

# ACTIVITY REPORT



**Natural  
Gas &  
Oil  
Technology  
Partnership**

**June 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)

This project is in "Inactive" status.

## Remote Sensing for Environmental Baseline and Monitoring

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

### Highlights:

- Calculating cluster statistics for designated regions
- Paper submitted to the International Petroleum Environmental Conference

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. Using two different cluster radii, both high and low-resolution geobotanical maps have been created. A central objective is to distinguish environmental damage from roads from damage caused by produced water. Using single-cluster maps, the USGS and ORNL have been searching for clusters that occur only in brine damaged areas. Software has been written to automate this search. After a region has been specified, the software counts the number of members of each cluster inside and outside the designated region.

For Site A, the designated area is 261 pixels. For the 46-cluster case, 24 clusters are in the region and 10 clusters have more than 10% of their members in the region, with 2 at 100% and a third at 31%. For the 100-cluster case, 47 clusters are in the region and 31 clusters have more than 10% of their members in the region, with 3 at 100% and a 12 more clusters above 30%. For Site B, the two designated areas have 135 and 1214 pixels. For the smaller area and the 82-cluster case, 29 clusters are in the region and the highest membership ratio is 22%. For the smaller area and the 219-cluster case, 54 clusters are in the region, with two above 30% and 20 more clusters above 10%. For the larger area and the 82-cluster case, 61 clusters are in the region, with five above 30% and 26 more clusters above 10%. For the larger area and the 219-cluster case, 141 clusters are in the region, with 21 above 30% and 47 more clusters above 10%. The high-resolution cases with more clusters do a much better job of distinguishing between the roads and the brine scars.

A paper "Hyperspectral signature of the salt scar and other oilfield disturbed areas at USGS Osage-Skiatook Petroleum Environmental Research (OSPER) Site A, northeast Oklahoma- a preliminary report" has been submitted to the 11th International Petroleum Environmental Conference (IPEC) to be held in Albuquerque, New Mexico, October 12-15, 2004.

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

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

Funding for the project has arrived and work will resume shortly.

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

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

There was limited activity on this project during the May-June reporting period due to a break in the funding. We look forward to receiving FY04 funding in July.

## Interactive Information System on Drilling Waste Management Practices

(ChevronTexaco, Marathon, and ANL)

### Highlight:

- Drilling Waste Management Information System Website open

The Drilling Waste Management Information System (DWMIS) Website was opened for public access on June 2.

The URL is: <http://web.ead.anl.gov/dwm>.

This website publication followed several rounds of internal review and a final review by an external review panel with representatives from industry and government.

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. Several additional presentations are scheduled for summer and fall of 2004.

The Oil & Gas Journal intends to publish an article on the DWMIS during July 2004.

This completes the activities and deliverables for this project. This also serves as the final progress report.

## Use of Ionic Liquids in Produced Water Clean Up

(ChevronTexaco, Conoco-Phillips, Shell, and ORNL)

### Highlight:

- Paper prepared on uptake of organics into ionic liquids from aqueous solution

The distribution between water and ionic liquid solvents was measured for nine room-temperature, hydrophobic ionic liquids (1-butyl-3-methylimidazolium bistrifluoromethylsulfonylemide, 1-hexyl-3-methylimidazolium bistrifluoromethylsulfonylemide, 1-octyl-3-methylimidazolium bistrifluoromethylsulfonylemide, 1-butyl-3-methylimidazolium PF6, trihexyltetradecylphosphonium bistrifluoromethylsulfonylemide, 1-butyl-1-methyl-pyrrolidinium bistrifluoromethylsulfonylemide, trihexyltetradecylphosphonium dodecylbenzenesulfonate, tributyltetradecylphosphonium dodecylbenzenesulfonate, and trihexyltetradecylphosphonium methanesulfonate) and polar organic compounds typical of water contaminants (organic acids, alcohols and aromatic compounds) associated with oil and gas production.

Ionic liquids and aqueous solutions of the organics were contacted under static conditions. Concentrations of organics in the aqueous phase and similarly treated controls were measured by gas chromatography and high performance liquid chromatography, and distribution coefficients were obtained by concentration differences.

