition, thus speciation of $PM_{2.5}$ is necessary to develop the model. Furthermore, some of the nonvolatile chemical components of outdoor $PM_{2.5}$, such as sulfate (and in many homes, carbonaceous aerosols), have no common indoor sources. These species provide an excellent means to trace transport of outdoor $PM_{2.5}$ into indoor air.

Physical processes monitored include infiltration, exfiltration, penetration, and deposition. Monitored chemical processes are phase changes, particle formation, coagulation, and hygroscopic growth. The model will be general enough to predict probability distributions for species-specific indoor concentrations of $PM_{2.5}$ (sulfate, nitrate, organic and black carbon constituents) based on outdoor PM, and gas-phase species concentrations, meteorological conditions, building construction characteristics, and heating, air conditioning, and ventilating conditions.

Instrumentation

Considerable progress has been made on a new instrument for automated 10-min resolution monitoring of fine-particle nitrate, sulfate, and carbonaceous aerosols in indoor and outdoor environments. Particle collection

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Fresno Field

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efficiencies for nitrate are greater than 95%, and the system operates for days with data recovery of 97%. Recovery of known standards for each sulfate and carbonaceous aerosol improved from less than 35% to approximately 80%. To take advantage of these enhanced recoveries, team researchers from Aerosol Dynamics constructed the multi-cell system running in the Fresno Field Site that provides simultaneous, time-resolved indoor/outdoor measurements for particulate sulfate, nitrate, and carbon (Figure 3).

Because there was no suitable off-the-shelf instrumentation that could provide detailed time resolution of gas-phase ammonia and nitrate, researchers constructed an ion chromatograph system capable of sub-ppb sensitivity. All instrument systems have been installed and field tested. Current efforts involve improving collection efficiency and field performance of the instrumentation.

Model Validation

Model validation is being accomplished through sensitivity and uncertainty analyses. Sensitivity analysis identifies the most influential parameters determining model behavior. Uncertainty analysis carefully quantifies errors in and distributions of parameters and determines the effects of propagating these errors throughout the model. Later experiments will identify and reduce the most consequential uncertainties in the model.

The model, which specifically addresses how indoor $PM_{2.5}$ is affected by differences between indoor and outdoor temperature and relative humidity, will be tested against field measurements made in approximately 30 residential buildings in California. Credibility of the model will be evaluated and established with respect to its real-world representation, accuracy, and limits of prediction.

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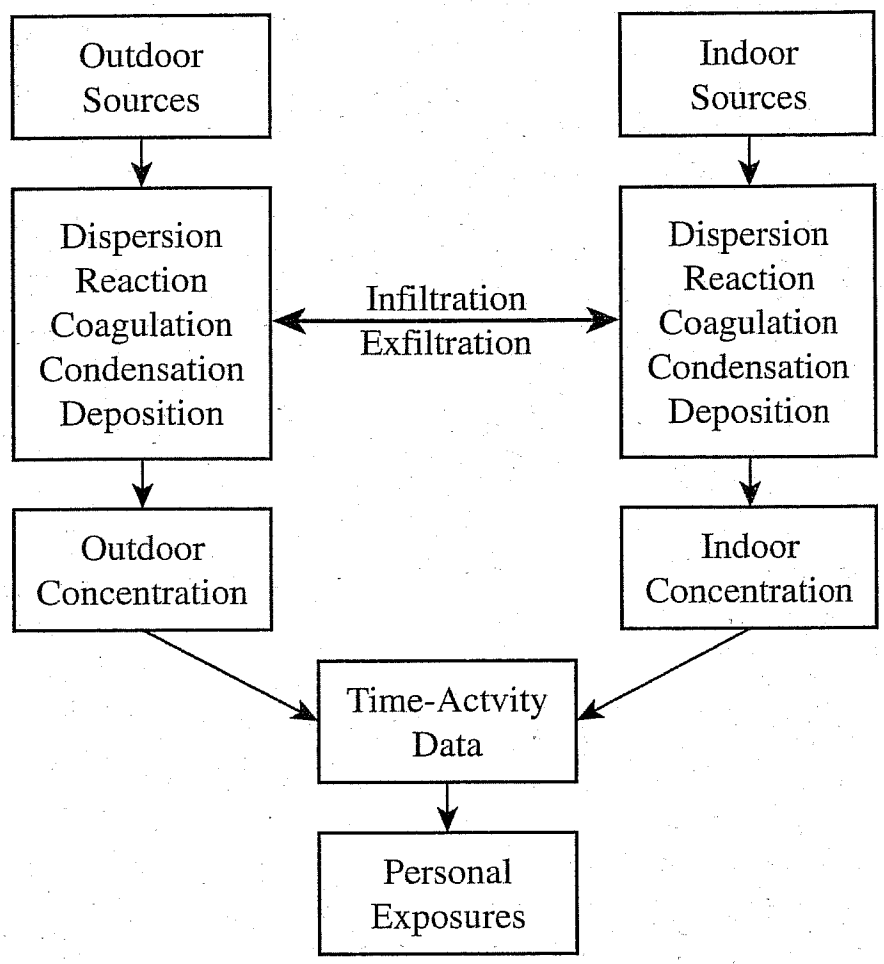

Figure 2. Interrelationship between indoor particles, outdoor particles, and human exposure.

Richmond Field Site

The project's initial experiments were performed in a "prototype" house—known as the Richmond Field Site—located at the University of California, Berkeley. The site is used for set-up/calibration exercises and preliminary study for equipment mobilization and experimental methods to provide input for the more advanced studies conducted at the Fresno Field Site.

For example, the description of relevant house characteristics and required house measurements obtained from the Richmond site were used to develop specifications for the purchase of meteorological equipment, a differential pressure measurement and control system, and an indoor environment characterization system for the Fresno site. Preliminary experiments investigating particle penetration and deposition performed at the Richmond site reduced the particle concentration indoors, then measured the concentration rebound over time. Results were used to refine experiment parameters at both the Richmond and Fresno sites.

Collaboration

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Project research is being performed in collaboration with other investigators in the California Regional Particulate Air Quality Study to benefit from their multi-year, multi-institutional detailed and intensive outdoor air study. The methodology, tools, data, and models derived from this study will be applicable to other areas of the United States, as well.

