

ACTIVITY REPORT



**Natural
Gas &
Oil
Technology
Partnership**

February 2003

bringing department of energy national laboratories capabilities to the petroleum industry

Los Alamos
Los Alamos, NM 87545
(505) 667-7811

Sandia
Albuquerque, NM 87185
(505) 844-7333

Lawrence Livermore
Livermore, CA 94551
(925) 422-5196

Lawrence Berkeley
Berkeley, CA 94720
(510) 486-5085

Argonne
Argonne, IL 60439
(202) 488-2415

Brookhaven
Upton, NY 11973
(516) 344-3819

Idaho
Idaho Falls, ID 83415
(208) 526-7004

Oak Ridge
Oak Ridge, TN 37831
(865) 574-4941

Pacific Northwest
Richland, WA 99352
(509) 372-4565

To: William F. Lawson, Associate Director
National Energy Technology Laboratory
One West Third Street
Suite 1400
Tulsa, OK 74103-3519

From: J. Albright, Los Alamos
D.J. Borns, Sandia
J. Ziagos, Lawrence Livermore
N. Goldstein, Lawrence Berkeley
D. Schmalzer, Argonne
A. Goland, Brookhaven
B. Reynolds, Idaho
J. McFarlane, Oak Ridge
B. Saffell, Pacific Northwest

cy: E. Allison, DOE Fossil Energy
L. Capitanio, DOE Fossil Energy
G. Dehoratiis, DOE Fossil Energy
A. Hartstein, DOE Fossil Energy
B. Hochheiser, DOE Fossil Energy
E. Subia-Melchert, DOE Fossil Energy
N.B. Woodward, DOE Office of Science
D. Alleman, DOE-NETL-Tulsa
J. Casteel, DOE-NETL-Tulsa
N. Comstock, DOE-NETL-Tulsa
D. Gurney, DOE-NETL-Tulsa
R. Lindsey, DOE-NETL-Tulsa
R. Long, DOE-NETL-Tulsa
K. Sterling, DOE-NETL-Tulsa
D. Sutterfield, DOE-NETL-Tulsa
J. Ammer, DOE-NETL-Morgantown
H. Guthrie, DOE-NETL-Morgantown
B. Gwilliam, DOE-NETL-Morgantown
J. Rogers, DOE-NETL-Morgantown
B. Tomer, DOE-NETL-Morgantown
F. Toro, DOE-NETL-Morgantown
M. Vargas, DOE-NETL-Morgantown

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
Upstream Environmental Technology
Downstream Environmental Technology
Natural Gas Technology

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

Upstream Environmental Technology

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:

- Draft manuscript completed.
- American badger landscape model improved.
- Three additional manuscripts in progress.

ORNL made the following improvements to the landscape model for the American badger: (1) the frequency of movement during winter months was reduced; (2) distances for movements within range and dispersal to the average distance between sightings for badgers were linked using an exponential distribution; (3) age-specific mortality rates were added; (4) immigration from outside the Tallgrass Prairie Preserve (TPP), OK was assumed to equal emigration, and; (5) the proportion of mate-finding females was calculated to quantify the role of Allee effects caused by habitat fragmentation. The badger model can now select from alternative spill landscapes for each replicate population, allowing all maps to be evaluated in one long simulation.

ORNL and LLNL completed a draft manuscript summarizing the ecological framework developed in this project. This manuscript will be published as a chapter in an ASTM Special Technical Publication resulting from a symposium on Landscape Ecology and Wildlife Habitat Evaluation: Critical Information for Ecological Risk Assessment, Land-Use Management Activities, and Biodiversity Enhancement Practices, to be held in Kansas City, MO, on April 1-9, 2003. In addition, two other manuscripts, the first describing simulation results and the second describing actual spills, are in internal review and will be submitted to the Petroleum Environmental Research Forum (PERF) for review in March 2003. A third manuscript on the vole model is near completion.

