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Introduction

This document is a report of work accomplished during FY 1987 for the Department of Energy (DOE) by the Energy Program of the Lawrence Livermore National Laboratory (LLNL). The goal of the LLNL Energy Program is to define and implement research and development projects for the DOE that will positively impact the nation's supply and utilization of energy.

The national economy is particularly dependent on efficient electrical generation and transportation. Electrical demand continues to grow and will increasingly rely on coal and nuclear fuels. The nuclear power industry still has not found a solution to the problem of disposing of the waste produced by nuclear reactors. Although coal is in ample supply and the infrastructure is in place for its utilization, environmental problems and improved conversion processes remain technical challenges. In the case of transportation, the nation depends almost exclusively on liquid fuels with attendant reliance on imported oil. Economic alternates—synfuels from coal, natural gas, and oil shale, or fuel cells and batteries—have yet to be developed or perfected so as to impact the marketplace. Inefficiencies in energy conversion in almost all phases of resource utilization remain. These collective problems are the focus of the Energy Program.

In this report, the individual programs making up the Energy Program are grouped into three sections: Nuclear Energy, Fossil Energy, and Nonfossil Energy. Figure 1(a) shows the primary funding from DOE to the programs. DOE funding of the programs per se was \$22 million; additional monies, however, were provided by the DOE Office of Basic Energy Science, by the Gas Research Institute, and from Institutional Research and Development funds provided by the Laboratory Director. Figure 1(b) breaks down the funding for Fossil Energy. Nonfossil Energy research includes work on the aluminum-air fuel cell, geothermal research, combustion chemistry, and abrasion studies relating to energy conversion processes and fuel transportation.

Throughout this report, the individual programs are first described in terms of their objectives and accomplishments, and then publications reporting on the year's progress are listed.

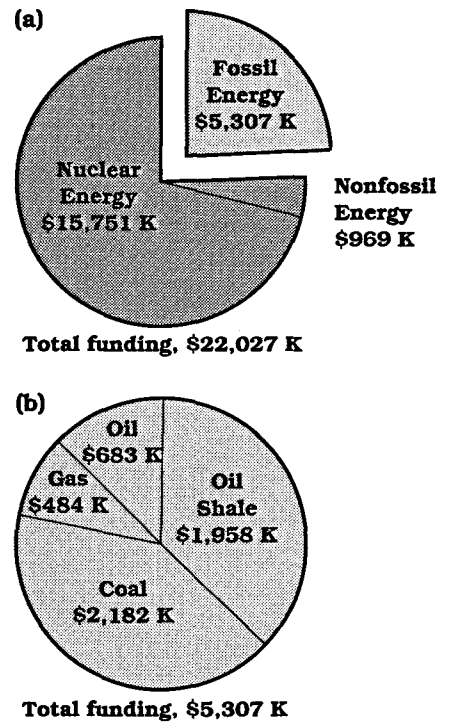


Figure 1. (a) DOE funding of LLNL's Energy Program for FY 1987. (b) Breakdown of DOE funding to Fossil Energy.



**Nuclear waste repository site,
Yucca Mountain, Nevada.**

Nuclear Energy

Nevada Nuclear Waste Storage

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Objectives


Background

The Lawrence Livermore National Laboratory (LLNL) is responsible for the design, development, and assessment of a container—which, together with the waste form, is called the “waste package”—to be used for the permanent disposal of high-level nuclear waste. The waste package is being developed specifically for the safe, permanent disposal of radioactive waste in a proposed tuff repository at Yucca Mountain, which is located on the southwestern boundary of the Nevada Test Site (NTS). In December 1987, Congress amended the Nuclear Waste Policy Act of 1982 so that if Yucca Mountain is found to be suitable, it will be the nation's first nuclear waste repository. The geologic horizon in which the nuclear waste would be stored is unsaturated rock, i.e., above the permanent groundwater level, so that there should be only minimal interaction between water and nuclear waste.

To develop the best design for the waste package, LLNL scientists are investigating four interrelated areas: the environment of the waste package, the design of the container, including structural materials, and testing and analysis of waste-package performance under expected repository conditions. Several container designs have been developed and analyzed covering a broad range of options associated with different repository designs, container materials, waste forms, etc. It is also the responsibility of LLNL to address the four areas of concern in sufficient depth and detail so that the repository can be duly licensed. That is, the modeling approach used to predict the long-term behavior of the container and radioactive waste must be validated to demonstrate that the safety criteria established by the U.S. Nuclear Regulatory Commission (NRC) for the licensing of nuclear waste repositories have, in fact, been met.

