# ACTIVITY REPORT

## April 2002

Natural Gas & Oil Technology Partnership

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** | **February, April, June, August, October, December** |
|---|---|
| Oil and Gas Recovery Technology<br>Drilling, Completion, and Stimulation Technology<br>Diagnostic and Imaging Technology | Upstream Environmental Technology<br>Downstream Environmental Technology<br>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, Rhorback Casasco, and ANL)

### Highlight:

- Efforts continue to transfer the ANL ECN corrosion probe technology to the refinery industry.

The purposes of this project are to 1) minimize the environmental discharge of hydrocarbons and treatment chemicals due to failures resulting from sustained localized pitting corrosion, 2) reduce the use of toxic treatment chemicals used by field operators to prevent those failures, and 3) identify treatment approaches that reduce the use of toxic chemicals. The approach in this project is to develop an on-line, real-time method to monitor sustained localized pitting so that treatment chemicals (e.g., biocides and chemical inhibitors) can be applied only when needed.

The joint effort between ANL and Ondeo (a chemical manufacturing and service company formerly known as Nalco) to test the ANL electrochemical noise (ECN) technology at a refinery site continues. The proposed test in Louisiana was cancelled due to schedule and field support conflicts. Evaluation of other potential test sites in the U.S. and Canada continues.

Researchers also initiated discussions with a corrosion monitor manufacturer in Texas. This firm makes a field-ready corrosion monitor system and it may be possible to incorporate ANL's ECN technology into their hardware components. A plan to test the ANL ECN probe at their facility in Texas or at ANL, with their technical personnel present, was proposed. Successful collaboration with this firm could result in the promotion of the ANL ECN technology for commercial applications and would enhance ANL's ability to conduct field tests with minimal (or no) field support requirements.

## Characterization of Soluble Organics in Petroleum Waste Water

(ChevronTexaco, Marathon, Phillips, Shell, Statoil, and ORNL)

ORNL has undertaken to characterize water-soluble organic compounds as they appear in produced water after contact with Gulf of Mexico crude oil samples taken from deep-well drill sites. Contact experiments were performed to determine the influence of physicochemical parameters on the extent of contamination of produced water. It was found that pH was the most important variable influencing solubility of organic compounds from both of the crude samples studied in the laboratory. This result is in agreement with the fact that most of the water-soluble material from the crude oil is polar.

Data from the characterization experiments are being incorporated into a predictive model for organic solubility in produced water brines.

Since recent focus was on the modeling program, there is no progress to report on the experimental program.

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

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

### Highlights:

- Prairie vole and badger populations in the Tallgrass Prairie Preserve simulated.
- Spill generator developed to simulate brine and/or hydrocarbon spills.

Project researchers continue the intensive modeling phase of the project. The goal is to develop generic models to determine the threshold frequency, size and/or distribution of spills that would lead to a density of herbivores and/or predators that cannot persist. Researchers also plan to use the models to quantify how the effects of exploration and production related habitat loss differs for species with different life history attributes, mobility, and spatial habitat requirements.

LLNL developed an individual-based model for simulating species with territorial preference and their relations to the spatial environment (herbivore-resource relationship) as well as with their predators. The first implementation of the individual-based model describes the birth, death, aging, feeding, and movements of individual prairie voles on a spatial grid consisting of spatial cells roughly corresponding to the home range of the vole, and containing vegetation that changes in mass due to production and herbivory. Simulations were performed using the prairie vole vegetation components of the code in artificial grassland habitats of 900 and 0.225 hectares. Preliminary results show a positive correlation between the size of the habitat and the persistence of the herbivore species. A predator and prey simulation of short-eared owl vole dynamics will be undertaken in the next few months.

ORNL focused on the development of a population model that uses a habitat suitability index as the basis for representing spatial variation in habitat. The population model recognizes six activities that individuals engage in during their lives: pre-breeding, mating, post-mating, birthing, rearing offspring, and dispersal. The model was parameterized for American badger, and preliminary runs are complete. ORNL anticipates generalizing this model in the future to represent other species of prairie birds and mammals with contrasting life histories to address the question of how life history and spatial ecology of a species influences its susceptibility to petroleum-related habitat loss.