The effort to generalize the landscape model for other species and enable it to run in Monte Carlo mode for sensitivity analysis progresses. The goal is to compare sensitivity of a highly territorial and solitary species (badger) with a social breeder (prairie chicken) to habitat loss by varying the influence of non-specific densities on perceived habitat quality.

LLNL completed initial simulations evaluating the effect of the total area of spills, fragmentation and predation on time to extinction (TE) of prairie vole (*Microtus ochrogaster*) populations. For these simulations, LLNL made an additional modification to the model to incorporate density-dependent predation, the first step in linking the model with a higher trophic-level predator. Sets of simulations with 50 and 100 randomly generated initial vole distributions were conducted and the resulting TEs averaged. The TE for vole populations generally decreases with increasing spill area, although the level of predation is important. A 10% reduction in habitat area due to spills reduced TE by approximately 25% when predation was relatively high and the vole population density was thus kept low. When predation was relatively low (and the vole population was correspondingly high), the presence of spills had negligible effect on TE. In addition, vole density was sensitive to the interaction of predation and fragmentation, with fragmentation causing population extinction in the presence of higher levels of predation and stabilizing the population when predation was absent or at lower levels.

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

- Manuscript submitted to Annual Review of Energy and Resources.
- Graphical tools evaluated and compared.

LANL improved emissions tables for the August 1990 ozone episode in the SARMAP. The tables are based on the research of Marr and Harley of the Department of Civil and Environmental Engineering Department of the University of California-Berkeley. The improved emissions are for motor vehicle (mobile) sources only and are derived with the aid of fuel sales data. A code was written that translates the emissions input files suitable for one modeling platform into another to produce an input file in the standard form of the SAPRC99 chemical mechanism, as it is used in the CMAQ code.

Researchers installed and evaluated AVS and Tekplot, two graphical tools used for visualization and post-processing. Tekplot appears to be more sophisticated than AVS, and is more amenable to allowing a user to implement his/her own graphical icons. Tekplot support is also more Linux-friendly than AVS.

The manuscript "Evaluating Uncertainties in Regional Photochemical Air Quality Modeling," by J.D. Fine, L. Vuilleumier, S. Reynolds, P. Roth, and N.J. Brown, was submitted as an invited paper to Annual Review of Energy and Resources 28, 2003. It is also in LBNL Report No. 52222.

Presentation materials were prepared summarizing findings from draft manuscript concerning the use of models and uncertainty in urban- and regional-scale air quality management that is based upon a case study of Central California planning in the 1990s.

Remote Sensing for Environmental Baseline and Monitoring(ChevronTexaco,
UC-Davis, and ORNL)

Report not received.

Modeling of Water-Soluble Organic Content of Produced Water(ChevronTexaco,
ConocoPhillips, Shell, Statoil, and ORNL)**Highlight:**

- Activity coefficients calculated with a functional group model (UNIFAC).

Thermodynamic equilibrium calculations were selected to model the solubility of organic compounds in brines, in order to predict the contamination of produced water by oil and grease. Semi-volatile components are of primary interest because of their residual presence in water that will be discharged back into the ocean (i.e., the Gulf of Mexico). Hence, ORNL used a liquid-liquid equilibrium model based on an activity coefficient description of the aqueous and hydrocarbon phases. This model allows one to predict partitioning into the produced water brine if the composition of the oil is known, as well as conditions of temperature, salinity, pH, and water cut.

The initial approach was to develop a model based on Non Random Two Liquid (NRTL) activity coefficients, a method already applied to hydrocarbon-brine systems as reported in the literature. The disadvantage of this approach is that NRTL parameters are inherently empirical, and although binary, do change when other components are present (e.g., in ternary systems, etc.). In addition, not all of the interactions of interest were measured in the laboratory. Hence, unless one is calculating solubilities for a well-characterized system, the selection of appropriate parameters is problematic.

A less restrictive method is to use UNIFAC to model activity coefficients in the aqueous and hydrocarbon phases. UNIFAC calculations are based on the breakdown of individual molecules into their constituent parts. In principle, interactions can be calculated for any pair of molecules that have their constituent functional groups represented in the database. Indeed, representations for most C-H-O-N molecules are possible. However, the representation of sulfur-containing compounds is quite restricted, and salts must be incorporated in the calculation using another approach.

