



# Mild Coal Gasification

Principal Investigator:  
D. W. Camp

## Objectives

The purpose of this project is to develop and apply coal devolatilization technology to the concept of mild gasification of coal. During mild gasification, coal is heated in an oxygen-free environment at near-atmospheric pressure to temperatures between 400 and 800°C. Under these conditions, 100 lb of coal pyrolyzes to produce approximately 20 lb of condensable oil vapor, 10 lb of medium Btu gas, and 70 lb of solid char product. The gas can be burned for process heat, the oil refined to liquid fuels, and the char burned in a power plant, briquetted for home heating, or upgraded for specialty carbon applications. Such "skimming" of oil from coal may be a way to produce liquid transportation fuels with minimal capital cost and implementation time.

The immediate objectives of this project were (1) to recommend promising processes for the continuous mild gasification of bituminous coals on the basis of our experience, creativity, and a survey of the literature, and (2) to provide technical assistance and advice to improve the operation, equipment, and data interpretation of a DOE batch process unit that is already in operation in Bristol, Virginia.

## Accomplishments

We surveyed a large number of processes and arrived at three that we identified as the best candidates for further development. An important consideration was the ability to handle highly volatile bituminous coals, most of which become soft and sticky just before and during pyrolysis. The first two processes are Occidental Petroleum Company's entrained bed and Lurgi-Ruhrgas's screw mixer, both of which involve flash pyrolysis. The coal is heated rapidly

during mixing with very hot, partially-burned recycled char. The third process uses a screw device, similar to a vented plastics extruder, to convey the coal, heat it by conduction through the barrel walls, and pyrolyze it. An especially promising way of doing this, conceived by our group, involves the use of a twin-screw devolatilizing extruder for the task. In addition to these process recommendations, we identified several ways by which the oil yield and product compositions could be improved during or after almost any process.

We provided considerable technical guidance and some interpretation of data for DOE's batch process unit.

### Publication

Camp, D. W., R. G. Mallon, M. S. Oh, T. T. Coburn, R. W. Taylor, and A. E. Lewis (1987), *A Review of Continuous Processes for the Mild Gasification (Pyrolysis) of Bituminous Coal, Including Ways to Improve the Product Characteristics*, Lawrence Livermore National Laboratory, Livermore, CA (in preparation).

# Enhanced Oil Recovery Sensing

Principal Investigators:  
E. F. Laine and J. G. Berryman

## Objectives

The objective of this research project is to develop a system to image a vertical two-dimensional plane between two boreholes using high-frequency electromagnetic transmissions and seismic transmission. The system is designed to operate in a steam-flood environment in an active enhanced oil recovery field. Interpretation of reconstructed tomographic images will aid the diagnosis of fluid saturations and movement.

## Accomplishments

Downhole electronics and materials were developed that will withstand long-term exposure to a hostile environment. It is thus possible to acquire data in an active steam-flood recovery zone and to construct tomographic images that delineate steam-flood override, shale layers, and oil- and water-saturated areas.

A system has been successfully deployed at Kern County,

California, in a commercial oil field undergoing a steam flood. High-frequency electromagnetic tomographic data have been obtained, and images have been reconstructed that show the lithology of the plane between the boreholes. A steam override shows in one of the tomographs. Thus, detailed high-resolution tomographic data have been obtained for the first time in a commercially active steam-flood

field. This system opens up the possibility of a better understanding of the underground steam-flood process and may suggest ways to increase the sweep efficiency.

## Publication

Laine, E. F. (1987), "Remote Monitoring of a Steam Flood Enhanced Oil Recovery Process," *Geophysics* **52**(11), 1457-1465.