ORNL also developed two stochastic models to describe the spatial distribution of brine spills. The first model attempts to produce spills based on typical well configurations. The second model is a simple statistical model that produces a specified spatial distribution of spills.

## Estimation and Reduction of Air Quality Modeling Uncertainties

Envair, EPRI, and LBNL)

### Highlights:

- Researchers participate in air quality model tutorial course.
- Progress continues on uncertainty visualization.
- Researchers continue to analyze interviews.
- Researchers meet with CARB representative to discuss research and potential collaboration.

Project researchers participated in the EPA's Community Multiscale Air Quality Model (CMAQ) tutorial course given by the University of California (UC) at Riverside in late March to gather information on obtaining, building, and running the program, as well as pre- and post-processing data. A new version of CMAQ was installed at LBNL.

Progress continues on uncertainty visualization. Researchers conducted a preliminary assessment of visualization methods being developed at the Computer Science Department of UC-Santa Cruz, for possible use as an approach for visualizing uncertainty. A few promising candidates were identified. The methods typically provide facilities to develop straightforward 2D spatial displays of 4D+ datasets. Promising candidates include uncertainty glyphs, spray rendering, and ribbon plots.

A table was created to associate NVivo codes with narratives. Researchers analyzed coded interviews to identify narratives and group respondents according to narratives. The narratives describe the way respondents view the air quality planning process in terms of the use of models, modeling capabilities, the significance of uncertainty, the potential utility of uncertainty informa-

tion, and methods for communicating uncertainty.

Project researchers met with a representative of the California Air Resources Board (CARB) modeling group to inform them of research plans and to discuss potential collaboration.

## Remote Sensing for Environmental Baselining and Monitoring

(ChevronTexaco, UC-Davis, and ORNL)

### Highlights:

- Field data from the Jornada Experimental Range received.
- White-reference radiance for the AVIRIS data calculated.

In April 2002, ORNL received data for 665 hyperspectral reflectance measurements made in September 2000. Agricultural Research Service (ARS) investigators collected the data at 5-m intervals along 150-m transects, for transects established in areas dominated by grass, creosote bush, or mesquite, and within a vegetation-transition zone. Data were also collected on a 30-m by 30-m grid located within the vegetation-transition zone. Separate radiometric measurements were made for the dominant plant species, litter, and bare soil within each transect. Using both field and remote data, ORNL will explore the resolution limits for pixel unmixing and plant species identification.

The airborne visible infrared imaging spectrometer (AVIRIS), used to obtain remotely sensed data, 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. As reported previously, ORNL used AVIRIS data for two regions near the spill site which appeared white in a three-band color image to approximate a white reference. For each of the 224 spectral bands, ORNL set the white-reference value as the maximum value of the radiance detected within the three spatial regions (road, plus the two white areas).

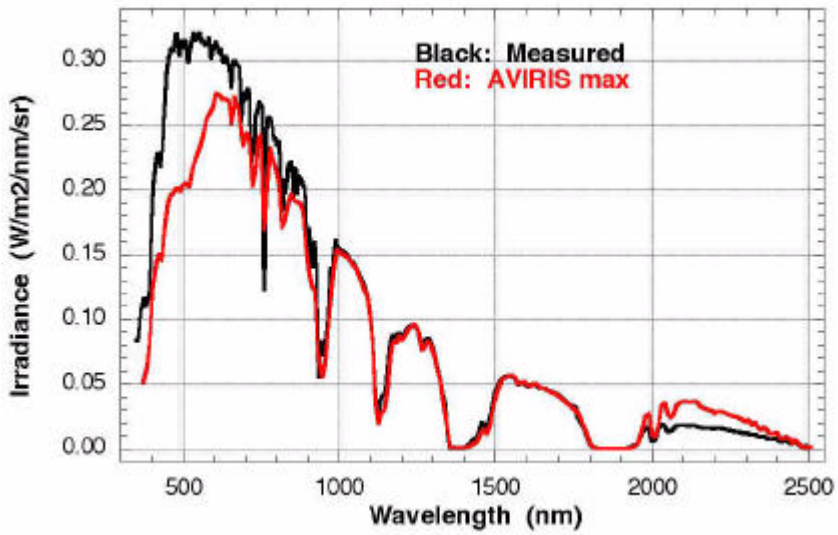


Figure 1. Comparison of two estimates of white-reference radiance: the black curve represents measured field data; the red curve is the maximum radiance for each wavelength, for a set of measurements made using the AVIRIS sensor.