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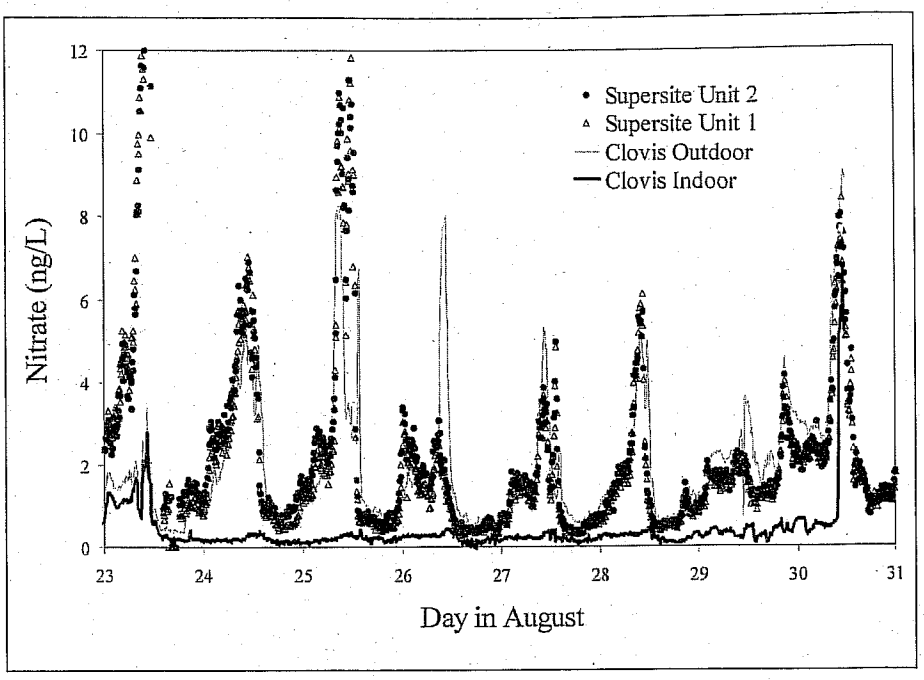

Figure 3. Automated nitrate measurements track well with Fresno Supersite.

Partnership News

Industry Panels

As the Partnership has added new technology areas over the last five years, these areas have been guided by industry panels. Through workshops and other venues, these panels have defined and prioritized industry needs in new technology areas. Their prioritized lists have provided the focus of subsequent Partnership calls for proposals in those technology areas.

The Partnership Office has received suggestions that we implement a similar process in the three traditional technology areas (Oil and Gas Recovery; Drilling, Completion, and Stimulation; and Diagnostic and Imaging). Implementation and ramifications of the suggestion are being studied. We invite your comments.

Ultra-Deepwater Research

In fall 2000, the DOE's Offshore Technology Roadmap was rolled out at three regional events (Galveston, TX; New Orleans, LA; and Washington, DC). This roadmap is the first step toward increasing oil and gas production from the Gulf of Mexico's ultra-deepwater sites.

The Partnership supports the DOE's effort as part of our organization's goals to develop and transfer exploration and production technologies from the national laboratories to the domestic oil and gas industry to increase critical and strategic production. The Partnership, in conjunction with DOE Fossil Energy, will seek ways to showcase Partnership technologies that apply to deepwater exploration and production. Included in this evolution of the Partnership will be a review of best practices for transfer of national laboratory technology to industry.

Changes

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responsibilities at LANL. Jim Albright, of LANL, will step into Earl's roles of lab representative and Partnership co-chair. In addition, Bernie Saffell has returned to serve as PNNL's representative.

The DOE has approved the Partnership's recommendations, which were based on industry panel input, for new and continuing projects. Ten new projects will start in the Upstream Technology area.

These projects will start later this spring. Future editions of this report will highlight the projects as participants begin to generate results.

Publications

Abate, J.M., P. Wang, and K. Sepehrnoori. "Parallel compositional reservoir simulation on a cluster of PCs," *International Journal of High-Performance Computing Applications*, Spring 2001.

Lu, Q., M. Peszynska, and M.F. Wheeler. "A parallel multi-block black-oil model in multi-model implementation," *2001 SPE Reservoir Simulation Symposium* , SPE 66359, 2001.

Peszynska, M., Q. Lu, and M.F. Wheeler. "Multiphysics coupling of codes," *Computational Methods in Water Resources*, eds. Bentley, Sykes, Brebbia, Gray, and Pinder, 175–182, 2000.

Wang, P., G.A. Pope, and K. Sepehrnoori. "Development of equation of state for gas condensates for compositional petroleum reservoir simulation," *In Situ Journal* 24 (2&3) 183–217, September 2000.

Wheeler, M. F., J.A. Wheeler, and M. Peszynska. "A distributed computing portal for coupling multi-physics and multiple domains in porous media," *Computational Methods in Water Resources*, eds. Bentley, Sykes, Brebbia, Gray, and Pinder, 167-174, 2000.

Project News

Oil & Gas Recovery Technology

Improved Waterflooding

Waterflood oil recovery increases significantly under certain conditions when diluted reservoir brine is injected in laboratory corefloods. Field applicability of this process is being tested in Utah's Uinta basin. Water samples taken from the Monument Butte region were analyzed to determine composition of the formation's brine and injection water. Laboratory corefloods using crude oil, sandstone, and simulated brine (all from or characteristic of Monument Butte) will determine whether modifying injection brine will improve waterflood oil recovery. Waterfloods on 3-in. cores should begin in early spring.

Berea sandstone cores will be used to determine whether the process can be scaled from 3-in. cores to larger cores and later to field scale. Minnelusa asphaltic crude oil (Gibbs) has been selected for use in these experiments. Researchers investigated imbibition of liquid into clean and dry Berea cores. Imbibition is affected by the size, shape, and boundary conditions of the core and viscosity of the liquid. Verified by experimental data for air/refined oil/rock systems, the empirical scaling equation in use has a modified characteristic length and a new term for the viscosities of the nonwetting and wetting phases.

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Improved Prediction of Multiphase Flow

Project completed.