# Tubing Wastage in Fluidized-bed Coal Combustors

Principal Investigator:  
C. E. Witherell

## Objectives

Unexpected and unexplained rapid wastage of outer heat-exchanger surfaces threatens implementation of the economical, clean, and efficient fluidized-bed combustion process as a means of generating electric power from abundant domestic coal supplies. Our goal was to supply a plausible explanation for wastage of the carbon-steel tubes in the low-temperature environment and to identify the failure mechanism(s). Bed temperatures are about 800°C, and steam (and therefore tube) temperatures are about 400°C.

## Accomplishments

We completed a comprehensive study of affected heat-exchanger tubes from the Grimethorpe (U.K.) fluidized-bed combustor. Our conclusions are that wasted outer surfaces are not typical of those produced by simple erosion processes and that there are at least two dominant destructive mechanisms that operate concurrently on susceptible regions of the fireside surfaces.

One of the wastage mechanisms is oxide spallation caused by abrasion by the bed material, which results in continual loss and reformation of the normally protective oxide layer. Metal loss

by this mechanism therefore proceeds at an unusually rapid rate governed by the kinetics of oxide formation at the temperature of the tube surface under the operating conditions of the combustor. A second related loss mechanism is direct metal loss. As oxide deposits are abraded by turbulent bed particulates, localized depressions of oxide remain embedded in the tube wall.

Repetitive impacting of the surface by dense particulates mechanically work-hardens the metal protrusions or metal islands remaining between the oxide pockets, causing loss of ductility and their eventual fracture from the tube wall. The results of this analysis are in

contrast to the general consensus before our examination, which was that the wastage was due solely to erosion.

## Publication

Witherell, C. E. and R. G. Meisenheimer (1987), "Tubing Wastage in Fluidized-Bed Coal Combustors, Examinations of Tubing from Test Series 2 NCB (IEA Grimethorpe) Ltd. Facility," *Proc. EPRI Workshop on Wastage of In-bed Surfaces in Fluidized-Bed Combustors*, Argonne National Laboratory, Argonne, Illinois, November 2-6, 1987 (in press). Also, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-97569.



# Probabilistic Seismic Hazard Analysis

Principal Investigator:

J. B. Savy

## Objectives

The prolific oil fields in the Lake Maracaibo region of Venezuela have been under production for decades. Dikes have been constructed to protect surrounding land areas from flooding; however, the dikes are susceptible to subsidence and seismic damage. At the invitation of the Instituto Tecnológico Venezolano de Petróleo (INTEVEP), the research branch of the national oil company, we agreed to provide the necessary computational tools for assessing the seismic hazard at dike locations quantitatively.

## Accomplishments

We had previously developed a methodology for calculating seismic hazards at nuclear plant sites in the eastern U.S. for the Nuclear Regulatory Commission. The approach that we developed has been well accepted and documented. The methodology uses expert opinion as well as data as input to the codes. We

adapted the methodology to the Venezuelan case by developing all necessary questionnaires, which are to be sent to appropriate Venezuelan experts by INTEVEP. These included a questionnaire on seismic zonation and seismic characterization and another soliciting information for ground-motion attenuation calculations. We also developed a new type of ground-motion calculational

model specifically for this study which relates the number of cycles to earthquake magnitude and distance. We further broadened the methodology by dealing with the uncertainty of fault rupture length as a function of magnitude. Both the software and the questionnaires are now in Venezuelan hands.

# Petrophysics Related to Compaction of Sediments

Principal Investigators:  
S. C. Blair and J. J. Sweeney

## Objectives

The national oil company of Venezuela has observed subsidence in some of its oil fields as a consequence of production. The Venezuelan heavy-oil sands, with an oil-and-water content as high as 80%, have very low structural strength and exhibit extensive compaction when pore fluid is withdrawn. The Instituto Tecnológico Venezolano de Petróleo (INTEVEP), the research arm of the national oil company, has commissioned an extensive research program to develop models that will predict underground subsidence and its effect on surface configuration. Under an agreement with INTEVEP, we undertook laboratory investigations of the mechanical properties of reservoir rocks to provide improved data as inputs to the model.