The Waste-Package Environment

In order to analyze the behavior of the waste package over long periods of time, a thorough knowledge of the environment under expected repository conditions is needed. Since characterization of the Yucca Mountain geologic environment is primarily the responsibility of the U.S. Geological Survey (USGS), LLNL geologists work closely with their USGS counterparts to develop the information required for waste-package design and development. The environmental parameters evaluated include: the geochemical properties of the Yucca Mountain tuff, composed of compacted volcanic ash, and of the vadose water present in the tuff (i.e., above the permanent groundwater level); the



variations in the thermal and thermomechanical properties of the tuff; and the response of the interstitial water that is not chemically bound to rock constituents to the thermal energy and the nuclear radiation emanating from the radioactive waste. The geochemical effort at LLNL is closely coordinated with work being done at Los Alamos National Laboratory, which has been given the lead role in characterizing the geochemical environment of the Yucca Mountain site.

The Waste Package

High-level waste packages contain three major components: the metallic containment barriers (the containers), the waste form, and other materials, such as packing material, emplacement hole liners, etc. The metallic containers are intended to provide substantially complete containment of the nuclear waste for 300 to 1,000 years after emplacement. During the waste isolation or postcontainment period that extends for thousands of years after the metallic containment barriers are breached, the waste form itself is expected to control the rate of release of radioactive nuclides into the immediate repository environment.

Candidate materials for metallic containers are austenitic stainless steel alloys and copper-base alloys. The corrosion properties of these materials have been intensively investigated under expected repository conditions (steam or vadose water at temperatures up to 150°C in the presence of tuff, with and without gamma radiation fields). The effects on corrosion rates of varying amounts of naturally occurring groundwater contaminants, as well as of radiolysis products, have been studied over a range of temperatures. In all cases a number of different types of corrosion of the containers were investigated, including uniform corrosion and corrosion focused at pits, crevices, and transgranular stress cracks. The data obtained from this experimental work will be used to estimate how long it will take before the Yucca Mountain groundwater penetrates the waste package metallic barrier and gains access to the radioactive contents of the waste package.

Also being investigated under expected repository conditions are the rates of release of radionuclides from two classes of waste forms: reprocessed waste contained in borosilicate glass, and spent fuel with zirconium-alloy or stainless steel cladding. The effects of such variables as groundwater composition and oxidation state of the fuel on release rate are being assessed over a range of temperatures. The extent to which spent-fuel cladding can be expected to delay the access of groundwater to the fuel is being studied, as is the rate of release of radioactivity from fuel with flawed or breached cladding. Evaluation of this work will be used to determine whether the rates of release of radionuclides from the waste package conform to the criteria established by the NRC for repository licensing.

Other materials may be present in the waste package; for example, it might be necessary to surround the container with a packing material to reduce the rate of release of radioactivity. To date, however, only preliminary experimental work has been carried out on such materials.

So far, a number of thermal, structural, and economic analyses of several alternative designs have been completed; other analyses are continuing. Preliminary designs of alternatives are being prepared in close collaboration with Sandia National Laboratories, Albuquerque, which has responsibility for the design of both the underground and aboveground Yucca Mountain repository structures.

Modeling

Modeling and code development are closely coupled with the experimental work in the near-field environment and with investigations of the long-term performance of the waste form. Near-field coupled flow and heat transport and water-rock-waste interactions are specific to the unsaturated tuffaceous rock environment of the Yucca Mountain site in the model under development. Such modeling activity is integrated with the overall task of assessing the performance of the Yucca Mountain repository, which is being carried out by several cooperating national laboratories. Final results will be of critical importance to the NRC repository licensing process.

Accomplishments

The scientific investigations that have focused on the development of a waste package suited to the underground environment at the Yucca Mountain site are integrated experimental and calculational efforts. Nonetheless, it is convenient to describe the accomplishments of FY 1987 in terms of laboratory, theoretical, and planning work.

Laboratory Experiments

Characterization of the high-level waste environment included completion of long-term tuff-water interaction tests at elevated temperatures, which were designed to establish the alteration expected in the vitric tuff below the repository horizon. Some of this work was done in cooperation with Los Alamos National Laboratory. Work continued on simulations of dehydration-rehydration processes in an effort to establish the hydrologic properties of a thermally perturbed environment.

In order to produce realistic numerical simulations of rock-water interaction, measurements of two-phase flow in tuff were planned, and studies were initiated on single-phase dissolution kinetics. Extraction techniques for obtaining samples of vadose water from tuff were examined and evaluated.

