

ACTIVITY REPORT



**Natural
Gas &
Oil
Technology
Partnership**

February 2002

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
Oil and Gas Recovery Technology
Drilling, Completion, and Stimulation Technology
Diagnostic and Imaging Technology

February, April, June, August, October, December
Upstream Environmental Technology
Downstream Environmental Technology
Ultra-Clean Fuels Technology

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

Upstream Environmental Technology

Development of an In-Well Oil/Water Separator for *In Situ* Recycling of Produced Water

(Baker Hughes, ChevronTexaco, CINC, Oak Ridge Tool & Engineering, Phillips, REDA Pump, Unocal, and ORNL)

No report received.

Reducing Chemical Use and Toxicity in Produced-Water Systems

(BP Amoco, Ondeo, and ANL)

Highlight:

- Initiated transfer of the ANL corrosion probe technology to a gas pipeline facility.

ANL and Ondeo (formerly Nalco), a chemical manufacturing and service company for corrosion control, identified a field test site in Louisiana to test the latest corrosion monitoring system. The proposed test site is the slug catcher in a gas pipeline facility. The electrochemical noise (ECN) probe will be tested in an oil and water liquid mixture to detect sustained localized pitting corrosion activity. Equipment preparation for the field test will be completed in the first week of March. The field test is scheduled to last for one month. If the test is successful, Ondeo plans to commercialize the technology.

Sulfide Removal in Produced Brines by Microbial Oxidation

(Phillips, U of Tulsa, and INEEL)

This project was not funded by the Partnership for FY2002. However, a non-DOE proposal is pending for program continuation. On successful continuation, progress reports will be submitted to the appropriate DOE office.

Characterization of Soluble Organics in Petroleum Waste Water (ChevronTexaco, Marathon, Phillips, Shell, Statoil, and ORNL)

Highlight:

- Data acquired describing pH effects on water-soluble organics.

Data was acquired for a second sample of Gulf of Mexico (GoM) crude oil that describes the effect of pH on the quantity and character of water soluble-organics (WSO) in brine. The solubility of WSO increases linearly with pH, from 29 ± 7 mg/L at pH=7.0 to 72 ± 3 mg/L at pH=9.5. This trend is clearer than that seen with the earlier crude sample. As with the earlier crude, the increase in solubility is dominated by the behavior of the polar fraction.

ORNL is characterizing WSO compounds as they appear in produced water after contact with a second in a series of GoM crude oil sources. A number of contact experiments were performed to determine the influence of pH on the extent of contamination of produced water, pH being the most important variable influencing solubility of WSO from the first GoM crude.

The method was unchanged from that used for the first deep crude, employing a Water Accumulated Fraction vessel (ASTM D6081). The tests were carried out at ambient pressure (1 Bar) and temperature (25°C). Contact times were approximately 4 d to ensure that equilibrium was established between the oil and the contact brine, and the mixture was stirred throughout. A water cut of 80% was used for all the pH tests, along with 300 mL of oil and 1200 mL of GoM brine simulant. Extraction of WSO from the contact brine was performed using methylene chloride (CH_2Cl_2), followed by a solvent change to hexane (C_6H_{14}). Saturated hydrocarbons, aromatic hydrocarbons, and polar molecules were sequentially eluted from a multilayered sorbent bed with pentane, CH_2Cl_2 /pentane, and CH_3OH , and were analyzed using gas chromatography (GC). Neat oil samples and a brine blank were analyzed similarly.

GC analysis showed that the mid-range sample set at pH = 8.5 had the highest WSO content. In all cases, however, the aliphatic and aromatic fractions were much lower than the polar fraction, and their percentages dropped with an increase in pH. The polar fractions showed the same increase with pH, by a factor of 1.7 relative to the total WSO in the hexane fraction. Results are also available for carbon ranges, C₆-C₁₀, C₁₀-C₂₀, and C₂₀-C₂₈. The low carbon range shows a small reduction in WSO content with pH, but the mid range C₁₀-C₂₀ shows a maximum at pH=8.5 both in terms of relative and absolute amounts. The amount of C₂₀-C₂₈ is too low to ascertain trends.