## Accomplishments

Two rock types were investigated: the oil-bearing sand and the shale cap rock of the Faja reservoir. More than fifty tests were performed, including 12 pressure-volume tests, 15 long-term creep/compaction tests, and 30 triaxial tests in compression. New apparatuses were constructed to perform the tests, which ranged in temperature and pressure from ambient to 250°C and 300 MPa, respectively. These apparatuses include a high-temperature triaxial vessel with pore-pressure control and several manual and automated pore-fluid volumometer systems.

Bulk moduli, strengths, and other mechanical properties were measured for the two rock types. Observations pertinent to compaction and subsidence include the fact that decreases in volume with increasing effective pressure result from the permanent pore compaction that occurs as pore fluid is expelled from the samples. The compressive strength of oil sands at a similar confining pressure varied insignificantly with temperature to 125°C. In pressure-volume tests, temperature had very little effect on oil sands, but the bulk modulus for shales was reduced by one-third by increasing the temperature

from 23 to 125°C. For both the sands and the shale, long-term creep compaction tests showed a linear change in sample volume as a function of the log of time, and the rate of change of volume with time increased with temperature.

## Publication

Blair, S. C., J. J. Sweeney, W. R. Ralph, and D. G. Ruddle (1987), *Mechanical Properties of Heavy Oil-Sand and Shale as a Function of Pressure and Temperature*, Lawrence Livermore National Laboratory, Livermore, CA, UCID-21093.

# Chemical Study of Tar Sands

## Principal Investigators:

J. G. Reynolds and

R. W. Crawford

## Objectives

Tar sands are a large untapped hydrocarbon resource whose exploitation has been impeded by lack of an economic and efficient recovery process. As a first step toward that goal, we have undertaken a detailed study of the basic chemistry of the tar sands and their behavior during simulated recovery processes.

## Accomplishments

Our approach has been from three experimental directions: laboratory pyrolysis of various tar sands, laboratory pyrolysis of model compounds, and the study of metal-containing compounds in the bitumens and in pyrolysis products.

Our initial results indicated that different tar sands have different behaviors during pyrolysis tests and that the behavior of each may constitute a characteristic signature of the deposit. Our first detailed experiments were on tar sands from Asphalt Ridge (Utah) and Big Clifty (Kentucky), which we pyrolyzed at temperatures from 0 to 900°C at a heating rate of 4°C/min. Gas evolution (of H<sub>2</sub>, CO<sub>2</sub>, CO, SO<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>S, and H<sub>2</sub>O, and alkanes, alkenes, and aromatics) was monitored using an on-line triple quadrupole mass spectrometer. Hydrocarbon

evolution was associated with two processes: release of entrained material (low temperature) and release during cracking reactions (high temperature). H<sub>2</sub>, H<sub>2</sub>S, H<sub>2</sub>O, and NH<sub>3</sub> are associated with hydrocarbon breakdown. The evolved carbon oxides relate to the decomposition of carboxylic acid at temperatures associated with the breakdown of hydrocarbons, the decomposition of carbonate minerals, the gasification of char, and the water-gas shift reaction. The origin of SO<sub>2</sub> is uncertain. We expect the gas evolution profiles to have an impact on the choice of recovery processes as well as on environmental considerations. In order to understand gas evolution, we began a systematic examination of the products from the pyrolysis of model compounds and pure materials such as carboxylic acid salt.

Because bitumens in tar sands have high concentrations of

deleterious impurities, such as organic complexes containing nickel and vanadium, we have concentrated on their identification and structural characterization and their behavior during pyrolysis. Our results to date indicate substantial amounts of nickel petroporphyrins in the Asphalt Ridge tar sand and only vanadyl petroporphyrins in the Big Clifty tar sand. Preliminary results for Arroyo Grande (California) tar sand indicate that some of the nickel petroporphyrins survive pyrolysis while the vanadyl petroporphyrins do not. We have begun to extract and separate metallo-nonporphyrins from the petroporphyrins in the same bitumens by alumina-column chromatography in order to predict the role each will have in recovery processes that might be envisaged and in the final products.