To obtain information on dissolution, spent fuel was leached at elevated temperatures in groundwater obtained from well J-13 at NTS, using bare-fuel specimens as well as Zircaloy-clad specimens both with and without induced cladding defects. Several Zircaloy-cladding degradation experiments were performed using defueled irradiated Zircaloy. Electrochemical corrosion experiments on Zircaloy were continued. In another series of experiments, Zircaloy specimens were subjected to stress in order to study stress corrosion cracking under simulated repository environmental conditions. In addition, studies of the distribu-

tion of ^{14}C in (or on) Zircaloy cladding were begun. Long-term oxidation tests of UO_2 at temperatures relevant to repository conditions were undertaken, and short-term thermogravimetric oxidation tests were continued.

Unsaturated leach tests of several borosilicate glasses doped with actinides, both with and without a gamma radiation field, continued, and we completed unsaturated tests of actinide-doped SRL 165-type glass. A major effort was made to identify secondary phases precipitated during the dissolution process using a variety of techniques, including Fourier transform infrared spectroscopy, scanning electron microscopy, x-ray diffraction, Raman spectroscopy, and secondary ion mass spectroscopy. We also studied the process of dissolution of natural basaltic glasses as a natural analogue for dissolution of nuclear waste glass in the repository environment.

In keeping with our focus on the container material as a metallic barrier to the release of radioactivity, we pursued possible methods of metallic degradation for a series of promising materials. We completed all of the experimental and analytical work on general, localized, and stress corrosion of copper and copper alloys in gamma-irradiated J-13 water and moist air. Similar studies were also undertaken on various stainless steels.

The near-field migration of radionuclides in tuffs was studied by measuring the depth of penetration of lithium, uranium, plutonium, neptunium, and americium in tuff disks using an ion microscope. Profiles were obtained both with and without the newly installed digital imaging system. Radionuclide migration data were also obtained in time-series experiments in which tuff disks were exposed to J-13 water doped with uranium and plutonium. The profiles were identical to those obtained in the borosilicate glass/tuff integrated tests.

In conjunction with planning environmental tests of the waste package that are slated for execution in the Yucca Mountain Exploratory Shaft, several assessments of techniques and equipment were conducted or started, e.g., an assessment of a method of high-frequency electromagnetic geotomography to characterize the distribution of water in the environmental tests. In conjunction with this technique, a test facility in a sand pit was constructed and tested at LLNL. Experiments carried out in the facility, as well as in the G-Tunnel facility at NTS, indicate that a zone of dehydration can be detected as it develops around a

heating element emplaced in the respective test media. The results of sensitivity tests of the method's capability to detect moisture as well as of the thermal stability of the U.S. Bureau of Mines gage have yet to be evaluated. Calibration and sensitivity tests of thermocouple psychrometers were conducted as well. The prototype tests of all proposed instruments and techniques will be conducted at the G-Tunnel facility at NTS.

Modeling Studies

Modeling has accompanied almost all phases of the experimental program associated with the design and development of a suitable waste package. The powerful EQ3/6 geochemical code is described in some detail below. It was used to simulate the dissolution of borosilicate glass into J-13 water. There were two types of simulations. The first simulated the reaction of glass with a fluid in which the glass dissolves into the fluid at a fixed rate. The composition of the solution was calculated as a function of the amount of glass dissolved together with the amounts and types of secondary precipitates that are predicted to form. The second type of modeling attempts to predict the actual rate of glass dissolution using chemical kinetics. These simulations are being optimized by matching predicted solution concentrations and secondary mineral precipitates with data from glass-leaching experiments.

Another group of simulations using the EQ3/6 geochemical codes involved the congruent dissolution of 1000-year-old spent fuel into J-13 water at 25 and 90°C. The evolution of fluid composition and the sequence of

solid precipitates were predicted as a function of the mass of dissolved spent fuel.

In conjunction with experimental studies on the degradation of metallic waste containers, work began on the formulation of a model treating localized corrosion. Degradation processes considered included stress corrosion cracking and hydrogen embrittlement. We are continuing to develop a model to predict the redox and corrosion potentials that will develop on a metal container surface during the containment period.

As noted above, computational efforts are being devoted to the development of a more consistent and detailed near-field flow and transport model. In addition, a systems-level model is being developed to integrate the more detailed codes into a code evaluating overall performance of the waste package. The model uses a systems analysis approach, and the code developed from the model uses structured analysis and software-quality-assurance techniques.