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New-Generation Petroleum Reservoir Simulator

Researchers are improving performance of the project's compositional simulator on a cluster of PCs. The original simulation represented a three-component model running 100 days of gas injection into an homogeneous reservoir, containing two wells, an injector located in one corner, and a producer installed in the opposite corner. Initial conditions and production scheme specified were (1) gas/oil/water were present throughout the simulation and (2) water was immobile. Grid dimensions were 16x22x8 (28,672 gridblocks and 229,376 unknowns). To carry out the parallel simulations, domain decomposition was in one dimension in the y-direction to decrease communication between processors.

The team has focused on the communication software for maximizing interprocessor communication efficiency. The P4 socket buffer size was tuned, changing the communication window from 7680 bytes to 4096 bytes during TCP communications, and the operating system in the cluster was upgraded to RedHat Linux v6.2. The same runs also were performed using a second cluster consisting of dual 400 MHz Pentium Xeon PCs. The tuned buffer size with 16 processors decreases total execution time several times over compared to the untuned system, making the P4 socket buffer size for PC clusters the most important tuning parameter.

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High-Resolution Reservoir Characterization

Partitioning tracer data (from Hill Air Force Base, UT) are being analyzed; an extensive set of the data was used to infer the permeability in a test cell. Work began on modifying the streamline approach to account for capillary effects and diffusion. Literature review indicates that the asymptotic approach, the basis of the inversion algorithm, may be extended to situations in which diffusion is present. Researchers are setting up a reservoir model—based on time-lapse seismic data and pressure, tracer, and water-cut observations—for simulation purposes.

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Fluid Identification Acoustic Logging Tool

Researchers are refining the automatic tracking electronics design that allows real-time measurement of oil composition. The system, which has a sensitivity of 0.2 ppm in resolving sound speed under static conditions, has not been tested under flow conditions. Participants are developing an integrated system that would derive all the required information acoustically and would rely on a separate capacitive measurement for the gas volume fraction measurement. The circuit requires further miniaturization and testing under more stringent conditions.

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Measuring Sucker Rod Pump Parameters Downhole

The prototype downhole instrumented pump is being assembled for testing in Austin, TX, where a unique video capability was added to the transparent laboratory sucker-rod pump. The camera rides up and down with the plunger, can zoom in on the traveling valve, and captures video in sync with the data measured. Video and data were recorded of two valves in action. The video shows that the two valves do not necessarily behave (open, chatter, etc.) in the same way. The data suggest that two types of valve chatter may occur: the first when the valve opens to balance flow with plunger movement, the second when the flow rate is so high that the turbulent flow tosses around the ball. Understanding valve chatter is a first step to mitigating the damage it causes. Researchers are developing a method to measure pressure between valves.

Two papers were presented at the Society of Petroleum Engineers Production Operations Symposium and the Southwestern Petroleum Short Course.

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Formation Logging Tools for Microboreholes

Researchers studied the advantages and technical challenges in making formation resistivity measurements in microholes. Advantages include moving to higher measurement frequencies and reduction of the uncertainties associated with resistivity measurements in commercial-size wells. Challenges include reduction of transformer size for the electrode-type resistivity tool and reduced rigidity of microhole resistivity tools if they were to be made using conventional designs.

Apparent (but physically impossible) shifts in gamma-ray spectral peaks were recorded by both commercial and microhole tools when casing sizes were changed. One casing was heavily magnetized, which affected performance of the photomultipliers in both commercial and microhole tools. Magnetic shielding resolved the discrepancy. New measurement sets were initiated to learn whether the respective intensity of the peaks was also affected, which would require repeating the tools' relative performance measurements.

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Coupled Geomechanical Deformation, Fluid Flow, and Seismic Modeling

The basic model consists of a single, 144-ft thick layer of Belridge Field, CA, diatomite located at a depth of 1188 ft. The layer is modeled as a square (330 ft/side) with a well at each corner; wells are completed to different depths. Mechanical loading is gravity plus the transient pore pressure field. The IPARS grid contains 7,938 cells; the JAS3D mesh has 42,875 elements. Model problems were run for a simulation time of ten years. Results clearly showed changes in the flow simulation pore pressure field because of dynamic porosity and permeability fields. Compaction caused decreased permeability which resulted in less flow (less fluid produced). These experiments served as initial checks on the dynamic permeability updates, but further validation is required because the magnitude of these differences depends on the exact relationship used to relate volume strain to porosity and permeability.

JAS3D was modified to calculate changes in relative density (porosity) from the total strain, rather than from changes in stress/strain. This new quantity (total volume strain) causes a bigger change in reservoir pore volume as either elastic or inelastic strain accumulates at every time step. The convergence behavior of the flow simulator (IPARS) changes when the total volume strain-calculated porosity changes occur. A modification to the

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Jacobian and conjugate gradient preconditioner will be made to allow the flow simulator to predict these large changes more accurately and to accommodate porosity and permeability changes coming from total strain change. Additionally, a suite of problems, including both analytical and computational solutions, was compiled to verify the staggered coupling scheme used in the IPARS/JAS3D code against a tightly coupled oil company research code for flow and geomechanics.

Using the same basic model, four simulations will compare results of various flow and geomechanic parameters: (1) flow simulation alone (porosity and permeability assumed fixed throughout the simulation), (2) coupled flow and geomechanics with fixed permeability and time-dependent (changing) porosity, (3) coupled flow and geomechanics with fixed porosity and time-dependent (changing) permeability, and (4) coupled flow and geomechanics with both porosity and permeability changing with time.

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Drill Cuttings Injection Field Experiment

Final reports include calculations of the stress changes induced by the injection series and tiltmeter and microseismic results.

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Drilling, Completion, & Stimulation Technology

Real-Time Coiled Tubing Inspection System

Nine samples of 1.25-in. 0.109 QT800 coiled tubing were fatigue tested. Four samples were plain; five were coated with magnetic strips. To compare the influence of the coating on fatigue strength, samples were cycled between a straight position and a curved position with a 48-in. radius of curvature, while maintaining constant internal pressure. Cycling continued until failure. The two pressure levels examined corresponded to (1) an average hoop stress of about 4% of the nominal yield strength (low pressure, nominally 638 psi) and (2) 40% of the yield strength (high pressure, nominally 6388 psi).