## Publications

Reynolds, J. G., and R. W. Crawford (1988), "Pyrolysis of Sunnyside (Utah) Tar Sand: Characterization of Volatile Compound Evolution," *Proc. Am. Chem. Soc., Division of Petroleum Chemistry, Toronto, Canada, June 5, 1988* (in press). Also, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-97719.

Reynolds, J. G., R. W. Crawford, and T. T. Coburn (1987), "Variable Temperature Pyrolysis of Domestic Tar Sands," *Pacific Conference on Chemistry and Spectroscopy, Irvine, CA, October 30, 1987*, Session 41, Paper 10-1 (Abstract).

Reynolds, J. G., R. W. Crawford, and T. T. Coburn (1987), "Variable Temperature Pyrolysis of Domestic Tar Sands—Asphalt Ridge (Utah) and Big Clifty (Kentucky)," *Proc. Eastern Oil Shale Symposium, Lexington, KY,*

*November 18, 1987* (in press). Also, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-97677.

Reynolds, J. G., E. J. Gallegos, R. H. Fish, and J. J. Komtenic (1987), "Characterization of the Binding Sites of Vanadium Compounds in Heavy Crude Petroleum Extracts by Electron Paramagnetic Resonance Spectroscopy," *Energy & Fuels* **1**, 36-44.

# Conversion of Methane to Liquid Hydrocarbons

Principal Investigator:

M. W. Droege

## Objectives

Our goal is to understand the basic chemistry of conversion of methane to more complex hydrocarbons and to use that understanding to develop a process that eliminates the need for the steam-reforming of methane to a synthesis gas as an intermediate step. The work focuses on development of novel catalysts. It is desirable that direct conversion be at reasonably low temperatures and pressures so as to be economically competitive with existing processes and amenable to implementation at remote sites. If successful, such a process would utilize large quantities of gas currently without access to markets via pipeline and increase the liquid-fuel supply.

## Accomplishments

We have identified several chemical reactions that show promise in accomplishing the conversion of methane. These reactions include schemes that form methyl radicals which can then dimerize and further react, resulting primarily in small olefins such as ethylene. Another scheme of interest is the formation of transition-metal alkylidene complexes that react directly with methane, resulting in higher hydrocarbons. The catalytic materials must be designed to optimize such reactions.

A packed-bed flow reactor has been constructed for studying the reaction of catalyst materials

with methane. The system consists of  $\text{CH}_4$ ,  $\text{O}_2$ , and Ar or  $\text{N}_2$ ; the catalyst; and a quartz-tube packed-bed flow reactor heated in a furnace. Product gases are either sampled on-line using a computer or collected in gas bottles for subsequent analysis. The reactor allows us to screen potential catalysts, determine important process variables, and follow the time evolution of the reaction. Data analysis includes product identification, production distribution, and analysis of reaction kinetics.

Using a flow and on-line mass spectroscopy detection system, we have observed the oxidation of methane under temperatures ranging from 25 to

800°C and flow rates of 40  $\text{cm}^3/\text{min}$  using a 3:1 mixture of methane to oxygen. In control experiments, the empty quartz reactor and the undoped silicon aerogel showed similar behavior for methane oxidation. Formation of CO,  $\text{CO}_2$  began at about 600°C and increased (CO is the favored product under these conditions) with increasing temperature. At 800°C, all available oxygen was consumed and both ethane and ethylene were observed. The production of these hydrocarbons will be further quantified and used as background values for comparison with results obtained using doped aerogel materials.





Experimental  
electric car.