Specifications were published for the computer program called PANDORA-1, which assesses the performance of the Nevada Nuclear Waste Storage Investigations (NNWSI)-specific waste package. Program design, module coding, and module integration were completed. Program debugging continues, as does integration of specific materials associated with the current project design and with near-field environmental data. A draft report was prepared on the needs and methodologies for characterizing uncertainties in the assessment process and in assessment

results. Two needs are: (1) quantitative characterization of the uncertainties in assessment results, and (2) identification of the most effective ways to reduce the uncertainties if they prove to be unacceptably large.

Planning Activities

The waste-package sections of the NNWSI Site Characterization Plan (SCP) were revised and completed. LLNL staff also participated in reviews of other draft sections of the SCP before it was submitted to DOE Headquarters (HQ) on January 15, 1987. A report on NNWSI strategy for showing compliance of waste-package performance with regulations governing the postclosure period was revised and completed after meetings with DOE HQ and was submitted to DOE HQ in January 1987. This report remains in draft status. Comments on the SCP were resolved, and logic diagrams were added for readability and to provide an easier overview of the SCP, leading to the submittal of the revised Chapter 8, SCP, to DOE on May 22, 1987.

DOE HQ directions on interpretation of the regulatory terms "substantially complete containment" and "boundary of the engineered barrier system" were issued on May 28, 1987. Substantial changes were then made to the waste-package strategy and to the choice and value of parameters to be used to monitor performance goals in order to make them compatible with the DOE interpretation of regulatory terms. Plans were made to revise the report on waste-package strategy for consistency with the revisions to the SCP and with the

final interpretation of regulatory terms. The resolution of HQ comments on the SCP and the updating of tables and schedule information led to the completion of the concurrence draft of the SCP and its submission to DOE HQ on August 17, 1987.

Systems engineering integration activities at LLNL have been directed toward implementing the requirements of the DOE's Office of Geological Repositories' (OGR's) Systems Engineering Management Plan (SEMP). First, in conjunction with other project participants, a draft NNWSI Project SEMP was prepared and submitted to the DOE Waste Management Program Office for review. Second, as part of the Yucca Mountain Mined Geologic Disposal System Requirements (SR) document, LLNL staff identified the functional requirements, performance criteria, and constraints for the pre- and postclosure waste-package subsystems. The SR document integrates these requirements for the site, repository, and waste-package subsystems, and provides a basis for the respective subsystem design requirements. Finally, NNWSI systems engineering staff from LLNL conducted a briefing for OGR's annual review (July 14-16, 1987) of the NNWSI Project Baseline Management and Systems Engineering activities.

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EQ3/6 Geochemical Code Development

Principal Investigators:

K. J. Jackson and T. J. Wolery

Objectives

The Geochemical Modeling Group at LLNL is developing the EQ3/6 computer code to model the complex chemical reactions that can occur between an aqueous phase and minerals, rocks, or another fluid phase. The EQ3/6 code package, which had originally been written to model the geochemical evolution of the seawater/basalt system in a mid-ocean ridge geothermal environment, is now being developed to address the geochemical problems posed by the disposal of high-level nuclear waste in a geologic repository. This work is being conducted as part of investigations of (1) tuff (a volcanic ash) as a repository medium at the Nevada Test Site, and (2) salt at the Waste Isolation Pilot Plant in New Mexico. At LLNL we use the code for modeling a wide variety of geochemical processes, and it is actively used by researchers at other national laboratories, at laboratories abroad, at several universities, and in private industry.

The EQ3/6 package centers around two large computer codes, EQ3NR and EQ6, which are supported by a common library of computer routines and a thermodynamic data base. EQ3NR is a speciation-solubility code that is used to compute a model of the thermodynamic characteristics of dissolved species in an aqueous solution. EQ6 is a reaction-path code that is used to track the progress of chemical interactions as they occur between rocks and an aqueous solution.

The models in the current version of the EQ6 code correspond to two physical scenarios: (1) a closed system, one that is not allowed to either gain material from or lose material to its environment, and (2) a flow-through (open) system, which follows the progress of a single "packet" of water as it traverses a reacting medium and is allowed to either gain material from or lose material to the enclosing rock. The EQ3/6 package also includes a data base that contains the thermochemical data for over 1200 minerals and aqueous species.

Laboratory experiments at LLNL are a way to attack the problem of validating EQ3/6 submodels and render the package useful for predicting the short- and long-term performance of a waste repository. Models developed from well-characterized experiments can: (1) help identify the important reactions and processes taking place in the experimental system, (2) test the consistency of assumptions involving thermodynamic and kinetic models of reactions, (3) help us develop

the ability to extrapolate experimental results to systems of, for example, different rock/water ratios; diverse starting conditions involving composition of both solids and solutions; and different temperatures, pressures, and time durations, (4) help us design new experiments, and (5) resolve differences between the results of laboratory experiments, field experiments, and theoretical calculations.