Sensitivity of the distribution coefficients to salinity, temperature, concentration, and pH was investigated. Partitioning into the ionic liquid varied considerably. Acetic acid did not significantly partition into the ionic liquid phase, except for the sulfonate-anion ionic liquids. Hexanoic acid, however, showed a strong uptake of the protonated form from aqueous solution for all of the ionic liquids studied. Other organics also showed high distribution coefficients, up to several hundred in the case of toluene and 1-nonanol.

The distribution coefficients for toluene, 1-nonanol, cyclohexanone,

and hexanoic acid were independent of ionic liquid-to-water ratio over the range from 0.05 to 1.0. The ionic liquids showed a large capacity for some organics, with solubilities measured above 100 g/L. Regeneration of the ionic liquids by rinsing and heating was studied, with mixed success. These experiments have shown that ionic liquids do have an affinity for aqueous organic contaminants, and therefore may be used to detect or remove selected water-soluble organics from the aqueous waste stream.

A paper has been prepared on the uptake of organics into ionic liquids from aqueous solution.

This concludes the first set of experiments investigating the use of ionic liquids in produced water remediation.

## Downstream Environmental Technology

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

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

Work during this period has involved a continuation of analysis of the behavior of outdoor carbonaceous aerosols that have entered the indoors. We have calculated the indoor concentration of both black carbon and total carbon aerosols with a time-resolved mass balance model using the measured air exchange rate with the outdoor concentrations as an initial condition. We use a mass balance model that only includes losses due to penetration and deposition to determine if other loss mechanisms exist. Comparing the modeled results with the measured indoor concentrations reveals if there are any additional loss mechanisms that may be important. A candidate loss mechanism is evaporative loss that we have shown to be important in determining indoor concentrations of ammonium nitrate aerosol. Results suggest that there are additional loss terms for the total carbonaceous aerosol, most probably resulting from the repartitioning of organic aerosol from the particle phase into the gas phase upon entrance to the house. The black carbon aerosol appears to be chemically conserved, on average. These new results are being combined with the previous observations concerned with comparisons between different carbon measurement techniques that were employed at the research house. We are computing the indoor/outdoor ratios for the different carbon fractionations for inclusion in a manuscript.

**Technology Transfer:** Dr. Melissa Lunden presented two invited talks on the conclusions of this study to the Department of Environmental Science at Rutgers University and the Department of Epidemiology at the University of California at Davis in May.

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

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

We have previously determined that, outside of ventilation, sorption is likely to be the most important process affecting indoor exposures to volatile organic hazardous air pollutants (HAPs) entering from outdoors. Variability in materials and surface areas among residences is likely to result in variations in sorption that will affect exposures. Estimating

these variations is an important task for this project. In response to this important need, further progress was achieved on a pilot field study to quantify material surface areas available for sorption in real residential environments. A methodology was developed to measure efficiently large material surface areas and estimate smaller material surface areas in occupied residential settings. A database was constructed in *Microsoft Access* to facilitate the recording of materials and areas by room and location. The database can also be used to determine total surface area by material and by room within each dwelling. A pilot survey of three dwellings was performed that included a dormitory room plus three occupied houses in Berkeley and Oakland, CA.

In order to better understand the potential variability of sorption in real environments, an experimental plan has been developed to quantify sorption rates of VOCs in residential rooms. This series of experiments is being partially sponsored by the Department of Homeland Security (DHS). For each experiment in this study an individual room will be isolated from the other rooms of the house. A VOC mixture containing compounds ranging in vapor pressure will be flash volatilized; compound concentrations will be measured as a function of time. Sulfur hexafluoride tracer gas will be used to quantify the room air change rate. Time-resolved VOC measurements will be fit to a previously developed sorption model using a custom LBNL sorption data fitting routine. Experiments are scheduled for July and August 2004; however, the conduct of experiments is contingent upon resolving several methodological challenges.

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

(ChevronTexaco, BNL, and ANL)

Project awaiting renewed funding.