The magnetic strips appear to have adversely influenced the fatigue strength during low-pressure cycling, but the opposite appears true for high-pressure cycling. For the low-pressure tests, the average life for the coated samples was 27% lower than the average for the baseline tests. The average life from two high-pressure coated tests was 23% higher. The life reduction imposed on the low-pressure samples is reasonable, because the surface is scored to prepare for coating. It is not surprising for the effect to be less influential at high pressure, but it cannot be concluded in general that "coating improves life for high-pressure service."

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Seismic Stimulation for Enhanced Production

Remaining tasks include completing field monitoring of the Lost Hills, CA, test; analysis of laboratory experimental data; and assessment of current modeling capabilities. Discussion includes publication of project results and future support of this work outside DOE/FE.

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In-Well Imaging and Heating: Multiple-Use Well Design

Researchers continue to evaluate different established petrophysical relationships to interpret the changes in electrical properties observed during stimulation, particularly with respect to production criteria. During the initial monitoring phase, prior to temperature increase, individual pay units displayed consistent changes: some units showed an increase in electrical resistivity, others a decrease.

Interpreting these changes using Archie's Law (with considerations given the reservoir characteristics based on independent data) permits an estimate of fluid movement in the vicinity of the imaged volume. In the simplest interpretation, increasing resistivity can indicate oil displacing formation fluid in the pore space; decreasing resistivity indicates oil being removed from the pore space. Initial evaluation supports net movement of oil out of the imaged zone perpendicular to the well.

Final models were run for different ohmic heating simulations for input into imaging forward models. Calibration runs are under way to assess combined ohmic heating/imaging for comparison to steam simulations.

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Perforation Dynamics in Geological Media

Future tasks will include (1) refining the fines migration and ablation model and validating with quantitative comparison to experimental data on Berea sandstone, (2) extending the model to harder and weaker sandstones and porous limestone, and performing x-ray computer-aided tomography experiments to measure fines distribution and permeability, and (3) deriving core flow efficiencies based on computer modeling and validating those with measurements to be made in API RP-43 flow tests.

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3D Analysis for Induction Logging in Horizontal Wells

Efforts have focused on three objectives: (1) research on borehole effect, (2) development of a localized inversion code and dataset analysis, and (3) optimization of modeling software.

Researchers developed a matrix-free version of the 3D finite-difference modeling software that greatly reduces the amount of computer memory required. Thus, inexpensive PCs can be used to solve relevant problems in horizontal-well induction logging. The code was ported for use on distributed-memory parallel clusters. Using the MPI parallelization library, each node of the parallel cluster independently computes a single logging point, permitting minimum interprocessor communication, and achieving nearly optimal performance.

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Acoustic Telemetry

Minor modifications being made to the downhole acoustic telemetry system will strengthen its components against vibration. During its first field test, the prototype will be deployed in a well to a depth of approximately 10,000 ft. The rotating receiver sub will be mounted at the top of the kelly, where it will sense acoustic waves in the drill string and use a commercial radio frequency (RF) modem link to transfer the data from the rotating kelly to a PC. Initially, data reception will be limited to periods when the drill string is not rotating.

Researchers are developing signal processing algorithms that can reduce noise, suppress echoes, and decode the modulated acoustic signal captured by the receiver sub. The algorithms have performed surprisingly well during testing on acoustic data obtained from integration tests of the downhole prototype at a surface facility. Data were acquired in excess of 20 baud in this relatively short (1400-ft) drill string, which riddles the acoustic path with numerous echoes. Using Windows NT, the algorithms appear capable of processing and decoding the raw data at about twice the acquisition rate.

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Chemically Bonded Ceramic Borehole Sealants

Initial American Petroleum Institute (API) Standard tests included a small amount of additive, and pumping times were varied at different temperatures. Slurry rheology was excellent. Fluid loss was minimal and was partially attributable to excess water added to the slurry. No free water was observed in the paste. A complete profile of pumping time, temperatures, and pressures will be developed.

Consistency tests established that the Ceramicrete formula meets API Standards for borehole temperatures and pressures up to 150° F and 6160 psig. The following were observed:

- Magnesium oxide, a prime ingredient in the pretreated binder, performed much better than a similar powder available commercially.
- Boric acid had a retarding effect when the ash contained calcium. Ash with very low calcium does not exhibit a retarding effect with boric acid.
- Boric acid decomposed at 120° F and exhibited no retarding effect at high temperatures.

Future tests will determine the extent of expansion/contraction of Ceramicrete during setting and curing, its bond strength to downhole materials, compressive and flexural strengths, and fracture toughness. Participants are developing formulations that will provide a pumping time in excess of three hours at higher temperatures and pressures.

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Look-Ahead Pore Pressure Prediction While Drilling

Project work resumed in May. Intial tasks include modeling the field data collected in November 2000 and developing prototypes for additional field testing.

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Coiled-Tubing Deployed Microdrilling with Real-Time, Downhole Monitoring

San Ysidro Demonstration

The third attempt to run in a 1.66-in. OD PVC casing to a depth below the flowing aquifers was successfully completed by running the casing inside NQ drilling rods and removing the rods. Attempts to circulate and condi-

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tion the hole for cementing were plagued by hole collapse or caving. After establishing good circulation at moderated pump pressure, neat cement was pumped down the casing. Pump pressure increased and the flow stopped just as the cement started up the annulus.

Hydraulic Calculations

A concept for a real-time fluid viscometer that is compatible with the microdrilling circulation system and the PC data acquisition and control system was demonstrated with three flow-rate pressure-drop datasets. The concept (1) calculated the correct rheology for an ideal theoretical dataset and the ideal dataset with up to 5% background noise added and (2) produced the rheologic constants for one real dataset that were within 5% of the values calculated with six-point Fann viscometer measurement. The concept assumes a yield-power-law (Herschel-Buckley) fluid and is thought to be adaptable to allow other fluid with other three-parameter models, if the yield-power-law model does not represent microdrilling fluid adequately.

Control System

The new hydraulics system performed well during the drilling demonstration that included the interface with the PC control system.

