ACTIVITY REPORT

December 2000

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 Drilling, Completion, and Stimulation Technology Diagnostic and Imaging 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

Continuous Monitoring of Particulate Matter and Particulate Matter Precursor Emissions from Stationary Sources (Chevron and SNL)

Project is in close-out phase.

Development of an In-Well Oil/Water Separator for *In Situ* Recycling of Produced Water (Baker Hughes, Chevron, CINC, Oak Ridge Tool & Engineering, Phillips, REDA Pump, Texaco, Unocal, and ORNL)

Highlights:

- System operated on feed stream containing 3 percent sand, 47 percent sea water, and 50 percent synthetic oil.
- Contract placed for manufacture of new centrifugal separator housing.

Bench-scale testing is continuing using a model V-2 (2-in. rotor) centrifugal separator (CINC, Inc.) and synthetic oil.

Solids/water/oil were separated using a hydrocyclone in combination with the centrifugal separator. The system worked well, producing a clean split of oil and water in the separator, after the solids had been removed in the hydrocyclone. The system was operated for approximately an hour. Adjustments were made to the hydrocyclone/separator system so that long-term operation (6–8 hours) is possible.

The housing for the separator was redesigned and will be machined in Plexiglas. The new housing will accept a longer rotor, which will allow for increased throughput capacity. The portion of the rotor housing that directs the exit of the separated streams was redesigned not to protrude from the side, but to extend down the side. Also, exchangeable parts for the internal parts of the housing were designed to allow adjustment of the collection well volumes.

Stationary Source Emission Control Using Plasma-Assisted Catalysis (Cummins Engine, Edison Chouest Offshore, and LLNL)

Project is in close-out phase.

Reducing Chemical Use and Toxicity in Produced-Water Systems (BP Amoco, Rhorback Casasco Systems, and ANL)

Highlight:

- Software for automatic online ECN monitoring developed and tested.

Development and testing of a user-friendly software package for automatic electrochemical noise (ECN) measurement, data interpretation, and corrosion monitoring was completed. The new software was designed to automatically measure and interpret signals from a single ECN sensor. This prototype software was written using an industrial-standard data acquisition-programming platform, LabVIEW from National Instrument, Inc. Corrosion status of the online monitored equipment is updated continuously and can be displayed every 5–10 minutes. The information displayed includes the corrosion mechanism (i.e., sustained localized vs. uniform corrosion), the corrosion current, and estimated uniform corrosion rate. It also includes the information obtained from high-order statistical analysis of the ECN signals (e.g., the Kurtosis and skewness values). Additional statistical analysis capabilities of the online-measured signals will be implemented in the future. This software analysis package will be used to determine whether it is possible to differentiate between chemically or bacterially influenced sustained localized pitting corrosion.

Further modification of the software to allow monitoring of multiple ECN sensors is about 80 percent completed. The modified software for multiple sensors will be used in the next series of experiments to verify the linear proportionality between the general corrosion rates of the non-surface-modified elec-

trode in the new noise probes and the total noise current. It also will be used in another experiment to find the optimal surface roughness of a surface-modified electrode to maximize the sensitivity of the electrode to sustained localized pitting corrosion in a microbially influenced corrosion environment.

Sulfide Removal in Produced Brines by Microbial Oxidation

(Phillips, U of Tulsa, and INEEL)

Experiments to evaluate the tolerance of the Coleville organism (CVO) to sulfate are nearing completion. Initial data indicate that pure cultures of the organism can tolerate more than 400mM of sulfate. This is in contrast to mixed-culture (dominated by CVO) experiments that indicate a more substantial sensitivity.

Evaluations concerning the potential protective nature of the counter ion of the polysulfide complex are ongoing. Efforts have focused on application of microscopy techniques to differentiate between live and dead cells.

Comparative experiments between *Thiobacillus denitrificans* and CVO are ongoing. Evaluations include immobilization strategies, cell washout, sulfide loading, and upset recovery.