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

(Marathon-Ashland and INEEL)

The effect of regeneration was examined over both Beta and USY zeolite catalysts. Reaction conditions were 60 °C, an isoparaffin to olefin ratio of 20:1, and an olefin weight hour space velocity of 0.1 hr<sup>-1</sup>. A regeneration pressure of 600 psi was examined. At those conditions both zeolite catalysts regenerated to initial activity levels while providing high levels of conversion and product yield for the full duration of testing: at least 120 hour, or 5 days of continuous operation. Based on the promising results obtained with the Beta zeolite, the USY catalyst test was scheduled for a longer duration. That catalyst was regenerated to initial activity levels for 250 hour, or over 10 full days of continuous operation.

### **Secondary Organic Aerosol Research in the Sierra Nevada Foothills**

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

Work continues to characterize the particle growth events observed in the forest during the 2002 field measurement season. In the last report, we mentioned that some data analysis routines have been developed to provide data regarding the change in the characteristics of the distribution as a function of time. Recent efforts have used these results

to more definitively define days when the fine particle growth events occurred and days where no event was observed. These days are characterized by the appearance of a small particle sized mode at around 20 nm, which subsequently increases in size. The influence of meteorology on growth events is being determined by correlating these two different types of days (new particle growth versus no growth) with parameters such as degree of vertical mixing, amount of photoactive radiation, and wind speed and direction. Similar correlations are planned with the anthropogenic particle markers to discern the effect of anthropogenic emissions on the growth events. A manuscript summarizing the basic aerosol behavior at the site, and the factors that influence the growth events, will be complete during the next reporting period.

As a continuation of the work understanding the influence of distant forest fires on the air quality at the Blodgett field location, we have begun to assemble the available monitoring data from Oregon, California, and Nevada. This data will be used in conjunction with the more detailed Blodgett data to (1) understand the effect of forest fires on air quality and (2) describe the geographic extent of the forest fire influence.

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

(Ceramatec, Inc. and INEEL)

A third 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).

The catalyst reactor system was modified slightly and used to test a new metal-modified zeolite catalyst under dehydrocyclization reaction conditions. A benzene yield of up to 3% was produced from a methane feed stream. In addition, a significant conversion of methane to hydrogen of over 50% transpired. Current efforts are examining hydrogen yields and catalyst stability.

### **Bioupgrading of Heavy Crudes Using Temperature and Oil Tolerant Enzyme Catalysts**

(ChevronTexaco and ORNL)

The Principal Investigator is in the process of writing the final report for this project. A summary of the report will be provided in the August 2004 Activity Report.

### **Laser Peening to Improve Fatigue and Corrosion Lifetime of Upstream Oil Pipe and Tubing**

(ExxonMobil, Metal Improvement Company, and LLNL)

Our efforts since the start of the program in March of 2004 have focused on interacting with our upstream oil partner, ExxonMobil and our industrial laser peening partner, Metal Improvement Company, to specifically define the data required and to develop an execution plan so as to impact lifetime extension of deep water well casings and tubing. We identified that it would be most beneficial to build a data base and work toward an engineering demonstration to show that laser peening could make a significant impact on the fatigue lifetime of 18" welded high strength steel pipe. With this plan in mind we began laser peening small, 2 inch square coupons of the appropriate high ksi strength steel and worked through an experiment program where we varied the processing

parameters and thus identified the optimum laser peening parameters to treat full scale pipe. This small coupon data demonstrates that we can indeed induce intense residual compressive stress to depths in excess of 1mm to the welded areas.

The next program step was to generate a data set using larger 12 inch welded fatigue bend bars to demonstrate lifetime vs. number of fatigue cycles (SN fatigue curve). In this work a significant portion of the coupons were untreated welded samples and a large number were laser peened welded samples. We have just completed this SN work and have achieved very positive, exciting results. The laser peened results provide approximately a 10x lifetime improvement factor over unpeened as-welded samples. An alternative view of this data is that the fatigue samples can achieve the same fatigue life but at a 50% higher stress loading at, for example, 60 ksi. This enhancement in lifetime and/or fatigue strength provides important operating margin and design flexibility.