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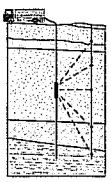

Diagnostic & Imaging Technology

Advanced Sensor Technology

A 1-5/8-in. PVC casing was run and cemented into a 600-ft microhole drilled for testing the 7/8-in. microhole seismic array. During cementing, no returns were observed at the surface. It was learned that only the lower 200 ft of the well had been properly cemented; a combination of lost-circulation material injected in advance of the cement and swelling clays prohibited cement return to the surface. The casing was washed over and retrieved from the well in preparation for a second attempt to cement the well.

Drilling the microhole did result in two noteworthy accomplishments: (1) A percussion bottomhole assembly adapted for use with the microhole drilling system was used to efficiently penetrate near-surface hard rock that had been impenetrable using the current PDM-bit combination. (2) Microhole sections of 1-3/4-in. diameter were drilled—to date, the smallest diameter microhole drilled using coiled tubing.

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Large Downhole Seismic Sensor Array

When the total passive design was tested (December 2000), two of the three receiver channels failed to activate; however, the working channel demonstrated the array's capability. The electronics were modified to improve durability of the array. Attempted testing in early January 2001 resulted in complete failure of the computer, but the array functioned with all channels. Response was poor for the horizontal phones, but the vertical phone worked without incident.

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Single-Well Seismic Imaging Technology

Computational simulations continue on the seismic reflections observed at the Bayou Choctaw, LA, salt dome test site. Anelastic effects, based on the standard linear solid formalism, were introduced into the 3D finite-difference wave propagation algorithm. Anelasticity is probably an important geophysical phenomenon at Bayou Choctaw, because of the fairly low quality factor (Q) values (for both compressional and shear waves) of Gulf Coast sediments. Preliminary modeling indicates that anelasticity reduces the amplitudes of the computed salt flank reflections so that they agree reasonably well with field-recorded data. However, incorporating anelasticity into the wave propagation algorithm substantially increases the computational burden.

Two papers about seismic wave propagation issues were presented at the Fall American Geophysical Union Meeting.

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Improved Prestack Kirchhoff Migration

Previous migrations completed were of numerical and field datasets using multiple-valued traveltime tables with

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and without amplitude and phase corrections calculated from ray tracing included in the migration operator. Current migrations employ the same datasets using single-value traveltime tables. These criteria were investigated: earliest arrival, most energetic arrival, and shortest travel path arrival.

The most energetic and shortest path arrivals give better images than earliest arrival for the Gulf of Mexico subsalt numerical dataset. For the field dataset, however, the earliest arrival image is the best when amplitude and phase corrections are added to the migration operator. Researchers theorize that the earliest arrival operator works best for the field dataset because errors in its velocity model make the prediction of later arrival times incorrect. Therefore, inclusion of later arrivals adds noise to the image rather than improving it. Investigation of this conclusion continues.

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Locating Geopressured Hydrocarbon Reservoirs

Three invention disclosure reports (IDRs) were submitted:

1. method for low-frequency seismic, sonic, and infrasound detection of acoustic and geopressure transition zones;
2. ahead-of-bit method for low-frequency seismic and infrasound detection of geopressure transition zones while drilling wells; and
3. method for using naturally occurring seismic amplitude or reflection strength variation with frequency boundaries for quality control of spectral balancing in geophysical seismic processing.

IDRs 1 and 2 protect intellectual property that demonstrates a method for locating geopressured hydrocarbon resources in young, active basins (e.g., Gulf of Mexico [GOM]) worldwide. These resources account for only 10% of GOM reservoirs but more than 50% of cumulative production. Applications include oil and gas exploration and ahead-of-bit detection of anomalous pressure regimes.

IDR 3 pertains to processing seismic survey data. Project studies on seismic processing of pressure-transition zones show that the different reflected frequency spectra between sharp and gradational acoustic contacts can be used to estimate the best frequency filters for a given dataset. Production of faster and more accurate imaging in seismic survey processing is IDR 3's expected benefit.

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3D Seismic Analysis Using SEG/EAGE Model Dataset

This project's final technical task is to select 3D image subsets of the marine survey and vertical cable datasets collected for the subsalt physical model. Selections will be based on data quality, regions of physical importance in the model, and reliability of the velocity model, which varies throughout the physical model. Results of this effort will be used to assess directions for future proposed physical model designs.

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Seismic Attributes of Fluids in Poorly Consolidated Sands

Researchers obtained a low-frequency approximation for the effect of a viscoelastic jacket on fundamental mode extension and torsional and flexural waves propagating in a jacketed sample. This expression will be used to analyze the effect of a plastic jacket on the attenuation of low-frequency waves propagating through a sand pack with low confining pressures.

Attenuation was added to the 3D cylindrical, time-domain finite-difference code. The modification used the memory-variable formulation to allow the bulk and shear moduli to be described as a superposition of relaxation mechanisms of the standard linear solid type. This code will be used with the low-frequency solution described (previous paragraph), to determine the effects of the plastic jacket in tests as the confining pressures are reduced below 1000 psi.

Assembly was completed of the combined extensional/torsional wave source, which is being tested on an acrylic bar. This test will determine the effects of the steel housing on the frequency response of the source over the 1–10 kHz range.

Steps were taken to measure the viscoelastic properties of unconsolidated sands in the 1–100 Hz range. Equipment assembled includes electronics, sensors, and a piezoelectric actuator to allow researchers to dynamically excite samples while measuring their quasi-static stress-strain properties.

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Inversion of Full Waveform Seismic Data for 3D Elastic Parameters

Full waveform inversion of seismic data entails finding a subsurface earth model that generates predicted seismic data that agree with the observed seismic data. Solution of the (nonlinear) full waveform seismic inverse problem, which involves continued updating of an initial estimate of a 3D earth

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model, continues until an acceptable match is obtained between observed and predicted (i.e., computed) seismic data. Extensive theoretical effort based on the seismic reciprocity principle identified two linear equations that can be used to determine the updates required for an elastic earth model.

Both a time-variant equation and a time-invariant equation were derived; characteristics of each are being investigated, particularly with regard to ease of computational implementation, memory demand, and algorithm execution speed. Although the time-invariant updating expression bears some similarity to existing full waveform-inversion approaches, the time-variant alternative appears to be novel.