Experiments to investigate the effects of increasing concentrations of sodium sulfate and sodium thiosulfate on the growth of CVO, as assayed by disappearance of sulfide (oxidation) have been completed. The first experiment, which tested various sodium sulfate concentrations up to 200 mM, found no effect on the rate of disappearance of sulfide. Additional experiments evaluated concentrations up to 500 mM. At time equal to 20 hours, sulfide had been reduced to zero in the 0, 200, and 300 mM sodium sulfate vials and was reduced by 80–85 percent at 400 mM sodium sulfate. Concentration of 500 mM sodium sulfate showed significant inhibition of sulfide oxidation after one day, but by day two the sulfide concentration was down to zero in this vial as well. Additional experiments investigated the effects of sodium thiosulfate concentrations between 0 and 8 mM. Thiosulfate itself has a depressing effect on the color development in the sulfide assay (approximately linear) as shown by assay after addition of thiosulfate but before inoculation. Nevertheless, the sulfide concentrations in all vials were reduced to zero after one day, showing that thiosulfate at these concentrations has no effect on sulfide oxidation by CVO. Evaluating concentrations above 8 mM thiosulfate will require different techniques because the 8 mM thiosulfate reduced the color yield of the sulfide assay by approximately 42 percent.

"Characterization of a novel biocatalyst system for sulfide oxidation," by C. McComas, K. L. Sublette, G. Jenneman, and G. Bala, has been accepted by *Biotechnology Progress*, pending minor revisions.

Characterization of Soluble Organics in Petroleum Waste Water

(Chevron, Phillips, Shell, Statoil, and ORNL)

Correspondence testing of chemical procedures used to analyze the chemical content of neat oil and produced water is under way. Statoil is providing characterization data derived from North Sea samples. Their primary protocol relies on the analysis of individual semi-volatile compounds, as defined by Environmental Protection Agency (EPA) Method SW-846 8270C, and total petroleum hydrocarbon (TPH) content, as defined by EPA Method SW-846 8015B. ORNL is supplying data derived from Gulf of Mexico (GOM) crude oil and brine. Rather than identifying individual chemical compounds, ORNL is characterizing samples based on carbon range content and chemical classes. It will be important to understand the equivalency of the North Sea and GOM

data when combining the information into a single mathematical model that will predict organic contamination in produced water.

ORNL submitted samples of GOM crude and synthetic produced water for standard EPA Methods testing. The same samples were also analyzed in house, using an open-column liquid chromatographic separation and gas chromatography (GC) flame ionization detection (FID), to determine the relative distribution of chemical classes and carbon content. The total petroleum hydrocarbon content in GOM crude, as defined by EPA Method SW-846 8015B, is 300 g/kg TPH-DRO C10–C28; 180 g/kg TPH-Oil C20–C28. Approximate ratios of carbon size by the EPA method are thus 37 percent, 21 percent, and 42 percent for C6–C10, C10–C20, and C20–C28 ranges, respectively. The relative distribution using a similar GC/FID procedure at ORNL found 50 percent, 42 percent, and 8 percent in carbon series.

The principal semi-volatile compounds in oil, identified by EPA Method SW-846 8270C, include acetophenone (0.6 g/kg) and methylnapthalene (0.4 g/kg). These particular constituents represent less than 2 percent of the total organic content in either sources of crude oil. Chemical classification by liquid chromatography helps to account for the remaining 98 percent of the organic character of either oil or produced water samples. Methylene chloride total extractable material (TEM) in oil is 200-400 g/kg. Approximately 35 percent of this material can be exchanged to a hexane matrix. The relative composition of the hexane matrix is 35 percent saturated hydrocarbons, 15 percent aromatic components, and 50 percent polar material.

The total concentration of water-soluble organics (WSO) in produced water is 20-30 ppm, using either EPA Method SW-846 8015B or ORNL GC/FID procedures. Identified semi-volatile compounds are 1-methylnaphthalene (10 ppb), 2-methylnaphthalene (9 ppb), naphthalene (14 ppb), and phenol (30 ppb). Again, compounds identified by EPA Method SW-846 8270C account for very little of the total WSO content. Chemical fractionation of the TEM suggests that 80–90 percent of WSO is present as polar compounds; the next largest fraction is that of aromatic materials. The visibly colored material appears to be present in the polar fraction.