## Natural Gas Technology

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

(ChevronTexaco, Virginia Commonwealth U, and BNL)

The objective of this project is to develop a gas filtration technology based on the Molecularly Imprinted Polymer (MIP) concept. The approach is to prepare a gas template imprinted on a polymer thin film to selectively and efficiently separate small gas molecules (N<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>S from CH<sub>4</sub>) to upgrade natural gas for direct application to gas fields. Earlier, we reported on the preparation and evaluation of three nanocoatings of polymeric thin films (MIP) derived from the diolefinic monomer 2,5-distyrylpyrazine (DSP) by the RESS (Rapid Expansion of Supercritical Solution) method. We now report successful preparation of various batches of diethyl p-phenylenediacrylate (EPA), a MIP prepared from the acrylate-based diolefinic monomer. The separation performance of EPA imprinted with various liquid vapors, methanol, ethanol, and water, was compared. The unit is now being modified to imprint gas templates such as butane and propane. Work also continues to prepare EPA samples for XRD, TEM, SEM, porosity, and XRD measurements. A laboratory-scale unit is being designed to demonstrate the gas purification efficiency of the MIP based systems.

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

(Nextant, NM Tech, and LANL)

#### Highlight:

- NM Tech bench test burner reached 65% of design fuel/air rate using the small exhaust nozzle that will produce a supersonic jet when design rate is achieved.

**Connector Subassembly.** Los Alamos completed an improved design for the connector subassembly (sub). This sub will attach the burner assembly to the coiled tubing and connect the fuel, air, and cooling water conduits in the coiled tubing to the appropriate ports in the burner assembly. It also must connect the conductors in the telemetry cable to the igniter and to the appropriate sensors in the burner assembly and sub. The improved design concept will reduce the fabrication cost and assembly time for the first prototype as compared to the original concept that is a better design for a very deep application.

NM Tech retained an experienced mechanical designer to produce design drawings based on the original concept. He has developed the improved design and is working with Los Alamos to produce the prelim-

inary fabrication drawings. The drawings are approximately 15% complete.

**10 ft Spallation Test Attempt.** NM Tech has had great difficulty starting the spallation drilling process on top of the rhyolite outcrop because large spalls are created which are not effectively removed from the hole. Two 18-inch deep, 2-inch diameter pilot holes were drilled with a portable electric percussion drill. The holes were placed near the drill frame and will be used to determine if the spalling process can be initiated more reliably from shallow pilot holes than it was from the surface of the rhyolite outcrop.

**Automation.** NM Tech decided to control and eventually monitor the shallow burner with LabView™ software operating on a surplus PC. The PC has been set up with software and programming of a fuel air controller with three modes: ignite burner, ramp fuel and air flow to rates desired for spallation, and support steady state spallation. Interface hardware needed to connect the PC to the fuel, air, spark controllers is being identified and purchased.

### Scintillating Fiber Neutron Detectors for Well Logging

(GeoLog Solutions, Inc. and PNNL)

#### Highlight:

- Additional tools are under fabrication

The new Electronics Staff are up to speed and we have a better understanding of the high temperature photomultiplier tubes. Some electrical components were underrated for the expected conditions and are being replaced. Signals from the photomultiplier tubes look good but the tube behavior with voltage is expected to change dramatically with temperature. Fiber was drawn for four additional detectors. Two will be made with high hydrogen moderator (Highgel) and two with a new high temperature epoxy. Compatibility tests with the new epoxy are better than the last and this material has been used downhole for other purposes. There are still some concerns about the high temperature epoxy affecting the optical quality of the fiber. An additional protective layer of RTV silicone may be needed around the fiber.

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

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

Project awaiting renewed funding.

## From The Partnership Office

### Upstream Environmental Technology Projects:

The proposals, presentations, recommendations and fiscal 2004 funding of the Upstream Environmental Technology Projects is now posted on the NGOTP website. The direct link is: <http://132.175.127.176/ngotp/projects/UETforum2004.cfm> . It can also be accessed by going to the NGOTP home page and clicking on the link titled: "**New!** Upstream Environmental Technology Forum 2004".

We will also be posting on the NGOTP Website the following two UET Annual Progress Reports:

1. "Modeling of Water Soluble Organic Content in Produced Water"
2. "Use of Ionic Liquids in Produced Water Clean Up"

These reports are scheduled to be posted by COB Thursday, July 15.