Proof-of-principle calculations were carried out on ten-component systems including saturated hydrocarbons, aromatic compounds, and polar molecules as well as brine. The calculation was able to reproduce the trend in pH observed in the ORNL water-characterization experiments. The next step is to perform calculations on systems that best mimic actual oil-brine systems. The composition of such a system will be developed from a literature review of crude oil compositions.

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

(ChevronTexaco,
Petroleum Environmental Research Forum,
UC-Berkeley, UC-Davis, and LBNL)

Highlight:

- Developed preparation method of spiked test soils.

Studies characterizing the uptake of pollutants from soil to vegetation can significantly be influenced by the method used to spike test compounds into soil. Researchers experimented with the soil spiking method recommended by Northcott and Jones, scaling up the process to work with the soil quantities necessary for growing wheat to maturity. The chosen approach blends wet field soil into acetone containing appropriate quantities of test chemicals. The acetone is then volatilized off the acetone while soil moisture is maintained. The spiked soil is then “aged” until the measured test chemical concentrations of test chemical stabilize. The use of organic solvent and blender is known to alter the natural organic material and natural structure of the soil, but it is a necessary trade-off for relatively homogeneous starting concentrations in the soil mixture.

Researchers were unsuccessful in acquiring an accelerated solvent extractor due to changes in funding, so the project is shifting the method development efforts toward the use of continuous Soxhlet extraction apparatus for both the vegetation and the soil samples. Researchers are also optimizing the gel permeation chromatography method for cleaning up extracts prior to analysis.

Interactive Information System on Drilling Waste Management Practices (ChevronTexaco, Marathon, ANL)

Highlight:

- Paper prepared and scheduled to be presented in March 2003.

ANL researchers are working on the state regulatory summaries and have discussed the decision-tree architecture for the technology identification module.

Project completion is based on two years of funding. Most of the Year 1 funds are spent. As of the end of February 2003, the project has not received any Year 2 funding, nor has there been word that Year 2 funds will definitely be available this year. As a result, project researchers elected to suspend most of project work in a manner that will allow them to quickly and efficiently come up to speed when funds become available.

Publication

Veil, J.A., J.R. Gasper, M.G. Puder, R.G. Sullivan, P.D. Richmond, B.R. Fidler, C.N. Fleming, R.F. Bernier, and F.V. Jones. “Innovative Website for Drilling Waste Management,” SPE/EPA/DOE Exploration and Production Environmental Conference, San Antonio, TX, March 10-12, 2003.

Downstream Environmental Technology

Kinetics of Biochemical Upgrading of Petroleum (Biocat, ChevronTexaco, Shell, and BNL)

Report not received.

A Predictive Model of Indoor Concentrations of Outdoor PM_{2.5} in Homes (Aerosol Dynamics, Western States Petroleum Association, and LBNL)

Highlights:

- Manuscript accepted for publication.
- Model development progresses.

The manuscript describing measurements of ammonia and nitric acid at the Clovis, NM, field site was accepted for publication in *Environmental Science and Technology*.

Researchers continue to develop the sub module of the mass balance model describing the transformation of ammonium nitrate aerosol inside the house.

A sub-model describing the kinetics of evaporation of ammonium nitrate aerosol particles is nearing completion. The sub-model includes a description of the effect that water uptake by the ammonium nitrate aerosol has on the size, evaporation rate, and equilibrium vapor pressure of the system. The dissociation and evaporation of the nitrate aerosol serves as a source term for ammonia and nitric acid gasses indoors.

A Predictive Model of Indoor Concentrations of Outdoor Volatile Organic Compounds in Homes (American Petroleum Institute, Western States Petroleum Association, and LBNL)

Highlight:

- Researchers preparing manuscript.