Accomplishments

In FY 1987 the fundamental basis of solution thermodynamics was investigated, resulting in the clarification of key relationships and the derivation of new models for activity coefficients in aqueous electrolyte solutions. Other published models were analyzed for thermodynamic consistency as part of this activity. Using these results, a simple, thermodynamically consistent method for averaging the ion-size parameter in the Debye-Hückel model of activity coefficients was derived. This method allowed the development of extended models applicable to concentrated salt solutions in which a different size can be fitted or assigned to each ion. Also during this period, the hydration theory of Stokes and Robinson was rederived using rigorous methods. Mutually consistent equations describing activity coefficients and the activity of water were obtained, something that was not done in the original derivation. Both ion size averaging and the optional addition of virial coefficient terms were introduced. Two new sub-models for activity coefficients in electrolyte solutions were added to the EQ3/6 codes: the modified

Stokes and Robinson hydration theory model described above, and the 1981 model of Helgeson, Kirkham, and Flowers. The latter model was revised to allow incorporation of LLNL's method of ion size averaging.

The EQ3/6 modeling effort was improved by changes in the thermodynamic data bases that support calculations. These data bases were improved by the addition of new data, the updating of existing values in the files, and better documentation of the sources and quality of data contained in the files.

The computers supporting the group were upgraded by the purchase of several Sun work stations and a Ridge 3200, which greatly facilitate the process of code development and maintenance. Because the task of maintaining such large codes occupies a great deal of our time, the addition of these machines to our computer network was a significant improvement.

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Technical Exchange with Atomic Energy of Canada, Ltd.

Principal Investigators:

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A. M. Wijesinghe, and
R. K. Thorpe

Objectives

Under Department of Energy-Atomic Energy of Canada, Ltd. (AECL) Subsidiary Agreement No. 1, a formal exchange of technical information relating to nuclear waste management began in FY 1982. The intent of this project was to share LLNL experience acquired at the Climax Spent Fuel Test at the Nevada Test Site as well as LLNL technical expertise. Of particular interest has been the evaluation of geomechanical and hydrologic responses to mining operations, the design of appropriate instrumentation and measurement techniques for monitoring these responses, and the development of numerical simulators for proposed waste-repository experiments at the test underground research laboratory in Manitoba, Canada.

Accomplishments

Proposed experiments in Manitoba, Canada, include a series of activities exploring rock-mass response to excavation, the sealing of boreholes and shafts, and the performance of the proposed artificial buffer around the waste container. Our contributions in FY 1987 were directed at developing a semianalytical approach to predicting hydrologic flow in fractured rock perturbed by excavations. This work has involved developing models of coupled, in situ hydrologic and mechanical rock behavior utiliz-

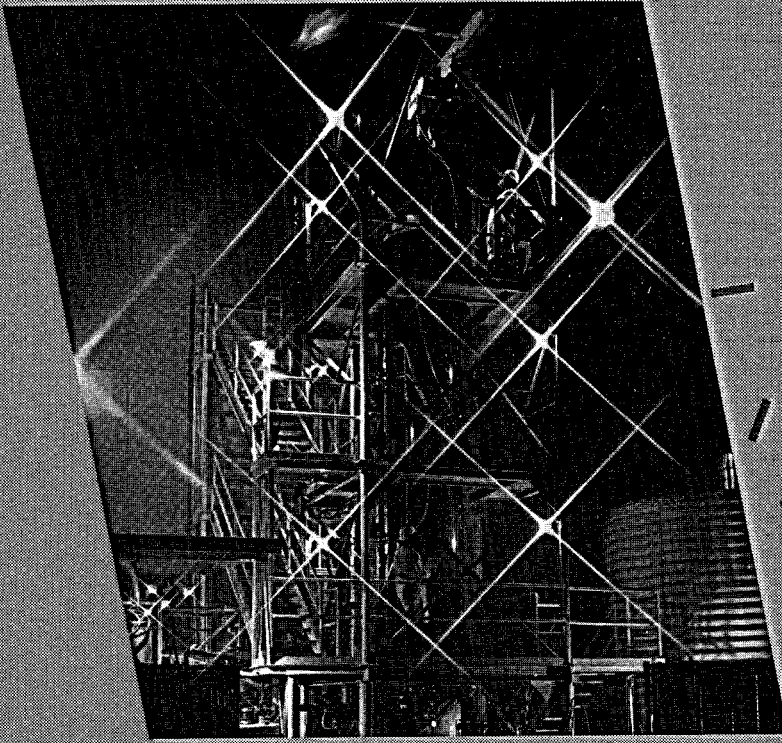
ing geological parameters measured at the site. To facilitate data acquisition, we developed specifications and began testing commercially available instruments designed to monitor geomechanical and hydrologic parameters. Ultimately, the calculated response of surrounding rock to mining will be compared with the measured response in order to improve the simulator.