The ARS data are radiance measurements and include 15 field measurements of a white-reference panel. The approximate white-reference radiance is compared to typical measured values in Figure 1. The two white-reference curves are very similar over the interval from 1000 nm to 1900 nm. However, the red curve is lower than the black curve initially (that is, at wavelengths less

than about 700 nm), and higher than the black curve at wavelengths greater than 2000 nm. These differences probably occur because the "white" areas are not 100% reflective below 700 nm and above 2000 nm. Each of the curves has three spectral regions characterized by very 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 and 2509 nm. ORNL contacted Dr. Greg Asner of Stanford University, and discussed the use of models for calculating white-reference values for AVIRIS data. Dr. Asner recommended using the model FLAASH; ORNL will obtain this model and evaluate it.

ORNL investigators are working with ChevronTexaco investigators to identify other sites where vegetation was exposed to oil, and where hyperspectral data was or could be collected. The Tall Grass Prairie Reserve (located in northeastern Oklahoma) is being discussed as a second study site. Chief advantages of this site are: 1) it is well vegetated; 2) it has a long history of exploration and production activities; and 3) it contains significant brine scars, some of which are being used in revegetation studies.

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

(ChevronTexaco, Phillips Shell, Statoil, and ORNL)

### Highlight:

- PERF characterization data analyzed.

This project will develop a model for the organic contaminant concentrations in produced water associated with oil production at deep well drill sites in the Gulf of Mexico (GOM). The modeling started with the analysis of data collected during the collaborative Petroleum Environmental Research Forum (PERF) project to characterize and evaluate water solubles. ORNL examined two independent GOM crudes, which were contacted with simulated brines. Organic solubility into the brines was measured gravimetrically. The organics were also separated into their aliphatic, aromatic, and polar fractions on an open column, and were analyzed using gas chromatography. Data from the characterization study indicate that of the variables studied in the laboratory, pH had the largest effect on organic solubility, followed by temperature. The influence of pressure and water cut were ambiguous. Hence, ORNL plans to compare these results with other datasets. Salinity did not appear to affect the solubility of the compounds under study.

To develop a model to explain the data, ORNL will take three different approaches. The first will be to develop an empirical model of organic solubility based on the activity coefficients of the organic in the aqueous and crude phases. The distribution of the organic between the two phases can be described as a ratio of the activity coefficients. This approach will be used to model the pH and temperature data that were observed in the laboratory.

In addition, the existing literature on organic solubility in produced water will be explored. In particular, the following information is needed to describe an oil/brine system:

- Oil characteristics - density, content (gas, oil, and diesel fractions);
- Brine characteristics - salinity, source, pH;
- Geochemistry - location of formation; type of formation, age, depth;
- Production variables - age of well, methods of production, additives, pressure and temperature.

For some of these factors, ORNL will be able to develop a mathematical correlation, as will be done with pH and temperature. But, it is likely that a statistical model will be required to predict organic solubility in brines. ORNL can apply multivariate analysis to the available data to show which variables are the most important in organic solubility, in addition to those already measured in the laboratory. Cross-correlations are also possible. With the understanding of

which variables are important, predictions can be made to the organic contamination in future wells, using statistical distributions provided from the examination of existing data.

# Downstream Environmental Technology

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

(ChevronTexaco, UOP, and INEEL)

### Highlights:

- Manuscript submitted to the ACS.
- Final report in preparation.

A manuscript entitled "Biocatalytic Treatment of Organosulfur Compounds in Emulsions in Supercritical Fluids" was submitted to the American Chemical Society (ACS) Fuels Division Preprint series. Authors were Marina A. Stanescu, Daniel M. Ginosar, Gregory A. Bala, and Raymond P. Anderson. An abstract with the same title and authors was submitted to be considered for presentation at the 224th ACS national meeting to be held in Boston in August 2002. The project final report is in preparation. All experimental efforts for this project are now complete.