LBNL continued and expanded data analysis of five multi-day experiments designed to investigate sorption in a 50-m³ room at three furnishing levels. The goal is to determine the simplest semi-empirical model that can be used to represent the sorption behavior of each of 20 compounds studied. The following models were investigated: (a) linear adsorption/desorption to/from a surface “sink”; (b) a surface sink with diffusion into a single layer of bulk material; and (c) two sequential sinks, including a surface layer and an undefined second layer that may represent a tighter binding (e.g. chemical) or diffusion with adsorption/desorption in the pores of the material. The data for all 20 compounds in each of the five experiments were fit to all three models using two minimization techniques; the first minimizes the sum of squares (giving more weight to higher concentration data points), and the second minimizes the sum of normalized squares (equal weighting for all points).

In parallel to the ongoing data analysis, researchers are preparing a manuscript describing the experiments and modeling of the data.

Developing Enzyme and Biomimetic Catalysts for Upgrading Heavy Crudes via Biological Hydrogenation and Hydrodesulfurization (ChevronTexaco and ORNL)

Highlight:

- Experimentation to purify the active center from *D. gigas* hydrogenase conducted.

ORNL scaled up the isolation procedure for the nickel-iron (Ni-Fe) active center peptide complex. Binding and activity studies will require at least a few microgram quantities of the complex, for which a larger-scale prep is required. Experiments were conducted with a 40 gm batch of cell paste, giving 100 mL of periplasmic extract containing 1.7 units/mL. This was digested with a protease in the presence of 6M urea. The extent of digestion was studied using gel-chromatography with Biogel P-2 (fractionation range 100-1800 Da), Sephadex G-25 (fractionation range 1000-5000 Da) and Sephadex G-50 (fractionation range 1500-30000 Da). The time of digestion and amount of protease necessary for digestion were optimized for a large scale digestion.

Digestion experiments were also conducted in the presence of ionic denaturants (unfolding enhancers) such as Rapigest-SF (Waters Corporation, Milford, MA) and sodium dodecyl sulfate (SDS) to increase rate of digestion. It was observed that the enzyme loses its activity merely in the presence of these unfolding agents. The unfolding agent urea (6M), however, did not cause loss of activity and was therefore used for further experiments. The temperature optimum for the digestion reaction in presence of urea is also being determined. The optimized conditions obtained from these experiments will be used for production of the complex for binding and activity studies.

Characterization and Reaction Behavior of Sterically-Hindered Sulfur Compounds in Heavy Crudes with Nano-Sized Molybdenum Disulfide (ChevronTexaco, BNL, and ANL)

Activity suspended pending receipt of FY03 funds, nothing to report for this period.

Development of a Solid Catalyst Alkylation Process Using Supercritical Fluid Regeneration (Marathon-Ashland and INEEL)

Highlight:

- Regeneration time requirements explored.

INEEL is exploring regeneration time requirements at reaction conditions of 0.26 hr⁻¹ olefin weight hourly space velocity (OWHSV) and an isoparaffin to olefin ratio of 20:1. The regeneration times are between 5 minutes and 2 hours. Preliminary data indicates that at a fixed reaction time increased regeneration times enhance catalyst longevity.

Biocatalytic Alkane Transformation for Viscosity Reduction (ChevronTexaco and LBNL)

Activity suspended pending receipt of FY03 funds, nothing to report for this period.

Secondary Organic Aerosol Research (Aerosol Dynamics, Western States Petroleum Association, and LBNL)

Highlight:

- Filter analyses complete.
- Observations presented at Blodgett Forest Research Workshop.

The aerosol measurement campaign for 2002 was completed in mid-November, and the instruments were removed from the field. Researchers evaluated the measurement technologies and data sets in use to determine if any change to the measurement protocol is desirable. For instance, one species was identified as potentially important is gaseous sulfur dioxide (SO₂). It was hypothesized that extremely small sulfuric acid particles (less than 3 nm) serve as the surface upon which organic gases (both biogenic and anthropogenic) can condense. While these small particles are extraordinarily difficult to detect, experimental evidence seems to suggest that their presence correlates with SO₂ concentration, even at the low levels expected in rural locations. As a result, researchers are searching for an organization that may be willing to loan an SO₂ analyzer for the next season. Two or three other types of measurements that may help with data analysis were identified and will be evaluated.