# Nonfossil Energy

# Aluminum-Air Power Cell

Principal Investigator:

A. Maimoni

## Objectives

Our objective is to develop an electrical power source as an alternative to the internal combustion engine, and to evaluate the extent to which it can provide general-purpose vehicles with the range, acceleration, performance, and rapid refueling capability of current vehicles powered by internal combustion engines.

## Accomplishments

Activities at LLNL as well as the activities of our subcontractors were phased down during FY 1987. Experimental work was carried out at ELTECH Systems Corp. and at Case Western Reserve University. Research at Case focused on developing a better understanding of the catalytic processes at oxygen electrodes and the development of improved and less expensive catalysts. The best catalyst continues to be pyrolyzed cobalt tetramethoxy-phenyl porphyrin (CoTMPP) on a carbon-black substrate. While a number of other less expensive catalysts were found, they are not as effective as CoTMPP.

Two series of experiments were carried out at ELTECH:

1. Determination of the effect of operating temperature, current density, and the carbon dioxide content of the incoming air on the life and performance of air electrodes. Carbon dioxide leads to precipitation of sodium

(or potassium) carbonate within the pores of the air electrode, decreasing its life and performance. A problem that had to be solved initially was the manufacture of air electrodes with very reproducible properties. The electrodes chosen have a much shorter operating life than normal electrodes; thus, while the conclusions of the study are important, they do not fully reflect the performance of future long-life electrodes. The main variables decreasing life and performance were found to be current density and temperature; the concentration of carbon dioxide had a surprisingly small effect. However, the conclusions of the study indicate that carbon dioxide will have to be reduced to about 5 to 50 ppm to obtain satisfactory electrode life.

2. Investigation of the effect of a number of alloying elements on the performance of aluminum anodes. Alloys containing In-Mg-Mn, In-Li-Bi, and In-Li in 99.99% pure aluminum were made at Reynolds Aluminum Co. and

tested at ELTECH. Although the three alloy families did not perform as well as anticipated, the results indicate that the concentration ranges chosen were not optimum. The In-Mg-Mn group of alloys continue to offer the most promise.

The principal activities at LLNL consisted of preparing the final reports. All work will terminate when the final reports from ELTECH and LLNL are distributed during FY 1988. The highlights of final LLNL reports in preparation are as follows:

1. *Crystallization of Aluminum Hydroxide in the Aluminum-Air Power Cell: Literature Review, Crystallizer Design, Results of Integrated System Tests* summarizes the results of all the research on aluminum hydroxide crystallization sponsored by the aluminum-air program, with particular emphasis on the most recent results obtained at LLNL. An important conclusion is that the crystallizer/product separation system for a full-size

electric vehicle need not exceed 40 L in volume and 60 cm in height.

2. *Aluminum-Air Power Cell: System Design Alternatives and Status of Components* describes the current development status of all the components of the aluminum-air system as well as the results of previous system studies. New material includes the effect of crystallizer performance on the steady-state operating-voltage power and energy-density characteristics of the battery; the implications of pressurized operation and/or oxygen-enriched air on the size of the carbon dioxide scrubber; and a summary of previously obtained information on the effect of aluminate concentration on the

polarization of the aluminum anode.

3. *Lamella Settlers: Behavior of Narrow Settlers*. Lamella settlers are a key component of the crystallizer system described above; they were used for the clarification of the electrolyte returning to the cells and for separation of the aluminum hydroxide product. Previous work using a 60-cm-long settler with 1-cm plate separation provided the basis for a predictive model and for the design of the crystallizer. Recent results using settlers of 0.635- and 0.317-cm plate separation confirmed the validity of the model. An 18-cm-long settler with 0.3-cm plate separation provides the same degree of separation as the 60-cm-long settler above, thus allowing for a

significant reduction of the volume and height of the system.

## Publications

Maimoni, A. (1987), *Aluminum-Air Battery Crystallizer*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-95923.

