

# ACTIVITY REPORT



**Natural  
Gas &  
Oil  
Technology  
Partnership**

**February 2004**

Bringing Department of Energy national laboratories capabilities to the petroleum industry.

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Note: Natural Gas and Oil Technology Partnership projects are reported according to the following schedule:

**January, March, May, July, September, November**  
Drilling, Completion, and Stimulation Technology  
Oil and Gas Recovery Technology  
Diagnostic and Imaging Technology

**February, April, June, August, October, December**  
Natural Gas Technology  
Upstream Environmental Technology  
Downstream Environmental Technology

**Natural Gas and Oil Technology Partnership on the World Wide Web: <http://www.sandia.gov/ngotp/>**

# Upstream Environmental Technology

## Estimation and Reduction of Air Quality Modeling Uncertainties

(Envair, EPRI, and LBNL)

Inactive

## Remote Sensing for Environmental Baseline and Monitoring

(US Geological Survey (USGS), and USDA Agricultural Research Service (ARS), and ORNL)

### Highlights:

- Analyzing nine sites in Osage County.
- Automatically find many clusters (38 to 174).
- Automatically prepare geobotanical maps.
- Can distinguish between roads and brine scars.

The US Geological Survey (USGS), the USDA Agricultural Research Service (ARS), and ORNL are collaborating to develop remote (airplane or satellite) hyperspectral sensor techniques to identify areas impacted by oil production. The last report mentioned that preliminary analysis had been completed for the USGS Site B with an area of 12,740 pixels. Subsequently, analysis has been completed for a total of nine sites. The sites are in all of the regions that were imaged: Tall Grass Prairie, Bluestem Ranch, John Zink Ranch, and the USGS sites. The USGS Site B remains the smallest area and the Bluestem Site 134 is the largest with 104,160 pixels (0.94 square kilometers). As new methods of analysis are developed, they are applied to all of the nine sites. The number of clusters depends on the cluster radius, which is: one minus the correlation. With a 1% radius (99% correlation), the number of clusters ranges from 38 for Site B to 124 for Bluestem 134. The USGS asked for more resolution at the Zink 131 site. Decreasing the radius from 1% to 0.4% (99.6% correlation) increases the number of clusters from 49 to 174 at Zink 131.

Since the two USGS sites are next to Skiatook Lake, their images have many water pixels. The water pixels have a negative correlation with green vegetation and were removed from the clusters by requiring that the root vectors for the clusters must have a positive correlation with the first root vector. Geobotanical maps assign each pixel a color that depends on the cluster. Consequently, the maps can be used to associate clusters with features: trees, forbs, grasses, dirt roads, paved roads, brine scars, etc. The primary method for associating clusters with features is to produce individual maps for each cluster. In a three color map, both roads and brine scars have high reflectance and are white. By associating clusters with features, ORNL and the USGS can distinguish: paved roads, dirt roads, edges of roads, brine scars, and recovering brine scars.

## Modeling of Water-Soluble Organic Content of Produced Water

(ChevronTexaco, ConocoPhillips, Shell, Statoil, and ORNL)

### Highlight:

- Produced water modeling presented at the GTI Natural Gas Technologies II Meeting in Phoenix, AZ.

Recent progress in the modeling of offshore produced water was presented at the the Gas Technologies Institute's Natural Gas Technologies II Meeting, held in Phoenix, AZ, February 9-11, 2004. The presentation covered recent progress in the thermodynamic and statistical model, and gave a brief summary of the produced water work done at ORNL and by North Sea producers. The presentation also mentioned similarities and differences between water contamination occurring with oil production versus that with water production.

## Science-Based Methods to Assess Risks Attributable to Petroleum Residues Transferred from Soil to Vegetation

(ChevronTexaco, PERF UC-Berkeley, UC-Davis, and LBNL)

### Highlights:

- Participated in NGOTP Review.
- Continued plant uptake data analysis.