In combining data from North Sea and GOM samples, it appears that data generated by EPA Method SW-846 8015B or ORNL GC/FID procedures correlate well to indicate the total organic content and relative carbon ranges from these two drilling sites. The toxicity of the organics can be estimated using data generated by EPA Method SW-846 8270C from North Sea samples, and the chemical nature of the material can be estimated using the liquid chromatographic method derived from GOM samples.

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

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

Highlight:

- Paper submitted to SPE symposium.

LLNL and ORNL submitted a symposium paper to the Society of Petroleum Engineers (SPE) for their February meeting in San Antonio, TX. The paper, "Current directions in screening-level ecological risk assessments," presents an overview of ecological risk assessment and soil-screening levels for ecotoxicity, as well as new tools and methods for potentially excluding exploration and production sites of a certain size or total petroleum hydrocarbon concentration in soil. A Chevron participant invited the paper, and Tina Carlsen of LLNL will present it.

ORNL drafted a review of terrestrial examples of population viability analysis (PVA), which can be used to evaluate the likelihood of persistence (or extinction) of biological populations. PVA considers up to four categories of extinction risk: (1) demographic stochasticity, (2) catastrophes, (3) environ-

mental variation, and (4) genetic risks. PVA or empirical vulnerability models will be combined with consideration of spatial factors (e.g., the patchiness of habitat) to provide recommendations for mitigation of exploration and production sites and/or their exclusion from state requirements for formal ecological risk assessment.

The national laboratories continue to identify and collect map layers for the geographic information system that will support the modeling effort at the Tall Grass Prairie Preserve in Oklahoma. The laboratories also continue to revise the draft Geographic Information Systems (GIS) data collection protocol authored by LLNL, which continues work on a literature review of about 300 papers on critical habitat size, fragmentation, and spatial modeling. LLNL is incorporating review comments on the Tall Grass Prairie Preserve trophic model. At the request of API, Exxon, and Chevron, LLNL prepared a white paper about field data collection activities recommended to determine whether 10,000 mg/kg of total petroleum hydrocarbons in soil will allow for ecological recovery.

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

We continued literature review to assess which methods for uncertainty analysis have been applied to grid-based modeling and with what success. The review identifies candidate methods and potential uses, evaluates the strengths and shortcomings of each, and recommends which methods should be applied and with what priority. Although the definition of performance evaluation depends on the intended use of the model simulation, a generic definition might be "assessment of the accuracy with which a model simulates observed phenomena." Methods are categorized as follows: (1) Operational Evaluation, identification and estimation of errors (or biases) through comparison of prediction and observation; (2) Sensitivity Analysis, estimation of responses of outputs to uncertainties in inputs that also can be used to analyze the interrelationships among variables; (3) Diagnostic Analysis, examination of the components of a model or the responses of components to dynamic changes; and (4) Corroborative Analysis, comparison of results with estimates produced through truly independent. One product of this review and other efforts will be a critical review paper. The paper has been outlined in substantial detail, and the research team is converging on the working outline. The review is also being used to initiate development of a comprehensive model system uncertainty analysis framework.

Under previous sponsorship (NPTO), stakeholders concerned with oil and gas development in southwest Wyoming were interviewed to ascertain their views on air quality modeling uncertainty. These interviews have been extended to others concerned with regulation (in Ohio and California) to ascertain their views concerning uncertainty and potential uses of model uncertainty information.

Remote Sensing for Environmental Baselining and Monitoring (Chevron, UC-Davis, and ORNL)

Highlight:

- Project meeting held.

A progress meeting was held at the UC-Davis on November 8, 2000. Researchers at UC-Davis are growing three plant species in hydroponic-solution culture in a controlled-growth facility and in a greenhouse. The plants are being exposed to several concentrations of several heavy metals. Hyperspectral data are collected on a regular schedule at the leaf and canopy level by both a spectrometer with hundreds of bands and an imaging spectrometer. Plans to grow plants that will be exposed to hydrocarbons were discussed at the project meeting.