Maimoni, A. (1986), "Aluminum-Air Power Cell Research and Development," *Technology Base Research Project for Electrochemical Energy Storage: Annual Report for 1986*, Lawrence Berkeley Laboratory, Berkeley, CA, LBL-23495, 35-38.

Maimoni, A. (1987), "Lamella Settlers: Material Balances and Clarification Rates," *Environmental Progress* (in press). Also, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-95924.

# Combustion Chemistry

Principal Investigator:

C. K. Westbrook

## Objectives

Engine knock occurs when unburned gases in an engine's cylinders prematurely ignite. Additives to gasoline reduce engine knock by slowing combustion. Eliminating the knock, however, requires a detailed understanding of the chemical reactions that take place. These reactions have remained elusive despite extensive research. We hope to provide some insight into antiknock processes through sophisticated computer modeling of engine processes coupled with experimental and diagnostic programs at other cooperating laboratories. Our modeling studies of engine processes also include research on flame propagation, temperature and pressure changes due to chemical reactions, chemical-pollutant formation, flame quenching at chamber walls, and heat transfer at cylinder walls.

## Accomplishments

Our foci have been the fundamental processes associated with engine knock and combustion properties in pulse combustors and direct-injected stratified-charge engines. The work on engine knock has centered on n-butane and isobutane because (1) these fuels are isomers of relatively simple hydrocarbon molecules, with knock properties that depend on the fuel structure, and (2) there is a considerable amount of relevant experimental data at hand. Combustion of more complex fuels, e.g., octane, appears to involve breakdown to butane, so they may also be amenable to analysis.

Premature ignition of the fuel results when the air and gas furthest removed from the igniting flame become compressed and

explode before the flame reaches them. Hydroperoxyl radicals, which are highly reactive molecules produced during combustion, must be reduced in order to limit knock. Lead additives slow the combustion mainly by removing hydroperoxyl radicals. Methanol is an effective additive because it reduces the ignition temperature of the mixture. For both butane isomers, our model accurately predicted all of the important intermediate- and final-product concentrations as well as the variation in the exact timing of the knock as a function of inlet manifold temperature and pressure and engine speed.

In the course of modeling knock phenomena, we determined that chemical reactions proceeded at much lower temperatures (below 800°K) and higher pressures (above 10–15 atm) than had

theretofore been thought possible. As a consequence, several low-temperature or "cool flame" modeling studies were carried out. We conclude that heat release during low-temperature periods raises the temperature of the end gases and leads to their ignition earlier than would normally have occurred, and that this also results in knock.

We have also studied pulse-combustion kinetics in parallel with an experimental program at Sandia National Laboratories. In pulse combustors, a mixture of fresh fuel and air mixes with the hot products of the previous combustion cycle. After a time delay, the mixture ignites, starting a new combustion cycle. The kinetic analysis combined with the experimental studies showed that the total ignition delay can

be divided into the sum of a mixing and a kinetics induction time. The overall operating characteristics of the pulse combustor can be materially altered by adjusting either to change the phase relationship between the time of peak chamber pressure and the time of maximum heat-release rate. Our prediction of improved performance through modification of the fuel and its ignition kinetics was verified in laboratory experiments.

### Publications

Chiang, C. C., K. M. Pamidimukala, G. B. Skinner, and C. K. Westbrook (1987), "An Experimental and Computational Study of the Oxidation of Ethane and Propane at Low Concentrations," *J. Phys. Chem* (in press). Also, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-96337.

Green, R. M., N. P. Cernansky, W. J. Pitz, and C. K. Westbrook (1987), "A Study of the Compression Ignition of N-Butane in an Internal Combustion Engine," *Proc. Western States Section of the Combustion Institute, Provo, UT, April 6-7, 1987* (in press). Also, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-96438.

Green, R. M., N. P. Cernansky, W. J. Pitz, and C. K. Westbrook (1987), "The Role of Low Temperature Chemistry in the Autoignition of N-Butane," *Proc. Society of Automotive Engineers Intern. Fuels and Lubricants Meeting and Exposition, Toronto, Ontario, Canada, November 2-5, 1987*, paper No. SAE-872108. Also, Lawrence Livermore National Laboratory, Livermore, CA UCRL-97547.