Lawrence Berkeley National Laboratory (LBNL) presented a detailed progress report at the NGOTP Upstream Environmental Technology review meeting. LBNL and University of California-Davis (UCD) researchers are continuing to analyze the grass, soil and air samples that were collected during the controlled plant uptake exposure study performed at UCD. LBNL is continuing work on the review paper looking at soil-to-plant transfers of petroleum-related hydrocarbons.

## Interactive Information System on Drilling Waste Management Practices

(ChevronTexaco, Marathon, and ANL)

### Highlights:

- Project paper presented at March 2003 Conference.

A paper describing the project was presented in March 2003 at the SPE/EPA/DOE Exploration and Production Environmental Conference in San Antonio, TX. The presentation was well received by the audience. We have received inquiries from around the world concerning the website and when it will be publicly available.

The Technology Identification module and Regulatory module are programmed. The fact sheets describing different technologies are completed and undergoing review by the industry partners.

We anticipate that a full draft website will be finished during March. This will undergo testing by a selected review panel during March and April. We hope to have a final, publically available website available by the summer of 2004.

## Use of Ionic Liquids in Produced Water Clean Up

(ChevronTexaco, Shell, Conoco-Phillips, ORNL)

### Highlight:

- Sulfonate ionic liquids demonstrate good uptake of organics.

Sulfonate ionic liquids diluted in 1-nonanol were tested against produced water simulated contaminants. Good uptake into the IL phase was demonstrated for organic acids and toluene. Further tests are underway to regenerate the ionic liquids using pH-controlled rinses and heating cycles.

# Downstream Environmental Technology

## A Predictive Model of Indoor Concentrations of Outdoor PM<sub>2.5</sub> in Homes

### Highlight:

- Completed winter intensive suite of measurements at our Fresno Field Site.
- Conducted extensive measurements to characterize duct system in the Fresno house.
- Organized data analysis associated with the two intensive measurement periods.

(Aerosol Dynamics, Western States Petroleum Association, and LBNL)

During the reporting period we completed the winter season measurements program and we are now in the process of preparing three scientific papers for publication that describe: 1) the ammonia measurement system, 2) the deposition and penetration processes, and 3) the differences between indoor and outdoor NH<sub>4</sub>NO<sub>3</sub> particle concentrations.

## A Predictive Model of Indoor Concentrations of Outdoor Volatile Organic Compounds in Homes

(American Petroleum Institute, Western States Petroleum Association, and LBNL)

### Highlight:

- Manuscript accepted for publication in Atmospheric Environment.

The manuscript entitled "Sorption of volatile and semivolatile organic gases in a furnished room," by Brett C. Singer, Kenneth L. Revzan, Toshifumi Hotchi, Alfred T. Hodgson, and Nancy J. Brown was accepted for publication in Atmospheric Environment.

Additionally, progress was made on a second manuscript describing sorption experiments and modeling for wallboard and carpet, and the relative importance of each as indoor sorption sites. Data from experiments in which the chamber contained both wallboard and carpet were analyzed and progress was made on the draft text. In support of this paper, we have also been reviewing the literature on small chamber experiments of individual material sorption rates and equilibria with indoor VOCs.

## Characterization and Reaction Behavior of Sterically-Hindered Sulfur Compounds in Heavy Crudes with Nano-Sized Molybdenum Disulfide

(ChevronTexaco, BNL, and ANL)

**Project suspended pending renewed funding.**

## Development of a Solid Catalyst Alkylation Process Using Supercritical Fluid Regeneration

(Marathon-Ashland and INEEL)

The effect of regeneration pressure was examined over a USY zeolite catalyst. Reaction conditions were 60 °C, an isoparaffin to olefin ratio of 20:1, and an olefin weight hour space velocity of 0.265 hr<sup>-1</sup>. Regeneration pressures from 600 to 2,000 psi were examined. It was found that the highest pressures resulted in the greatest number of high-activity reaction/regeneration cycles, however a significant number of cycles could be achieved even at the lowest pressures.