Downstream Environmental Technology

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

(Texaco, UOP, and INEEL)

September 2000 experiments demonstrated that the polyethylene glycol (PEG) - cytochrome c (CYT c) conjugate, supplied by ORNL, successfully facilitated the oxidation of thioanisole in a supercritical trifluoromethane/ethanol solution. November 2000 experiments explored the PEG-CYT c conjugate for the oxidation of dibenzothiophene (DBT). DBT conversion to its sulfone product ($DBTO_2$) over PEG-CYT c was 58 percent in a liquid acetate phosphate buffer (pH=5.2)/ethanol (80/20) solution. However, no conversion of DBT was observed in supercritical trifluoromethane/ethanol solutions at 40° C and at various pressures ranging from 1820 to 2950 psi.

In December 2000, CYT c was immobilized on agarose beads according to a Sigma procedure. The amount of immobilized protein, determined indirectly by the Bio Rad method, was 60.4 mg CYT c immobilized on agarose out of 100 mg used, when starting with 5 ml of the p nitrophenyl agarose suspension in isopropanol. The resulting product mass was 200 mg of immobilized protein/agarose beads.

Oxidation of DBT catalyzed by CYT c immobilized on agarose was studied at 40° C, 200 rpm for a reaction time of two hours. Solvent systems included acetate-phosphate buffer/ethanol (80/20), hexane, carbon dioxide, and ethane. Each nonaqueous reaction was accompanied by an aqueous buffer reaction to ensure the catalyst was still active. A 10 mg/ml wet biocatalyst was used in all reactions. Conversion to product obtained in the aqueous media was 85 percent. When the reaction was run in supercritical carbon dioxide (2150 psi) no product was obtained. Dehydration of the biocatalyst was observed in carbon dioxide. Reactions run in hexane and in supercritical ethane (2100 psi) also resulted in no conversion to product. In these two solvents, the biocatalyst did not dehydrate.

Modifications to the small-volume high-pressure view cell reactor were undertaken in November 2000. Cartridge heaters were installed, allowing elimination of the temperature-control water bath. Recovery of DBT from the view cell reactor using supercritical fluids demonstrated some reproducibility problems. $DBTO_2$ appeared to be partially soluble in supercritical carbon dioxide. In addition, a literature search on biocatalysis in various reaction media was updated. Protein biooxidation in supercritical reverse micelles and microemulsions appears to be a promising research area for the project.

A cooperative research and development agreement with UOP was signed in December 2000, and one with Texaco is being finalized.

Biological Upgrading of Heavy Oils for Viscosity Reduction

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

The objective of this project is to develop novel biocatalytic agents for the terminal oxidation of alkanes. These agents will be evaluated for use in biological upgrading of crude oil. Researchers currently have 42 pure bacterial cultures capable of oxidizing alkanes. The majority of these appear to be actinomycetes that do not match known phylogenic databases, which suggests that they are novel organisms.

Sixteen sRNA analyses will be conducted to determine with a higher degree of accuracy the phylogenic uniqueness of these organisms. Several strains possess promising characteristics for development of a controllable bioprocess. For example, one bacterium appears to oxidize dodecane but not decane, tetradecane, or pentadecane. The results will be confirmed, and the unique character of this enzyme system will be investigated. The project is on schedule.

Kinetics of Biochemical Upgrading of Petroleum

(Biocat, Chevron, Shell, and BNL)

In October 2000, the biochemical upgrading of petroleum studies were presented to a panel of program reviewers in Houston, TX. Regretfully, some members of the panel had not been updated on the recommendations and conclusions of the panels from the previous review (Berkeley, October 1999). Specifically:

- It was recommended that a 10 percent total sulfur removal should be accepted as proof of concept. This was to be accomplished with oil and biochemical strains to be chosen by BNL. Proof of concept was accomplished by BNL using Boscan crude. Although total sulfur removal was 11 percent, surpassing the goal of 10 percent, some participants were disappointed by the result, which seemed small to them. However, desulfurization of Boscan crude, containing 55,000 ppm (5.5 percent) total sulfur in macromolecular fraction, is a more difficult task than desulfurization of diesel fuel with 200 ppm sulfur content.
- The extreme difference in sulfur content and the complexity of current studies indicate that our understanding of metabolic capability is based on model compounds and diesel. While scientifically useful, this limited understanding does not mean that the information when extrapolated to whole heavy crude processing will lead to a successful process.