Green, R. M., C. D. Parker, W. J. Pitz, and C. K. Westbrook (1987), "The Autoignition of Isobutane in a Knocking Engine," *Proc. Society of Automotive Engineers Intern. Congress and Exposition, Detroit, Michigan, 23-27 February 1987*, paper No. SAE-870169. Also, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-95644.

Keller, J. O., J. E. Dec, C. K. Westbrook, and T. T. Bramlette (1987), "Pulse Combustion: The Importance of Characteristic Times," *Combustion and Flame* (in press). Also, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-96756.

Keller, J. O., T. T. Bramlette, C. K. Westbrook, and J. E. Dec (1987), "Response of a Pulse Combustor to Changes in Total Ignition Delay Time," *1987 Spring Meeting of the Central States Section of the Combustion Institute, Argonne, IL, May 11-12, 1987*. Also, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-96437.

Lavid, M., J. G. Stevens, and C. K. Westbrook (1987), "Analytic Modeling of Enhancement of Premixed H<sub>2</sub>/Air Flames with Photochemically Produced Radicals," *2nd ASME-JSME Thermal Engineering Joint Conference, Honolulu, HI, March 22-27, 1987*. Also, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-96272.

Westbrook, C. K., and W. J. Pitz (1987), "Detailed Kinetic Modeling of Autoignition Chemistry," *Proc. Society of Automotive Engineers Intern. Fuels and Lubricants Meeting and Exposition, Toronto, Ontario, Canada, November 2-5, 1987*, paper No. SAE-872107. Also, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-97082.

Westbrook, C. K., and W. J. Pitz (1987), "High Pressure Autoignition of Natural Gas/Air Mixtures and the Problem of Engine Knock," *Proc. Joint Meeting of the Western States and Japanese Sections of the Combustion Institute, Honolulu, HI, November 22-25, 1987* (in press). Also, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-97180.

Westbrook, C. K., W. J. Pitz, M. M. Thornton, and P. C. Malte (1987), "A Kinetic Modeling Study of N-Pentane Oxidation in a Well-Stirred Reactor," *Combustion and Flame* (in press). Also, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-96163.

Westbrook, C. K., M. M. Thornton, W. J. Pitz, and P. C. Malte (1988), "A Kinetic Study of Ethylene Oxidation in a Well-Stirred Reactor," *Proc. 22nd Intern. Symposium on Combustion, August, 1988*. Also, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-97985.

Westbrook, C. K., J. Warnatz, and W. J. Pitz (1988), "A Detailed Chemical Kinetic Reaction Mechanism for the Oxidation of Iso-Octane and N-Heptane over an Extended Temperature Range and its Application to Analysis of Engine Knock," *Proc. 22nd Intern. Symposium on Combustion, August, 1988*. Also, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-98090.

Wilk, R. D., N. P. Cernansky, W. J. Pitz, and C. K. Westbrook (1987), "Propene Oxidation at Low and Intermediate Temperatures: A Detailed Chemical Kinetic Study," *Proc. Western States Section of the Combustion Institute, Provo, UT, April 6-7, 1987* (in press). Also, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-96404.

# Abrasion- and Impact-Resistant Coatings

## Principal Investigators:

W. A. Steele, P. B. Mohr, and  
H. R. Leider

## Objectives

The aim of our abrasion studies is to develop cost-effective coatings that extend the life of solid components of granular-flow systems. There are numerous potential applications in energy conversion involving solids such as coal and oil shale. The basic approach is to reduce the intensity of interaction between flowing media and container by the use of a compliant coating on the surface to be protected. The coatings showing promise are made up of hard, brittle ceramics in the form of fibers with high aspect ratios that are fabricated into a pile woven onto a mesh backing.