During the year, we were active in the planning phase of Canadian experiments, participating in the Excavation Response, Buffer/Container, and Borehole

and Shaft Sealing Experiment Planning Committees. Our contributions dealt with the data requirements and the evaluation of modeling results in light of the objectives of the several planned experiments.

Publications

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Cascading-bed Oil Shale
Retort, Lawrence Livermore
National Laboratory.

Fossil Energy

Oil Shale

Principal Investigators:

A. E. Lewis, R. G. Mallon,
R. W. Taylor, R. J. Cena,
C. J. Morris, T. Coburn,
D. W. Camp, R. W. Crawford,
H. R. Gregg, and M. S. Oh

Objectives

Our goal is to provide a technical base that will contribute to the advance of oil-shale retorting technology. A better understanding of oil shale itself will lead to more efficient processing techniques that are both economically viable and environmentally acceptable. There is a current lack of industrial interest in oil shale utilization. Because of this lack of interest and the usually long time intervals between research, innovation, and implementation of a technology, our role in providing an in-depth understanding of the processes involved is important in ensuring that liquid fuels from the nation's large oil shale resources become available in the future.

LLNL has over 10 years of experience in oil-shale retorting research. Our approach is a combination of and an iteration between laboratory investigations of chemical reactions and their kinetics, mathematical modeling of reactions and retorting processes, and operation and testing in a 1-tonne/day pilot oil-shale retort of our design (Cascading-bed Oil Shale Retort). At this juncture we have reasonable confidence in our models, which are used to recognize areas within the retorting process in which fundamental knowledge of various types is lacking or imperfect. Our laboratory research is thus focused. In addition, we can use models to simulate retort operations at full-scale plants and to recognize problems not necessarily encountered in our 1-tonne/day test retort. This retort is used to test our understanding on a small scale, to identify phenomena whose importance may have been underestimated, and to facilitate decisions relating to process operation when more than one option is available. The profitable interaction of our chemical and modeling work with retort operations will provide insight for selecting the most promising second-generation retorting process for future development.

Accomplishments

We have continued to pursue an understanding of the interrelations between process fundamentals and operation. Our study of the retorting process in the Cascading-bed Oil Shale Retort

included research on the effect of imperfect mixing of solid streams entering the retort. A monitor for on-line determination of oil yield during retorting was designed and tested for general application and will be used in our system as well. We developed a concept of a

method for cooling spent shale from hot-solid retorting processes which leads to efficient heat transfer and minimizes H₂S production. To test the concept, appropriate equipment was designed, constructed, and

successfully tested. And understanding of the interaction of water droplets with hot solids is necessary to further this research. The next step is to construct a bench-scale cooler to test design concepts that may lead to a practical shale-cooling apparatus.

Coking and cracking reactions are important processes that lower oil yield, especially when a process is scaled to a larger size. As a consequence, we have continued to study the stability of shale oil vapors in the presence of hot oxidized shale and in the various gas atmospheres encountered in a retort. For the same reasons, we have also studied the effect of clay content on possible loss of oil due to cracking.

Our modeling work focused on adapting our RETORT model to the processing of Eastern oil shale. Our first task was to identify the critical information that was needed for the adaptation. Appropriate enthalpy relations for Eastern (and Western) oil shales were incorporated into the RETORT model. After studying the sulfur chemistry of Eastern shale under both pyrolyzer and combustor environments, we were able to outline a preliminary model of the sulfur chemistry in a solids-recycle combustor such as our pilot retort. Finally, we have begun to study the behavior of Eastern shales in our pilot retort.

The RETORT and lift-pipe process models were improved by the incorporation of a better model for carbonate decomposition. In response to a request from DOE's Morgantown Energy Technology Center, we adapted our latest models for use in the Center's ASPEN process-system simulation program.

Recognizing the potential importance of fluidized-bed technology in oil shale retorting, we completed the experimental investigation and modeling of chemical reactions involved in the rapid pyrolysis of char and in sulfide oxidation for a small fluidized-bed unit. This research included a study of the free-radical equilibrium in such a retort, which is an important determinant of the amount of oil produced. We extended a parameter study of a commercial-scale hot-solids recycle retort consisting of a fluidized-bed pyrolyzer and a lift-pipe combustor that had been begun earlier. The impetus for this work is to answer the important question as to which type of pyrolyzer is most satisfactory—a gravity-flow unit as used in the cascading-bed process or a staged fluidized-bed pyrolyzer as used in the Chevron process. The answer, which is not yet in hand, depends on obtaining much comparative information, in particular, data on cracking reactions and heat transfer.