The analyses of the filters collected last fall are complete. The data provides important information about the near source aerosol emissions from the forest fires that occurred during that time, and will serve as an interesting comparison for filters that will be collected during the upcoming summer.

Researchers presented observations on nuclei mode formation events as measurements from the near source aerosol emissions data for forest fires at Blodgett Forest Research Workshop.

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

(Ceramatec, Inc. and INEEL)

Highlight:

- Ceramatec, Inc., agrees to provide proton exchange membranes and conduct tests.

INEEL fabricated and leak tested a second palladium membrane. This membrane will serve as a surrogate for the proton-conducting ceramic membrane until the ceramic membrane is available. Hydrogen permeation will be measured and compared to published literature to confirm the operation of the membrane test system.

Dave Swank and D.C. Haggard of INEEL visited Ceramatec, Inc., to learn about their membrane test reactors and discuss what Ceramatec could provide in the way of membranes and testing. Ceramatec agreed to provide proton exchange membranes that operate in the 800°C-900°C range. They also are willing to test a few proton conducting materials to operate in the 300°C- 400°C range. In addition, they agreed to perform a limited amount of electrically driven membrane testing in parallel with the INEEL.

The INEEL researchers were able to observe Ceramatec's membrane test fixtures and sealing techniques. These techniques will help INEEL improve their membrane test system by moving all but one sealing surface outside of the heated zone. Ceramatec agreed to provide the ceramic cement for the hot zone seal after testing it with the new membrane materials.

Natural Gas Technology

Molecular Engineering: Next Generation of Gas Purification Technology (ChevronTexaco, Virginia Commonwealth U, and BNL)

Highlight:

- Tentative experiment protocol set up.

BNL and Virginia Commonwealth University (VCU) teams have visited each other to acquaint members with the space and equipment. In addition, a tentative experiment protocol involving many trial and error tests was set up. The following protocol is subject to change pending the outcome of the subsequent tests:

1. Existing equipment will be modified and calibrated.
2. A syringe pump will be used to pressurize a solvent/substrate mixture to supercritical pressures at controlled temperatures. The concentrations, pressure, and temperature of the process will be systematically studied to define the supercritical states. Initially the phase diagram of common solvents, i.e. CO₂, CH₄ and C₂H₄, will serve as guidelines.
3. The mixture will be sprayed onto the surface of a solid support. The rate of expansion, distance, temperature and pressure will be systematically varied to achieve a coating that ranges from micro- to nanometer on the surface, a factor that affects the permeability and durability of the coating. Many tests will be needed to optimize the performance of the coating formed.
4. The coating will be imprinted with the template molecules by using ultraviolet (UV) light to polymerize the coating with the template in place. The concentration of template molecule will be systematically changed to study their effect on the properties of the formed coating.
5. The template will be removed from the polymerized surface under reduced pressure and then tested for molecular selectivity. The product will be analyzed with SAW, electron microscopy, and Fourier Transform Infrared (FTIR) spectroscopy for surface structure studies.

Higher hydrocarbons, such as hexanes C_6 and heptanes C_7 , consist of a small percentage (up to 1%) in natural gases which need to be removed in the production of natural gas. Project researchers used hexane as the template vapor in an attempt to reduce the pore size and, correspondingly, increase the efficiency of the polymer material for separating C_5 to C_8 from small molecules. The ultimate project goal is to extend this work to very small molecules such as methane.

The vapor affinity decreases as the size of the alkane molecule is increased. Furthermore, the hexane-imprinted materials, as expected, exhibit a lower affinity to all alkanes in comparison to the heptane-imprinted material. This is strong evidence that researchers are successfully reducing the material porosity by reducing the size of the template vapor. Researchers plan to investigate processing variables to optimize the process, extending it to smaller template vapors.