These data indicate that pH is an important predictor of WSO solubility. However, more information is required (around pH = 8.5) to ascertain whether the observed behavior is characteristic.

Ecological Framework to Evaluate the Effect of Size and Distribution of Releases at Upstream Petroleum Sites

(American Petroleum Institute, BP Amoco, ChevronTexaco, Exxon, Gas Technology Institute, Unocal, LBNL, ORNL, and LLNL)

No report received.

Estimation and Reduction of Air Quality Modeling Uncertainties (Envair, EPRI, and LBNL)

Highlight:

- Principal investigator visits EPA.

The following tasks were completed:

- Interviews were transcribed and coded using Nvivo software.
- Coding of archival documents for the purposes of analysis begun.
- Researchers continue to work on a draft of a review paper titled, "Treatment of Scientific Uncertainty in Urban Air Quality Regulation."

The principal investigator (PI) visited the Environmental Protection Agency (EPA) in Research Triangle Park, NC for two days in February to inform them of the project modeling work. In addition, the PI prepared and gave poster and platform presentations on air quality modeling uncertainty to visitors from the California Energy Commission and the Air Resources Board.

Remote Sensing for Environmental Baseline and Monitoring

(ChevronTexaco, UC-Davis, and ORNL)

Highlight:

- AVIRIS June 2000 data analyzed.
- Alternate sources of data explored.

On June 1, 2000, a road grader damaged an oil pipeline at the Jornada Experimental Range (JER), near Las Cruces, NM, causing oil to spray over a five-acre area. The airborne visible infrared imaging spectrometer (AVIRIS) was used to collect data at the JER on June 10, just nine days after the oil-spray accident. The AVIRIS image covers a strip that is 614 columns wide and more than 4000 lines long. Each of the 2.5 million pixels is 17.4-m by 17.4-m in size. The image has 224 bands of radiance data for each pixel. Unfortunately, the five acre sprayed area was 236-m west of the image. However, the oil ran down a dirt road located within the imaged area, so pixels of the image that are crossed by the road are expected to contain an oil "signature." To look for this signature, ORNL studied a 221-pixel region of the image (17 columns wide, 13 lines long), centered on the road near the oil spill.

Several research issues were resolved during the preliminary analysis of the AVIRIS data. First, the AVIRIS sensor provides radiance data (power, measured in watts) rather than reflectance data (percentage of the incident power that is reflected). To calculate reflectance, the radiance values must be divided by the radiance from a white reference surface having 100% reflectance. To approximate a white reference, ORNL used AVIRIS data for two regions that appeared white in a three-band color image near the spill site. For each of the 224 spectral bands, the white reference value was set as the maximum value of

the radiance detected within the three spatial regions (road, plus two white areas). ORNL did not calculate reflectance for three spectral regions characterized by low radiance (i.e., spectral regions dominated by water absorption). For the AVIRIS data, 32 of the 224 bands had low radiance. These included nine bands from 1354-nm to 1433-nm, 18 bands from 1802-nm to 1961-nm, and five bands between 2469-nm to 2509-nm. The bands are not evenly spaced, and are not numbered in order of increasing wavelength. When sorted by wavelength, for example, the bands between 28 and 35 have the following sequence: 28, 32, 29, 33, 30, 34, 31, and 35. ORNL is reading the AVIRIS spectral calibration file to determine the wavelengths for each band. When the AVIRIS reflectance data are normalized, the values for the ultraviolet and blue bands appear to be too high. Until more a more suitable set of white-reference values are found within the UV and blue bands, information in the first 13 bands (from 374 nm to 491 nm) will not be analyzed.

ORNL is currently exploring alternative sources of hyperspectral data. A Landsat 7 image of the JER is being acquired, and investigation will determine if 14-band ASTER data were acquired for the JER site. ORNL is working with ChevronTexaco to identify other sites where vegetation was exposed to oil, and where hyperspectral data was or could be collected. At the most recent Petroleum Environmental Research Forum (PERF) meeting in San Ramon, CA, an ORNL project representative met with LLNL investigators and discussed the possibility of imaging the Tall Grass Prairie Reserve as a second study site. Areas around the exploration and production sites on the Tall Grass Prairie Reserve are well vegetated and there are significant brine scars that are now being remediated, but damage due to oil spills is expected to be minimal.