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

(Chevron, Phillips, Texaco, ORNL, and INEEL)

The objective of this program is to develop new technologies for upgrading of heavy oils, using novel enzyme-based bioprocessing concepts. Enzymes, naturally occurring in aqueous environments, will be modified through genetic engineering or chemical processes to make them stable and active in organic media.

To produce mutants of the lignin peroxidase (LiP) enzyme, the gene for the enzyme was first isolated from one of the previously created clones. New primer pair was designed. The forward primer bore a S*fi*l restriction site complementary to the sequence at the 5-ft-end of the *lip* gene (about 113 base pairs down from the start codon of the leader sequence)—a naturally occurring unique restriction site located in the proximity of the start codon of the native gene. The primer pair was used to create the *lip'* gene sequence using polymerase chain reaction (PCR). However, the amounts of product generated in the reaction were insufficient for further manipulations, and optimization of the PCR conditions was required to generate sufficient amount of the gene product. The product was then cloned into the PCR2.1 vector and transformed into *E. coli* strain TOP10. Researchers are analyzing the recombinant clones for correct insertion and orientation of the mutated gene.

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

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

Highlights:

- Continued analysis of intensive data.
- Improved and initiated Winter Intensive sampling plan.
- Began analysis of Fall Intensive filter samples.

During November and December 2000, researchers continued analysis of data from Fall Intensive measurement period and began analysis of the filter samples. Although analysis of the filter data is incomplete, preliminary results from the carbon filters showed intriguing differences between the carbon composition indoors and outdoors. During the Winter Intensive measurement period, additional types of filter samples are being taken to determine whether these differences are from filter artifacts or actual particle composition changes. The Winter sampling plan was modified to include a wider range of indoor air exchange rates, differential pressures, and house operating conditions. Explo-

ration of a wider range of parameters and the inclusion of step function changes in the operating conditions will enhance our ability to determine causal mechanisms for the particle transformation processes and improve the applicability of the project model to a wider variety of conditions.

The Winter Intensive sampling period began in December 2000 and will continue into January 2001. During this period, time-resolved measurements have been collected for $PM_{2.5}$ nitrate, sulfate, carbon, and black carbon; particle sizes between 0.1 and 10 microns, and gas-phase ammonia and nitric acid. Filter samples were taken for seven days during December and will be taken for an additional seven days in January, weather permitting. Because of differences in particle composition, particle loading, emissions, atmospheric chemistry, and weather conditions between the Fall and Winter periods, this additional sampling will allow us to explore a broader range of parameters and conditions that are crucial for developing a more generally applicable modeling system.

Real-Time Characterization of Metals in Gas and Aerosol Phases

(BP Amoco, Equilon, Marathon, Phillips, Shell, Eastman Chemicals, and ORNL)

No report received.

Partnership Office

Welcome to the New Year!

PNNL Representation

There has been a change in laboratory representation at PNNL. The Partnership thanks Bruce Reynolds, who has taken a new position at INEEL, for his efforts on behalf of our organization. We welcome Bernie Saffell, who rejoins the Partnership as PNNL's representative.

Upstream Technology Review

The leaders for the three Upstream Technology areas—Diagnostics and Imaging; Oil and Gas Recovery; and Drilling, Completion, and Stimulation—are completing the final draft of the industry rankings and Partnership funding recommendations for FY01. As several reviewers remarked, there was exceptionally high quality in both new and continuing projects during the FY01 reviews. Issues remain about how we can serve both independent and major producers in the selection and funding of projects.

The Partnership will make every effort to address these issues and evolve. A major effort also continues in considering how the Partnership can develop its Offshore Technology Program.