## Accomplishments

Carbon or graphite fibers were selected to perform proof-of-concept studies because of their strength and chemical inertness at moderate temperature, their cost, and their availability. After sand-blasting tests in the laboratory on fiber piles, an "industrial test" was conducted at the LLNL experimental oil shale retort. Sections of a 2-in. polyvinyl chloride pipe were lined with a pile consisting of 8-mm carbon fibers that had been woven to a packing density of 40%, carbonized, and attached to the pipe with epoxy. For 200-mm particles, survival of the lining was excellent below a maximum air velocity of 15 m/sec—measured in days—but erosion was extensive in minutes at higher veloci-

ties. Failure of the lining at high velocities was anticipated since the packing density was less than 50%, which we had earlier determined was necessary in order to withstand abrasion. Failure of the fibers in the pile proved to be by catastrophic fracture rather than by gradual attrition.

We have continued to study the details of fiber failure in order to perfect the coatings. This work has included examining the relation between particle properties and filament size and strength. We have assessed pressure differences across the test sections and drag phenomena in general. Our studies also included the investigation of new materials. For example, nickel-coated carbon fibers soldered to stainless steel, copper, or alumi-

num backing provide a broader capability to utilize the fibers as abrasion-resistant liners.

## Publications

Hirschfeld, T., G. Haugen, and W. Steele (1987), *Abrasion and Impact Resistant Coatings*, Lawrence Livermore National Laboratory, Livermore, CA, UCID-20795.

Steele, W. A., P. B. Mohr, and H. R. Leider (1987), *Abrasion and Impact Resistant Coatings*, Lawrence Livermore National Laboratory, Livermore, CA, UCID-20839-87-3 and UCID-20839-87-4.

Steele, W. A., P. B. Mohr, and H. R. Leider (1987), *Anti-Abrasion Protection with Highly Organized Materials*, Lawrence Livermore National Laboratory, Livermore, CA, UCID-20839-87-2.

# Geothermal Investigations

## Principal Investigators:

P. W. Kasameyer, J. J. Zucca,  
S. P. Jarpe, and T. Hauk

## Objectives

Our program has two principal directions: to geophysically monitor injected fluids at geothermal sites, and to develop and test innovative seismic tools for locating and characterizing underground magma and associated hydrothermal systems.

## Accomplishments

By deploying seismic instruments around injection sites, microseisms can be recorded that give insight into the location of moving thermal and chemical fronts, the location of zones of highest pressure, fracture orientation, and other information about subsurface processes during injection. Using both microseismicity and self-potential data collected at the Casa Diablo Hot Springs area near Mammoth Lakes, California, we have begun interpretation and analysis. Casa Diablo is an excellent site to test new assessments, methods, and models of seismic response to injection because background data were collected before injection by a high-resolution seismic array and because data have been gathered continuously over a period of years from the same seismic stations. Results of initial findings will not be released until reviewed by the operators of the geothermal field. A similar study was begun at the Salton Sea geothermal field in California in conjunction with a 30-day injec-

tion test at the State 2-14 geothermal injection well. A 12-station array using digital telemetry to the recorder will record the full waveform.

Our second major geothermal program resulted in tomographic images of the upper 5 km beneath the Medicine Lake caldera in northern California. These images were produced from seismic and attenuation data collected in conjunction with the U.S. Geological Survey and were based on data from 8 explosions recorded on 140 closely spaced seismographs. A 4-km<sup>2</sup> area at a depth of 3 to 5 km was identified as a possible magma chamber from its low velocity and attenuating characteristics. At shallower depths, a high-velocity core surrounded by lower-velocity rock was interpreted to be magma that had moved outward from the magma chamber and subsequently crystallized.

We believe that we have successfully tested the use of innovative seismic imaging tech-

niques on problems that have not been amenable to standard seismic reflection methods.

## Publications

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