Modeling of Water-Soluble Organic Content of Produced Water (ChevronTexaco, Phillips Shell, Statoil, and ORNL)

Highlight:

- Field work proposal prepared and submitted to DOE. Project will begin once funding arrives.

Large amounts of brine are often associated with oil and gas production. Because these produced waters are in contact with oil at high pressures, they can become contaminated with water-soluble organic compounds. The discharge of produced water in the Gulf of Mexico is regulated by National Pollutant Discharge Elimination System (NPDES) permits, which specify that total oil and grease in the water be below a daily maximum of 42 ppm. Analysis of the produced water for total petroleum hydrocarbons by EPA methods 413.1 or 1664 does not distinguish between carboxylic acids and other polar compounds, and more environmentally harmful hydrocarbons. Hence, remediation of the billion barrels of produced water per annum is based on aqueous organic concentrations that exceed the actual content of oil and grease. ORNL, Chevron-Texaco, Shell, Phillips and Statoil initiated a collaborative Petroleum Environmental Research Forum (PERF) Project to characterize and evaluate water solubles aimed at reducing future production of these contaminants.

There are two tasks associated with the project:

1. Task 1 is to provide a computational tool, based on analysis and modeling of oil/brine samples, to predict the water-soluble organic content in brines associated with deep-well production. Such a model could be used prior to production from new facilities to assist in the development of a more selective and focused approach to produced water clean up, leading to cost savings and reduced environmental impact.
2. Task 2 is to summarize and publish results of the PERF collaboration that led to the study of water solubles in produced water.

Downstream Environmental Technology

Bioprocessing of High-Sulfur Crudes via Application of Critical Fluid Biocatalysts

(ChevronTexaco, UOP, and INEEL)

Highlight:

The project's experimental work is complete. The final report is in preparation.

- Final report in preparation.

Biological Upgrading of Heavy Oils for Viscosity Reduction

(BP Amoco, ChevronTexaco, EPRI Chemicals, Natural Gas Center, Texaco, and LBNL)

Highlights:

- Experimental work complete.
- Final report being prepared.

Project researchers evaluated diversity among alkane monooxygenases and developed methods for selecting and evaluating biocatalytic agents for use in viscosity reduction and chemical manufacture. Researchers also investigated differences between well-characterized alkane oxidizing bacteria and novel environmental isolates.

Bacteria from petroleum-contaminated environments were isolated based on their ability to utilize octane as a growth substrate. This bacteria was compared to the alkane degrading bacteria, *Pseudomonas putida* (*oleovorans*) *GPo1*. Strain *GPo1* contains a well-characterized alkane monooxygenase enzyme (AlkB) that oxidizes linear alkanes to 1-alcohols, the *alkB* gene codes for AlkB enzyme. *GPo1* is a benchmark organism, and most of what is known about the genetics and enzymology of alkane oxidation was discovered using AlkB system or closely related proteins.

The alkane oxidizing bacteria isolated as part of this study was compared to *GPo1* for differences and similarities in genetics, kinetics, substrate specificity, and phylogeny. This study shows that there is considerable diversity among alkane oxidizing bacteria and opportunities for the development of novel biocatalysts. Five bacterial strains characterized in this study were selected for further development. The bacteria are considered to have potential as biocatalytic agents due to their substrate specificity, kinetic properties, or their probability of harboring novel enzyme systems.

As currently conceptualized, crude oil bioprocessing will be operated under non-sterile conditions and the directed oxidation of long-chain alkanes will be affected by a combination of biocatalyst selection and engineering controls. The results of substrate specificity and kinetic analysis suggest that there is significant potential for the development of a biocatalytic process that can oxidize less valuable, longer chain alkanes, without damaging valuable, gasoline range alkanes.