Activity maintenance studies using a Beta zeolite were performed at an olefin weight hour space velocity of 0.1 hr<sup>-1</sup> and an elevated reaction temperature. At those conditions the Beta zeolite catalyst regenerated to initial activity levels for 120 hour, or 5 days of continuous operation, while providing high levels of conversion and product yield.

Discussions were held with Marathon Ashland Petroleum and with ConocoPhillips on paths forward and CRADA issues.

## Secondary Organic Aerosol Research in the Sierra Nevada Foothills

(Aerosol Dynamics, Independent Petroleum Association of Mountain States, and LBNL)

Recent progress has been directed toward bringing the 2002 particle data set to Level I (precision) and Level II (accuracy) condition. The data provide information on particle number concentration, particle size distributions, particle optical properties, and black carbon concentrations. We now have concentration data for the gas phase trace species that are monitored at the Blodgett Forest site. These have been measured by our collaborators under different

sponsorship. The data include volatile organic compounds and their oxidation products that are emitted from both anthropogenic and biogenic sources, and nitrogenous species, NO<sub>x</sub> (nitric oxide and nitrogen dioxide) and some NO<sub>y</sub> (NO<sub>x</sub> + HNO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, NO<sub>3</sub>) compounds. The data analysis is ongoing. We have received data from our collaborators that contain measurements of detailed meteorology and speciated NO<sub>y</sub> for 2002. These data will be used to predict the rate at which the gas phase biogenic emissions are converted to secondary organic aerosol precursors.

Data analysis has focused on characterizing the particle growth events observed in the forest. We see bursts of large numbers of particles whose optical diameters are less than 20 nanometers. We have elucidated characteristics of the growth events and they are:

- Temperature is very influential
- Particle growth correlates in time with decreasing temperatures
- Total particle number is dominated by smaller particles
- Volume of particles in nuclei mode can be as high as 10% of total particle volume
- Lifetime calculations show growth processes occur in forest
- Coagulation of small particles with larger ones is significant pathway of SOA into ambient aerosol
- Aerosol mass associated with growth events is same order of magnitude of measured concentrations of hydrocarbon oxidation processes.

We have also begun to determine how distant forest fires in Northern California and Southern Oregon, the so-called "Biscuit Forest Fire" that occurred between July and November, 2002 influenced particle characteristics at Blodgett as a result of long distance transport of particles and their processing in the atmosphere.

Nancy Brown gave a talk entitled "Characterizing the Formation of Secondary Organic Aerosols" at the project review in Houston on February 25, 2004.

## **Proton Exchange Reactive Membranes for Conversion of Light Alkanes to Clean Liquid Fuel**

(Ceramatec, Inc. and INEEL)

A new proton exchange membrane was received from Ceramatec Inc. This membrane had significantly better hydrogen transport properties than the previous membrane. Sufficient hydrogen was transported through the membrane to be quantitatively analyzed with a Residual Gas Analyzer (RGA). Several experiments were run to characterize the transport properties of the membrane with an applied potential. The objective was to determine if the hydrogen flux through the membrane could be controlled in a way that would satisfy the requirements of a catalyst reaction on the reactant side of the membrane. The hydrogen flux was controlled as a function of the applied current through the membrane. At approximately -30 mA of reverse bias the hydrogen flow through the membrane was shut off. As the reverse bias was decreased and eventually applied in the positive direction, the hydrogen flow increases and ultimately a pumping effect was produced.

Delivery of a third, thinner membrane from Ceramatec is expected in March for testing at lower temperatures that coincide with the requirements of the catalyst.

## Bioupgrading of Heavy Crudes Using Temperature and Oil Tolerant Enzyme Catalysts (ChevronTexaco and ORNL)

### Highlight:

- Cloned P450 enzymes into a alternate expression vector.

Previously, we reported cloning of CYP119 and hybrid enzymes into pCWori vector. The enzyme produced by the pCWori-119 plasmid, however was truncated due to the presence of a second restriction site, not present in the sequence reported for the gene CYP119. Therefore, a different cloning vector had to be used. We selected pET30a, since it has been used previously for P450 cloning. Currently, we are testing the expression of CYP119 and hybrid enzymes using this vector. These enzymes will be characterized by NMR to determine potential mutations in the enzyme to study structure-function relationships. Polyaromatic as well as alkyl hydrocarbons will be used as substrates for these studies.