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Underground Coal Gasification

Principal Investigators:
R. W. Hill, C. B. Thorsness,
J. A. Britten, and R. J. Cena

Objectives

The goal of LLNL's underground coal gasification (UCG) program is to advance UCG technology along many fronts toward its eventual commercial application. Our efforts include fundamental theoretical and experimental investigations aimed at understanding the complex thermochemical and physical processes associated with in situ combustion and gasification of a coal seam; design and engineering of equipment and processes crucial to initiation, maintenance, and analysis of UCG field tests; technology transfer and consultation with organizations, both domestic and foreign, in regard to design and operation of UCG field experiments; and maintenance and expansion of a global UCG data base. LLNL's UCG program, in existence since 1975, has evolved into a position of international prominence in the technical aspects of UCG. The technology has advanced to the point that UCG of subbituminous coals is believed to be competitive with other sources of energy and with gaseous chemical feedstocks, and a commercial development is presently under way. The future efforts of LLNL's program will focus on developing the technology for bituminous coals of the eastern U.S., which, because of their location, are an important energy resource but whose quite different physicochemical properties will impact UCG processing characteristics.

Accomplishments

By far our largest effort during FY 1987 was the Rocky Mountain I UCG field experiment, which is presently in operation. Our responsibilities included (1) design, engineering, and construction of processes for remotely igniting coal in vertical and horizontal boreholes, for cleaning a product-gas slipstream for analysis, and for automatically measuring rates of water produc-

tion, (2) technical consultation regarding construction and operation of the plant, and (3) development of an automated data-acquisition system. The latter task required several months of software development and testing because of the procurement of a new computer and operating system, the development of powerful data-retrieval and display software, and the large number of data-recording instruments associated with the test.

We were also involved as consultants in test planning and core analysis for a proposed UCG field test in Brazil. This project, technically very promising, is currently under review for advancement into a second, more detailed planning phase.

During the fall of 1983, a UCG field test was performed by the LLNL UCG program at the site of an active coal mine near Centralia, Washington. Normal

mining activities at the site in the spring and summer of 1986 permitted the careful excavation of the UCG cavity with small earthmoving equipment. This excavation, in which we participated, provided unique data on the details of the shape and rubble-fill of a mature UCG cavity, and the early part of FY 1987 was spent analyzing the data. These data provided profoundly important insights into the dynamics of UCG cavity growth and have largely guided subsequent modeling of cavity growth. It was thus possible to improve and refine the three-dimensional axisymmetric UCG cavity-growth model, CAVSM, developed in 1986, by adding a model which describes water influx by gravity drainage, incorporating faster and more stable solution algorithms in several submodels, and reformulating some of the basic ideas concerning oxidant flow distribution in the rubble-filled portion of the cavity. Model results compared very well with data on gas production and on cavity shape for this test, and it is now felt that the model is capable of describing UCG phenomena in semiquantitative terms. A description of a simple method for approximating temperatures and gas compositions at the exit of one-dimensional packed-bed coal gasifiers, which is used in the global model CAVSM, was also developed.

On another modeling front, an economic model for estimating size and costs associated with a UCG plant for a user-specified final product has been coupled to a simple UCG process model based on thermodynamic constraints with a few user-specified

process parameters. It will provide a code which can quickly and easily bracket UCG economic characteristics for a wide variety of conditions using a personal computer.

Two small-scale experimental efforts were undertaken. One involved measuring the reactivity of coals of UCG interest to carbon dioxide and steam for ranking purposes and for quantifying rate parameters in the absence of mass- and heat-transport effects. These parameters largely determine the temperature in the gasification region of a packed bed of char particles and thus the temperature of certain regions of the UCG cavity undergoing gasification. Another study provided much-needed data on the variation of thermomechanical properties, in particular ultimate tensile strength and expansion characteristics, of several coals of UCG interest as a function of heat-treatment temperature. Small-scale failure of coal at an unsupported face exposed to high thermal fluxes, as at the roof of a growing UCG cavity, is a very important and a little understood phenomenon. This type of failure involves the interaction of small-scale, locally high stresses caused by drying and thermal contraction (or expansion) and the large-scale lithostatic stress field in the area of the cavity.