All experimental work for this project is complete and a final report is being prepared. The final activity report for this project will be issued in April, 2002. A summary of this research is available on the internet from the website: http://esd.lbl.gov/ESD_staff/stringfellow/.

Kinetics of Biochemical Upgrading of Petroleum

(Biocat, ChevronTexaco, Shell, and BNL)

No report received.

Enzymatic Upgrading of Heavy Crudes via Partial Oxidation or Conversion of PAHs

(ChevronTexaco, Phillips, ORNL, and INEEL)

No report received.

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

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

Highlights:

- Analysis of possible gas losses completed.
- Size-resolved transient model of non-volatile indoor PM_{2.5} of outdoor origin completed.
- Four papers written and submitted for publication.

The analysis of possible gas losses on the sample inlet of the denuder/ion chromatograph (IC) system has been completed. Researchers conclude that inlet losses on the short (4cm) glass inlet tubes used in the field 1) were not significant for relative humidity below ~ 20%, and 2) at high relative humidity the loss of nitric acid could reach ~ 50% (a limit given by the Gormley-Kennedy equation for gas loss in a cylindrical denuder tube). However, the lower solubility of ammonia makes it unlikely that ammonia losses were significant during the field measurements at the Clovis house. Researchers are incorporating a discussion of these results in the manuscript describing the gas measurements.

Researchers completed the work on the size resolved transient model of non-volatile indoor PM_{2.5} of outdoor origin. The principal result of this work confirms the observations that the reduction in indoor relative to outdoor PM_{2.5} is largely due to loss of nitrate particulate matter. A paper describing these results was submitted to *Indoor Air 2002*. Currently, researchers continue to explore the best model representation for the dissociation of ammonium nitrate and loss of nitric acid on indoor surfaces.

Four papers were written and submitted for presentation and publication: Fischer M.L., Lunden M.M., Thatcher T.L., Sextro R.G., and N.J. Brown 2002. "Predicting Indoor PM_{2.5} of Outdoor Origin: Testing a Transient Size Resolved Model Using Intensive Measurements from a Residence." *Indoor Air 2002, Proceedings of the 9th International Conference on Indoor Air Quality and Climate*. Indoor Air 2002, Monterey: Indoor Air, July 2002.

Lunden, M.M., Thatcher, T.L., Littlejohn, D., Fischer, M.L., Hering, S.V., Sextro, R.G., and Brown, N.J., "The Transformation of Outdoor Ammonium Nitrate Aerosols in the Indoor Environment." *Indoor Air 2002, Proceedings of the 9th International Conference on Indoor Air Quality and Climate*. Indoor Air 2002, Monterey: Indoor Air, July 2002.

Hering, S.V., Lunden, M.M., Kirchstetter, T.W., Thatcher, T.L., Revzan, K.L., Sextro, R.G., Brown, N.J., Watson, J., and Chow, J., "Indoor, Outdoor and Regional Profiles of PM_{2.5} Sulfate, Nitrate and Carbon." *Indoor Air 2002, Proceedings of the 9th International Conference on Indoor Air Quality and Climate*. Indoor Air 2002, Monterey: Indoor Air, July 2002.

Thatcher, T.L., Lunden, M.M., Sextro, R.G., Hering, S., and Brown, N.J., "The Effect of Penetration Factor, Deposition, and Environmental Factors on the Concentration of Changes in House Environment on the Concentration of PM_{2.5} Sulfate, Nitrate, and Carbon Indoors." *Indoor Air 2002, Proceedings of the 9th International Conference on Indoor Air Quality and Climate*. Indoor Air 2002, Monterey: Indoor Air, July 2002.

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

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

Highlights:

- Researchers modify the alpha model.
- PI visited EPA.

To account for different surface types and surface areas in indoor environments, project researchers are modifying the alpha model by incorporating the LBNL model of sorption interactions with indoor surfaces. The model tracks simultaneous interactions of several compounds with several materials of varying projected surface areas with a user-specified emissions schedule. Appropriate components of this model are being incorporated into the modeling system for tracking indoor fate of volatile organic compounds (VOC) generated outdoors.