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Next-Generation Seismic Modeling and Imaging

The project team is in the final stages of licensing its 3D seismic modeling capabilities to an oil service provider. The team is implementing additional physics (particularly anisotropic functionality) into its modeling capabilities. Researchers have begun investigating wide-aperture propagation through and below a subsalt model, using a technique that creates angle gathers with amplitudes that correctly indicate the changes of reflectivity as a function of incidence angle. Used after wave-equation migration, the method is equivalent to a radial trace transform in the Fourier transformed offset image gathers.

After the successful testing of narrow-azimuth migration on a V(z) model, the technique is being tested on the SEG/EAGE salt dataset. Preliminary results are promising, but more conclusive results will require running the technique on the soon-to-be-installed cluster of Linux computers.

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High-Speed 3D Hybrid Elastic Seismic Modeling

The local boundary condition approach was tested to see how it handles steep topography models. Introducing extra grid nodes at intersections of the topography function and rectangular model grid yielded high stability of computations, so the approach will be used on the 3D elastic algorithm.

Both second- and fourth-order in time finite-difference schemes were tested on the T3E and IBM massive parallel supercomputers. Changes in run times were measured as the number of subdomains was increased, along with the total model size and number of CPUs used. The T3E computer's better performance (compared to the IBM machine) results from its more effective internal data flow and communication. The fourth-order time-differencing scheme showed progressive improvement over the second-order scheme as the number of CPUs increased.

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Integrated Reservoir Monitoring Using Electromagnetics

A paper, "Crosswell electromagnetic and seismic imaging: An examination of coincident surveys at a steam flood project," was submitted to *Geophysics*. Another article, "Reservoir characterization using crosswell EM inversion: A feasibility study for the Snorre Field, North Sea," will be published this summer in *Geophysics*.

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Upstream Environmental Technology

Development of an In-Well Oil/Water Separator

Bench-scale testing is continuing using a model V-2 (2-in. rotor) centrifugal separator (CINC, Inc.) and synthetic oil. The housing for the separator will accept a longer rotor to increase throughput capacity. The portion of the rotor housing that directs the exit of the separated streams was redesigned to extend down the side. Exchangeable components for the internal parts of the housing were designed to allow adjustment of collection well volumes.

Solids/water/oil were separated using a hydrocyclone in combination with the centrifugal separator. The system worked well, producing a clean split of oil and water in the separator, after the solids had been removed in the hydrocyclone. The system was operated approximately an hour. The hydrocyclone/separator system was adjusted to make long-term operation (6–8 hours) possible.

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Ecological Framework to Evaluate the Effect of Size and Distribution of Releases

Project researchers presented work completed on the Tall Grass Prairie Preserve study site (Figure 1) at the Petroleum Environmental Research Forum (Richmond, CA, October 24–25, 2000). LLNL completed a draft Geographic Information Systems (GIS) data collection protocol and will provide it to ORNL for input. LLNL will incorporate the oil industry's request to list the minimum data layers necessary to allow landscape analysis of exploration and production sites. LLNL continues work on a literature review, which includes approximately 300 papers, on critical habitat size, fragmentation and modeling. ORNL is working to obtain additional data layers for the Tall Grass Prairie site, including Airborne Visible Infrared Imaging Spectrometer multispectral data and Landsat data. The laboratories also continue to revise the draft Geographic Information Systems (GIS) data collection protocol authored by LLNL, which is incorporating review comments on the Tall Grass Prairie Preserve trophic model.

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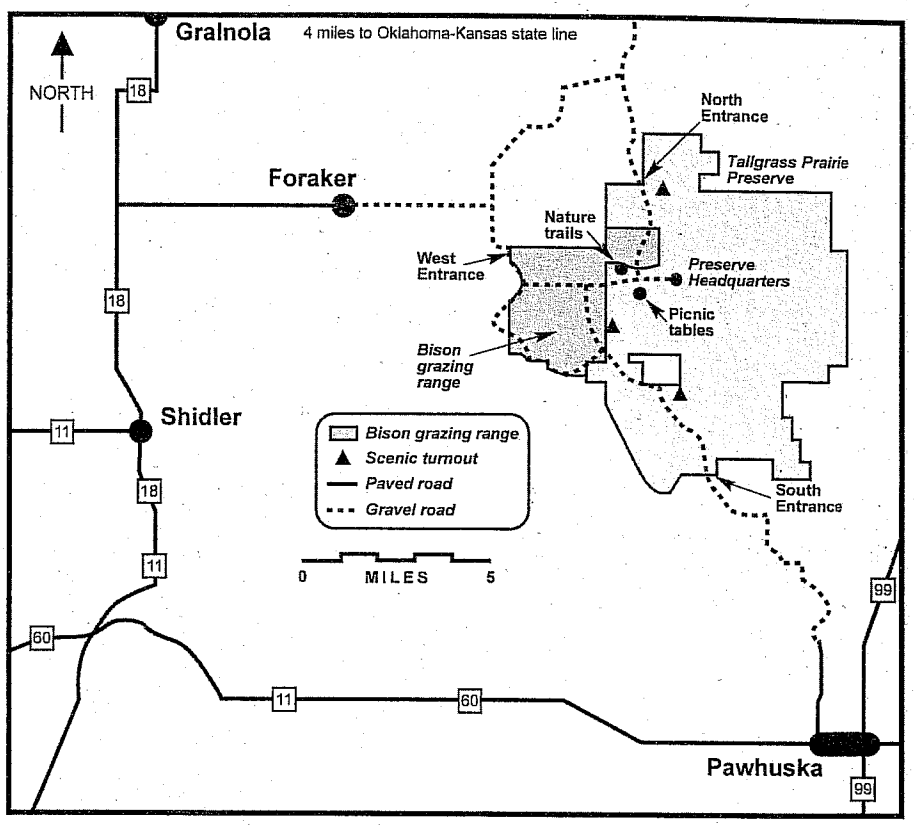

Figure 1. TheTall Grass Prairie Preserve in Oklahoma is the case-study site for the Ecological Framework to Evaluate the Effect of Size and Distribution of Releases project. Project researchers will develop an ecological framework that would assist in the evaluation of ecological impacts by considering land use and the types and attibutes of ecological receptors in relationship to size and distribution of impacted areas at upstream exploration and production sites at ecologically meaningful scales.