## 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)

### Highlight:

- Final CRADA report submitted to DOE.

The objective of this program was to investigate new enzyme-based technologies for upgrading of heavy oils. Enzymes were selected for screening from those capable of conversion of polyaromatic hydrocarbons (PAHs) reported in the literature. Oxidative reactions of PAHs using hydrogen peroxide as an oxidant with conversion to partially oxidized products were used. The enzymes (lignin peroxidase [lip], cytochrome c) were tested in various organic solvents and found to lose activity in pure organic solvents. A thermodynamic analysis revealed lack of effective interaction between the substrate and enzyme as the cause for low activity. The protein cytochrome c was modified to work in organic media by chemical hydrophobic group attachment. Two different modifications were made: attachment of polyethylene glycol (PEG) and alkyl groups. Alkyl groups, being small could be attached at interior locations within the core of the enzyme and possibly near the active site. Increase in the threshold solvent concentration where maximum enzyme activity occurred indicated potential of this strategy for effective enzyme-substrate interaction. Further improvements in enzyme activity called for other diverse methods due to the unavailability of sufficient chemical modification sites. Genetic techniques were therefore explored for further improvements. These experiments focused on cloning of a gene for the fungal enzyme lip into yeast *Pichia pastoris*, which would allow easy manipulation of the gene. However, differences in the fungal and yeast cellular machinery impeded significant expression of the fungal enzyme. Several strategies were explored to allow higher level expression of the enzyme, which was required for enzyme improvement. The strategies used in this investigation are described in the report.

Industry in-kind support was available throughout the project period. Review of the research results was carried out on a regular basis (bimonthly reports and annual meetings) followed by suggestions for improvement in

ongoing work and direction for future work. A significant portion of the industry support was in the form of technical consultation and expert advice via meetings and phone conversations.

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

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

### Highlights:

- Progress continues on interpretation of real-time gas phase measurements.
- Five papers accepted for publication and presentation.

Analysis of the expected equilibrium relationship between aerosol $NH_4NO_3$ and $HNO_3$ is complete and was incorporated into a revised manuscript describing the gas phase measurements. The results show that the outdoor aerosol-gas system was generally close to equilibrium and that low outdoor and $HNO_3$ concentrations were due to the high $NH_3$ concentrations in the San Joaquin Valley area. The results also show that the measurements of indoor $HNO_3$ are not consistent with aerosol-gas equilibrium, suggesting that a significant sink (most likely deposition to interior surfaces) is removing $HNO_3$ at a rate that is rapid compared to building ventilation.

Work on the model is now focused on developing a sub-model for nitrate aerosol vaporization and on incorporating the detailed time record of mechanically driven building ventilation conditions into the existing transient model. Recently, calculations were begun to estimate the rate constant for aerosol vaporization in the indoor environment. These initial results (which require further work) provide estimates of yield rates of 2–8 $hr^{-1}$, with the variation dominated by uncertainty in the size distribution of the nitrate aerosol. These initial estimates of vaporization rates are roughly consistent with that necessary to affect the order-of-magnitude observed reduction in indoor to outdoor nitrate aerosol concentrations.

Five papers were accepted for presentation and publication:

M.L. Fischer, M.M. Lunden, T.L. Thatcher, R.G. Sextro, and N.J. Brown. "Predicting Indoor $PM_{2.5}$ of Outdoor Origin: Testing a Transient Size-Resolved Model Using Intensive Measurements from a Residence" (in press) *Proceedings of the 9th International Conference on Indoor Air Quality and Climate* (Indoor Air 2002). Also Lawrence Berkeley National Laboratory Report No. LBNL-49615, 2002.

S.V. Hering, M.M. Lunden, T.W. Kirchstetter, T.L. Thatcher, K.L. Revzan, R.G. Sextro, N.J. Brown, J. Watson, and J. Chow. "Indoor, Outdoor and Regional Profiles of $PM_{2.5}$ Sulfate, Nitrate and Carbon," (in press) *Proceedings of the 9th International Conference on Indoor Air Quality and Climate* (Indoor Air 2002). Also Lawrence Berkeley National Laboratory Report No. LBNL-49980, 2002.