## Natural Gas Technology

### Molecular Engineering: Next Generation of Gas Purification Technology

(ChevronTexaco, Virginia Commonwealth U, and BNL)

**No Report Received.**

### Coiled-Tubing-Deployed Hard Rock Thermal Spallation Drill and Cavity Maker

(Nextant, NM Tech, and LANL)

### Highlights:

- Flame igniters tested.
- Rededigned burner assembly tested.

Los Alamos conducted a series of tests to evaluate the feasibility of driving spark plugs from the surface power supply through the 200-ft long coiled tubing to power a spark plug on the bottom of the coiled tubing. The test results are mixed and inconclusive at this time. Additional testing will be conducted to determine if the early prototype connector sub can be used as a place holder for a downhole spark plug power source and thus defer the design of the downhole generator for a flame igniter until a deeper system requires it.

It has been assumed that the connector sub for a deep drilling system will have to include a downhole electrical converter to power an igniter in the flame-jet burner. A high-voltage source will be needed for a spark plug type igniter or a high current source for a glow plug igniter. Small off-the-shelf spark plug coils have been identified that may fit inside a connector sub but dimensional data and required clearances are not specified in sufficient detail.

New Mexico Tech had successfully demonstrated that a very small motor cycle spark plug would light their propane burner. A NGK Spark Plug Co. LTD ME-8 was procured by Los Alamos to evaluate the plug's performance when it is energized through a 200-long telemetry cable.

Precision Tube Technology completed the factory-fabricated, 200-ft long, coiled tubing with internal umbilicals and shipped and delivered the tubing to Los Alamos. Los Alamos tested the telemetry conductors for continuity and shorts to ground. All of the conductors passed the continuity test but one of the eight conductors shorted to ground. Some of the insulation on the telemetry cable may have been damaged when the cable was pulled through the 1/2-inch OD tubing beside the 3/16-inch OD tubing.

The pipe fittings needed to complete the manifold and connect the supply lines to the rotating union were received and assembled.

For the 10 ft Spallation Test Attempt, the redesign of the mixer mount was completed and the burner assembly was reassembled with the larger diameter nozzle to resume testing. The flame was successfully ignited and an air rate of 550 slpm was achieved on the first test. This is about 60% of the target air rate for stoichiometric combustion of 10 lb per hour propane flow. The flame was

more stable than in previous demonstrations at that air flow rate. A second test achieved 650 slpm air flow by carefully increasing the air flow and the air supply pressure at the airflow regulator in gradual increments. Attempts to light the burner after reassembling it with the smaller 0.339 inch diameter nozzle were not successful at any air flow rate. The redesigned static mixer mount and the longer burner chamber did not solve the stability problems with the drill stem mounted burner.

### **Scintillating Fiber Neutron Detectors for Well Logging**

(CompuLog, Precision Drilling, Technology Services Group, and PNNL)

#### **Highlight:**

- Samples of high time epoxies obtained.

The preamplifier board for the photomultiplier tubes was redesigned to minimize noise and optimize power distribution. Samples of high temperature epoxies were obtained for fiber compatibility testing. These epoxies are rated to 150 C and will survive at 200 C for shortened mechanical life. Further neutron testing is pending until electronics issues are resolved.

### **225° C MWD Using Silicon-On-Insulator (SOI) Electronics**

(Baker Oil Tools, Eagle-Picher, Honeywell SSEC, General Atomics, Noble Engineering, Quartzdyne, and SNL)

**No Report Received.**

## Partnership Office

The Upstream Environmental Technology Forum held a review on existing projects on February 25, 2004 in Houston. Details of venue and schedule will be announced when available. Existing projects requesting

fiscal year 2004 funding were due by January 16, 2004. Due to budget constraints, no new-start projects will be solicited for fiscal year 2004.