LLNL will develop a GIS data-collection protocol for the two study sites, construct the basic GIS database, and conduct a literature review related to patch-to-patch interactions within a single trophic level and minimum habitat requirements. Other work will include conducting simulation modeling to evaluate the effect of size and distribution of the impacted sites on the larger ecosystem. The project supports the Petroleum Environmental Research Forum's "Ecological Evaluations for Upstream Site Remediation Programs" project (PERF-99-01).

Reducing Chemical Use and Toxicity in Produced Water Systems

A corrosion experiment, ECN36, was run to demonstrate the increase in sensitivity to sustained localized pitting (SLP) corrosion on electrochemical noise (ECN) probes by using surface-modified electrodes (SME) in a microbially influenced corrosion (MIC) environment. The original ECN probe included two non-surface-modified electrode NSMEs. Each loop in the experiment included one original and one newly designed ECN probe.

None of the NSMEs developed significant localized pitting corrosion. The two SMEs developed severe localized pitting corrosion. Only uniform pitting corrosion (small pits uniformly seen all over the electrodes surface) was observed. The uniform pitting corrosion rates in these NSMEs were smaller than their general corrosion rates. ECN37 is planned to verify linear proportionality between the general corrosion rates of the NSMEs in the new ECN probes and the total noise current.

Development and testing of a user-friendly software package for automatic ECN measurement, data inter-

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pretation, and corrosion monitoring was completed. The new software automatically measures and interprets signals from a single ECN sensor. Information displayed includes the corrosion mechanism (i.e., sustained localized vs. uniform corrosion), the corrosion current, and estimated uniform corrosion rate. The software will be used in an experiment to find the optimal surface roughness of a surface-modified electrode to maximize the sensitivity of the electrode to sustained localized pitting corrosion in a microbially influenced corrosion environment.

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Sulfide Removal in Produced Brines by Microbial Oxidation

Evaluation of alternate sulfur compounds resulted in two unique metabolic observations:

1. Coleville organism (CVO) (*Thiomicrospira* sp. strain CVO) appears to form an inclusion complex when grown on a specific polysulfide complex—evident in direct microscopic evaluations of DAPI (4',6-Diamidino-2-phenylindole dihydrochloride hydrate) stained cells.
2. The counter ion of the polysulfide complex potentially affords a protective mechanism that results in more robust biomass.

Experiments to evaluate CVO tolerance to sulfate are near completion. Experiments concerning the potential protective nature of the counter ion of the polysulfide complex continue. Comparative experiments between *Thiobacillus denitrificans* and CVO continue.

Experiments to investigate the effects of increasing concentrations of sodium sulfate and sodium thiosulfate on the growth of CVO, as assayed by disappearance of sulfide (oxidation), were completed. Sodium sulfate concentrations from 200 mM up to 500 mM were tested. Additional experiments investigated the effects of sodium thiosulfate concentrations between 0 and 8 mM. The sulfide concentrations in all vials were reduced to zero after one day, showing that thiosulfate at these concentrations has no effect on sulfide oxidation by CVO. Evaluating concentrations above 8 mM thiosulfate will require different techniques because it reduced the color yield of the sulfide assay.

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Characterization of Soluble Organics in Petroleum Waste Water

ORNL is identifying water soluble organics in produced water from Gulf of Mexico (GOM) crude oil/brine contacts. The primary classes of organic compound being identified in produced water samples include total extractable material (TEM) by methylene chloride solvent extraction, hexane-extractable material (HEX), total saturated hydrocarbons (TSAT), total aromatic hydrocarbons (TARO), and total polar hydrocarbons (TPOL).

Methylene chloride-extractable material in the equilibrated produced water is typically present at 20–30 ppm. Chemical fractionation of TEM content suggests that 80%–90% of WSO is present as polar compounds; the next largest fraction is of aromatic materials. The visibly colored material is present in the polar fraction. The chemical character of the water soluble material does not vary with water cut.

Correspondence testing of chemical procedures used to analyze the chemical content of neat oil and produced water is under way. Statoil is providing characterization data derived from North Sea samples. ORNL is supplying data derived from Gulf of Mexico (GOM) crude oil and brine. Rather than identifying individual chemical compounds, ORNL is characterizing samples based on carbon range content and chemical classes. ORNL submitted samples of GOM crude and synthetic produced water for standard EPA Methods testing. The total petroleum hydrocarbon content in GOM crude, as defined by EPA Method SW-846 8015B, is 300 g/kg TPH-DRO C10–C28; 180 g/kg TPH-Oil C20–C28. The relative distribution using a similar GC/FID procedure at ORNL found 50%, 42%, and 8% in carbon series.

Chemical classification by liquid chromatography helps to account for the remaining 98% of the organic character of either oil or produced water samples. Methylene chloride total extractable material (TEM) in oil is 200-400 g/kg. The relative composition of the hexane matrix is 35% saturated hydrocarbons, 15% aromatic components, and 50% polar material.

The total concentration of water-soluble organics (WSO) in produced water is 20–30 ppm, using either EPA Method SW-846 8015B or ORNL GC/FID procedures. Identified semi-volatile compounds are 1-methylnaphthalene (10 ppb), 2-methylnaphthalene (9 ppb), naphthalene (14 ppb), and phenol (30 ppb). Again, compounds identified by EPA Method SW-846 8270C account for very little of the total WSO content.

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Estimation and Reduction of Air Quality Modeling Uncertainties

Ongoing literature review to assess which methods for uncertainty analy-

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sis have been applied to grid-based modeling and with what success will identify candidate methods and potential uses, evaluate their strengths and shortcomings, and recommend which methods should be applied and with what priority. The review will help researchers develop a comprehensive model system uncertainty analysis framework.

Stakeholders concerned with oil and gas development in southwest Wyoming were interviewed about air quality modeling uncertainty. These interviews have been extended to others concerned with regulation (in Ohio and California) to ascertain their views concerning uncertainty and potential uses of model uncertainty information.

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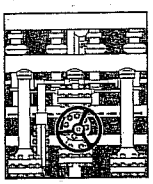

Downstream Environmental Technology

Biological Upgrading of Heavy Oils

Researchers found broad diversity among alkane-oxidizing biocatalysts, which will have far-reaching impacts on commercial development of bioprocessing systems. FY01 plans include expanding the project to include genetic characterization of the biocatalysts and beginning to isolate thermophilic alkane-oxidizers.