M.M. Lunden, T.L. Thatcher, D. Littlejohn, M.L. Fischer, S.V. Hering, R.G. Sextro, and N.J. Brown. "The Transformation of Outdoor Ammonium Nitrate Aerosols in the Indoor Environment," (in press) *Proceedings of the 9th International Conference on Indoor Air Quality and Climate* (Indoor Air 2002). Also Lawrence Berkeley National Laboratory Report No. LBNL-50158, 2002.

T.L. Thatcher, M.M. Lunden, R.G. Sextro, S. Hering, and N.J. Brown. "The Effect of Penetration Factor, Deposition, and Environmental Factors on the Indoor Concentration of $PM_{2.5}$ Sulfate, Nitrate, and Carbon," (in press) *Proceedings of the 9th International Conference on Indoor Air Quality and Climate* (Indoor Air 2002). Also Lawrence Berkeley National Laboratory Report No. LBNL-50160, 2002.

M.M. Lunden, T.L. Thatcher, D. Littlejohn, M.L. Fischer, T.W. Kirchstetter, K.L. Revzan, R.G. Sextro, N.J. Brown, M.R.Stolzenburg, and S.V. Hering. "Time-Resolved Determination of Indoor-Outdoor Concentration Relationships for PM2.5 Nitrate, Sulfate and Carbon," (in press) *Proceedings of the Sixth International Aerosol Conference*, 2002. Also Lawrence Berkeley National Laboratory Report No. LBNL-50161, 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 improve mass balance model.
- User interface improved.

Project researchers continue to improve the mass balance model. The ability to treat indoor surface chemistry was added, and the time-dependent species mass-balance equations were modified to include air exchange, and surface adsorption and desorption. Indoor and outdoor calculations are not directly coupled, but approximately so, since outdoor concentrations are read from a previously-created file. The user interface was improved to allow the choice of indoor or outdoor run, the air exchange rate, the number of interior surfaces and their surface-to-volume ratios, and the adsorption and desorption rates for each species of interest. The base chemical mechanism, SAPRC-99, was modified to include several species of interest explicitly, namely, benzene, toluene, xylene, naphthalene, acrolein, butadiene, and MTBE. Testing of the code proceeds.

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

(ChevronTexaco, ORNL, and ANL)

This project is aimed at investigating 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.

During the last two months, the setup for purification of *D. gigas* hydrogenase was prepared. This consisted of two DEAE-Sepharose chromatography columns, one Ultrogel AcA 44 gel filtration column and a Biogel-HTP hydroxylapatite column to be used for a four step purification process. A crude cell extract was prepared from a 1L cell culture. Hydrogenase activity was measured using a hydrogen utilization assay. The cell extract prepared from three grams of wet cells will be used to test the purification system. The thermophilic hydrogenase from *Pyrococcus furiosus* was also obtained from Dr. Mike Adams. Modification experiments for the two enzymes are currently being planned.

## Ultra-Clean Fuels Technology

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

(Marathon-Ashland and INEEL)

**Highlights:**

- New project funding received.
- Manuscript accepted for publication.

New project funding was received in March. The project experimental system was inactive since November. Efforts in March focused on reactivating the experimental system and checking instrument calibration. The system is expected to be operative and experiments are expected to be running in April.

A revised manuscript, describing the on-line addition of inert supercritical fluids for catalyst activity extension, was sent to *Industrial and Engineering Chemistry Research* for review and was accepted for publication.

# Partnership Office

The new Natural Gas Technology Area is off and running. In April, the laboratories submitted 14 new proposals in the drilling and gas storage areas of the call. The industry panel review and ranking will take place in Houston on May 30. Our thanks to John Rogers, of NETL, and Larry Myer and Norm Goldstein, of LBNL for pulling the proposal call and review together.

The FY2002 funding based on the autumn review cycle was distributed to the laboratories in April. Continuing and new projects will now be able to start. The new projects will commence reporting in this monthly series by this autumn. Thanks again to the industry reviewers, NPTO and NETL technology area managers, and the laboratory representatives for completing the FY2002 cycle.