Initially, sorption parameter values available from the literature will be used

to investigate compounds and compound classes that have substantial interactions with surfaces. Project researchers are also consulting with other researchers who performed experiments to determine sorption parameter values to identify and fill key gaps in the knowledge base. As a result, project researchers are focusing on the interactions between very volatile reactive and/or polar toxics, such as acrolein with painted wallboard. The experiments will focus on the importance of relative humidity and temperature.

Researchers also analyzed data from a related project examining the sorption of organics from indoor sources on indoor surfaces. These emissions provide a good analogy to the daily cycle of elevated concentrations associated with outdoor VOC. The initial analysis suggests that for many organic compounds, including naphthalene, phenol, and cresols, a steady daily cycle of sorption and re-emission is achieved for carpet and other furnishings, whereas the more porous gypsum wallboard continues to act as a net sink over longer periods of time.

The principal investigator visited the Environmental Protection Agency (EPA) at Research Triangle Park in February 2002 to learn of the research on Hazardous Air Pollutants.

Developing Enzyme and Biomimetic Catalysts for Upgrading Heavy Crudes via Biological Hydrogenation and Hydrodesulfurization

(ChevronTexaco, ORNL, and ANL)

Highlight:

- Researchers meet with Dr. Mike Adams.

This project investigates the potential of enzymatic and biomimetic catalysts for hydrogenation of oil compounds, with the goal of upgrading crudes via sulfur removal and potentially molecular weight reduction.

The setup for conducting anaerobic microbiology and enzymology work, including an anaerobic chamber and a gassing station, was completed. A *Desulfovibrio gigas* (*Dg.*) culture was initiated from an American Type Culture Collection (ATCC) sample (strain #19364) in serum bottles and later grown on a 1L scale. The cells were harvested and saved at -80°C. An inoculum was also prepared and sent to University of Georgia-Athens (UGA), Bioexpression Research Facility and about 400 g of cell paste was produced. This cell paste will be used to isolate the enzyme *Dg.* hydrogenase.

Researchers met with Dr. Mike Adams, also of UGA, to discuss potential methods to develop a biocatalyst from the hyperthermophilic hydrogenase enzyme from *Pyrococcus furiosus* (*Pf.*). The following tasks were identified:

- Screening of *Pf.* Cultures to investigate capability of the organism/enzymes to reduce organosulfur compounds including, but not limited to: dibenzothiophene, thiophene, benzothiophene and phenyl sulfide.
- Identification of the sulfur docking site in *Pf.* hydrogenase during reduction of elemental sulfur with hydrogen.
- Physical modification of the *Pf.* enzymes including hydrogenase as well as other electron transport proteins such as ferredoxin to bind and react with dibenzothiophene.

These tasks will be conducted in collaboration with UGA. Initial screening will be conducted using a guanine cytosine (GC)-based assay of the organosulfur compounds. During the trip to UGA, the *Pf.* Hydrogenase enzyme was isolated from the organism at Dr. Adams laboratory.

Ultra-Clean Fuels Technology

Development of a Solid Catalyst Alkylation Process Using Supercritical Fluid Regeneration

(Marathon-Ashland and INEEL)

No activity to report during this period. Experimental efforts were put on hold until FY02 funding is received.

Partnership Office

The Natural Gas and Oil Technology Partnership established a new Gas Issues forum focused on applied research and development in gas exploration, production, and storage. This year the focus of the forum will be limited to gas storage issues and drilling, completions, and stimulation issues.

The schedule for the first call in this forum will be as follows:

- The official "Call for Proposals" is sent via email to the Partnership Office representatives on or before March 15, 2002.
- Two-page proposals with at least one letter of industry support are submitted electronically to the Forum Lead on or before COB April 26, 2002. The Forum Lead is Larry Myer, lrmeyer@lbl.gov.
- The Forum Lead distributes proposals and the review instructions to the Industry Review Panel no later than COB 2002 May 1,.
- A one-day review of proposals will be held in Houston, TX during the third week of May. Information on the date and location of the meeting will be issued by the Forum Lead at a later time.