The objective of this project is to develop novel biocatalytic agents for the terminal oxidation of alkanes. Researchers currently have 42 pure bacterial cultures capable of oxidizing alkanes. Several strains possess promising characteristics for development of a controllable bioprocess. The project is on schedule.

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Bioprocessing of High-Sulfur Crudes

Experiments focused on polyethylene glycol (PEG) - cytochrome c (CYT c) conjugate and biocatalyst immobilization. Studies using the PEG-CYT c conjugate showed that no measurable transformations of dibenzothiophene took place in toluene solvents. Very slight conversion of thioanisole to the sulfoxide products occurred in a liquid benzene solvent, but transformation was evident in supercritical solvents. Carbon dioxide (CO_2), ethane, and trifluoromethane were explored as supercritical fluids. Reaction pressures ranged from 2,000–2,300 psi at a temperature of 40°C. No transformation was observed in supercritical ethane. Slight levels were observed in supercritical CO_2, but transformation was clearly evident in supercritical trifluoromethane.

Support material was used in protein immobilization studies; proteins investigated included horseradish peroxidase, CYT c, and hemoglobin. Dibenzothiophene (DBT) transformation in toluene was not observed. However, thioanisole conversion was measured in both the aqueous buffer and benzene solvent.

Experiments demonstrated that the polyethylene glycol PEG-CYT c conjugate successfully facilitated oxidation of thioanisole in a supercritical trifluoromethane/ethanol solution. Additional experiments explored the PEG-CYT c conjugate for the oxidation of DBT. DBT conversion to its sulfone product ($DBTO_2$) over PEG-CYT c was 58% in a liquid acetate phosphate buffer (pH=5.2)/ethanol (80/20) solution. CYT c was immobilized on agarose beads according to a Sigma procedure. The resulting product mass was 200 mg of immobilized protein/agarose beads.

Solvent systems included acetate-phosphate buffer/ethanol (80/20), hexane, carbon dioxide, and ethane. A 10 mg/ml wet biocatalyst was used in all reactions. Conversion to product obtained in the aqueous media was 85%. When the reaction was run in supercritical carbon dioxide (2150 psi) no product was obtained. Dehydration of the biocatalyst was observed in carbon dioxide. Reactions run in hexane and in supercritical ethane (2100 psi) also resulted in no conversion to product. Recovery of DBT from the view cell reactor using supercritical fluids-demonstrated some reproducibility problems.

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Kinetics of Biochemical Upgrading of Petroleum

In October 2000, the biochemical upgrading of petroleum studies were presented to a panel of program reviewers in Houston, TX. Regretfully, some members of the panel had not been updated on the recommendations and conclusions of the panels from the previous review (Berkeley, October 1999).

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Specifically:

It was recommended that a 10% total sulfur removal should be accepted as proof of concept. This was to be accomplished with oil and biochemical strains to be chosen by BNL. Proof of concept was accomplished by BNL using Boscan crude. Although total sulfur removal was 11%, surpassing the goal of 10%, some participants were disappointed by the result, which seemed small to them. However, desulfurization of Boscan crude, containing 55,000 ppm (5.5%) total sulfur in macromolecular fraction, is a more difficult task than desulfurization of diesel fuel with 200 ppm sulfur content.

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Enzymatic Upgrading of Heavy Crudes via Conversion of PAHs

A *Pichia pastoris* strain has been developed and engineered for expression of extracellular lignin peroxidase enzyme (LiP). Researchers investigated various optimization methods to improve recombinant enzyme production such as optimization of the fermentation conditions as well as media composition; however, success has been marginal. Work to improve enzyme production is being focussed on the use of error-prone polymerase chain reaction (PCR) to introduce point mutations in the LiP gene. The PCR products are cloned into a PCR2.1 plasmid and transformed into TOP10 *E. coli* strain using the original TA cloning kit (Invitrogen, Carlsbad, CA).

To produce mutants of the LiP enzyme, the gene for the enzyme was first isolated from one of the previously created clones. The forward primer bore a SfiI restriction site complementary to the sequence at the 5-ft-end of the lip gene (about 113 base pairs down from the start codon of the leader sequence)—a naturally occurring unique restriction site located in the proximity of the start codon of the native gene. The primer pair was used to create the LiP gene sequence using PCR. The product was then cloned into the PCR2.1 vector and transformed into *E. coli* strain TOP10. Researchers are analyzing the recombinant clones for correct insertion and orientation of the mutated gene.

All participants signed the cooperative research and development agreement. Separate meetings were held with industry participants and INEEL to discuss collaborative activities.

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A Predictive Model of Indoor Concentrations of Outdoor $PM_{2.5}$ in Homes

The project's research is the focus of this newsletter's feature article (see cover).

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Real-Time Characterization of Metals in Gas and Aerosol Phases

The project objective is to develop a high-precision field-portable instrument for real-time measurement of elemental composition in gas and airborne particulate matter in source emissions. Spectroscopic investigation of the portable laser-induced plasma spectrometer (LIPS) for lead- and nickel-laden aerosols was performed in the laboratory to evaluate the prototype instrument's response. Aerosol particles were produced by nebulization, charge neutralized, and dried before they were analyzed by LIPS.

Particle-size distribution and the elemental composition of the particles were measured in sequence. Maximum particle sizes were found to be smaller than 500 nm. In preliminary data, the dynamic linear range for the measurements was three orders of magnitude. Calibration curves were virtually linear (R2 value: 0.99 for lead and 0.98 for nickel species).

ORNL researchers are moving into the next phase of field testing the prototype instrument.

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Remote Sensing for Environmental Baselining and Monitoring

Researchers at UC-Davis are growing three plant species in hydroponic-solution culture in a controlled-growth facility and in a greenhouse. The plants are being exposed to several concentrations of several heavy metals. The hyperspectral data are collected on a regular schedule at the leaf and canopy level by both a spectrometer with hundreds of bands and an imaging spectrometer.

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Industry Participants

The Partnership's World Wide Web site includes a complete list of industry participants and their project affiliations:

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