Coil-Tubing-Deployed Hard Rock Thermal Spallation Drill and Cavity Maker (Nextant, NM Tech, and LANL)

Highlight:

- Drilling model and burner design progresses.

LANL made a rough prediction of drilling performance for the New Mexico Tech burner design using the burner calculations. The spallation drilling model will predict the heating of the formation due to jet impingement and radiant transport below the burner annulus, convective transport and radiant transport in the annulus.

Preliminary results indicate that heat transport by jet impingement will be greater than any of the other transport mechanisms modeled. Radiant transport might also be significant directly below the burner nozzle if (1) the actual burner chamber temperature is as hot as the theoretical combustion temperature and if (2) the combustion products produce a black body radiation or the chamber acts a black body emitter and the combustion products are transparent. Because none of these conditions are considered to be applicable for a propane air burner, researchers expect that radiant heating will be considerably less important than jet impingement. Therefore the spallation drill advance rate will be primarily influenced by the impingement heat transfer efficiency (a strong function of burner standoff from the bottom of the hole). This result agrees with field results for fuel oil and diesel burners used in previous downhole spallation demonstrations. Methods to monitor and maintain proper standoff will be one of the more challenging features of a downhole burner design.

New Mexico Tech's preliminary design of a connector sub and burner assembly was reviewed by the project team at a LANL meeting on January 10, 2003. Some initial feedback was provided to Ed Williams, the principal designer, and additional feedback will be forthcoming.

Researchers located a potential pressure sensor for the annular pressure measurement and some spark plug sources that might fit in the micro burner assembly. Several concepts for maintaining standoff were proposed but none are readily applicable to the present burner design. Additional concepts and quotes for swivels and slip ring assembly designs were prepared by LANL. Researchers believe they have a feasible concept that precludes the possibility of air propane mixing inside the coiled tubing, unless the breach of two internal tubing lines occurs.

Scintillating Fiber Neutron Detectors for Well Logging (CompuLog, Precision Drilling, Technology Services Group, and PNNL)

Highlight:

- Prototype detector construction begun.

Most of the parts purchased for the prototype detector were received, and most of the custom mechanical parts are finished. Half-inch well logging photomultiplier tubes will allow approximately 3,300 fibers to fill the detector active region. The maximum operating temperature of 200°C forced selection of a high-temperature epoxy for the moderator within the detector. This polymer has half the hydrogen content of polyethylene. The detector efficiency will be reduced by a factor of two, predicted from calculations based on polyethylene. However, the efficiency will still be significantly higher than cadmium shielded ^3He tubes of the same diameter and active length. This is true for all neutron energies above 0.1 MeV. The prototype detector will be run simultaneously with a cadmium shielded 10 atm ^3He tube. The components for the readout electronics are on hand. The target date for testing is mid-April 2003.

225° C MWD Using Silicon-On-Insulator (SOI) Electronics (Baker Oil Tools, Eagle-Picher, Honeywell SSEC, General Atomics, Noble Engineering, Quartzdyne, and SNL)

New FY02 project: Reporting will start three months after the DOE FY02 funding arrives at the laboratories.

Partnership Office

The Partnership completed its funding recommendations for FY03.

These recommendations are based on the reductions of funding from \$9 million in FY02 for the three upstream technology areas and the gas issues forum to \$4 million for FY03. These reduced funding levels resulted in the Partnership not starting any new projects this year in the upstream areas, ending some ongoing projects moving into their third years, and continuing some second-year projects on greatly reduced funding. The Partnership is attempting to move forward with its highest performing

projects to provide a foundation for future years.

In the Upstream Environmental Technology Area, the Partnership selected three new projects for funding in FY03. These three projects address the issues related to produced water associated with oil and natural gas, including coal bed methane production.

Finally, the reduction in funding for FY03 will affect Partnership reporting. The Partnership will suspend publication of the Partnership Progress Report after this issue for one year. The constantly updated web site and monthly reports will continue.