The UCG program also supported a study by the University of Colorado involving determination of failure characteristics of overburden rock exposed to large thermal gradients. Further experiments are planned in the laboratory coupling both localized thermal stresses and applied external loads to blocks of coal to simulate small-scale failure.

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Flow of Granular Solids

Principal Investigators:

O. R. Walton, R. L. Braun, and
A. J. C. Ladd

Objectives

The goal of the Granular Solids Flow project is to develop a fundamental understanding of the flow behavior of granular solids. This research utilizes discrete-particle computer simulation to determine how stresses in flowing granular solids depend on such parameters as shear rate, density, particle size, and frictional and elastic properties of the individual grains. A lack of understanding of the basic rheologic properties of bulk granular solids and their interactions with boundaries is hindering design efforts for coal gasification, liquifaction processes, surface oil shale retorting, and the development of other energy resources. A recent Rand Corporation study of solids processing technology cited evidence that plants processing or producing solids consistently perform much more poorly than comparable plants dealing strictly with liquids and gases. The primary reason for this poor performance is the poor theoretical understanding of the behavior of solids. New technologies to produce synthetic fuels will require extensive processing of solids, e.g., for coal, oil shale, or tar sands; thus, improving our understanding of the fundamental rheologic behavior of granular solids is an important step in the development of those technologies.

Accomplishments

The two- and three-dimensional discrete-particle modeling work under this project is providing new insight into the micro-mechanisms occurring during deformation and flow of granular solids. The models agree with laboratory measurements when such data are available, and they agree with theories when comparable approximations are made in the model, such as assuming frictionless and nearly elastic particles. The models are capable of including more

complex interparticle interactions than are most existing theories. During FY 1987, these models were extended to examine the effects of size distributions and boundaries on the stress-tensor components during steady flows.

Calculational studies with these models have shown that stresses generally vary as the square of the shear rate and the square of the particle radii and depend strongly on inelasticity and the solid's packing (porosity) and less strongly, but still significantly, on the friction coefficient. Less sensitive are dependences on

particle stiffness, shear-to-normal stiffness ratio, and details of the transition to full sliding during frictional collisions. Mixtures of two different-sized particles are found to behave, for small size ratios, like a weighted average of a system of all small and all large particles. We have also started to develop new models that incorporate the effects of an interstitial fluid, thus taking into account the interparticle forces that are transmitted by the flow of the fluid.

The discrete-particle models developed and utilized in this project act as a bridge between experimental measurements and advancing theories by providing details on internal flow parameters not normally available from laboratory tests. They also provide a means of directly testing the sensitivity of calculated flow behavior to various approximations used in developing theories and thus provide a direct test of the utility of new approximate theories of granular-flow behavior. These discrete-particle computer models were also utilized in developing the design of the solids flow aspects of LLNL's pilot Cascading-bed Oil Shale Retort.

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Unconventional Gas

Objectives

The objective of LLNL's unconventional gas program is to improve the understanding of the mechanics of gas stimulation in lenticular and jointed tight gas reservoirs. Stimulation of tight, impermeable gas reservoirs requires either large hydraulic fractures that drain gas-bearing sandstones or propellant-driven multiple fractures such as those that maximize drainage areas around wells in shales. The analysis of these processes is complicated by the natural fractured state of the formations before stimulation and by the layered or lenticular nature of the Western tight gas sands. This project is a combined experimental and numerical modeling effort.

Accomplishments

We have developed a model that can describe the mechanics of fluid-driven arbitrary (mixed-mode) fracture propagation in discontinuous media. In expanding our quasi-static, finite-element, coupled fracture and flow model, called FEFFLAP (finite-element, fracture and flow analysis program), we have developed the capability of doing time-dependent tracking of the fluid-driven fractures at the borehole inlet under a constant pressure for gas-driven fractures or under a constant flow rate for hydraulically induced fractures. Time-dependent analyses are important for hydraulically induced fractures because the histories of flow rate and pressure at the borehole are typically measured.

Our model is also designed to predict crack propagation in

arbitrary directions; to account for joints and interfaces, including their nonlinearities; and to follow the evolution of fluid flow in cracks and joints.

FEFFLAP now calculates time-dependent fluid flow by coupling with the FAST module for gas dynamics in fractures. Solutions to problems are obtained from coupled elastic-fracture equations and fluid-flow equations; each provides boundary conditions to the other. The flow model's method of solution is accurate to within a few percent for a broad range of test problems, including laminar and turbulent flows, incompressible liquids and ideal gases, permeable and impermeable media, prescribed inlet pressure, and prescribed flow rates. The model's results compare favorably with field results.

Principal Investigators:

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A. M. Wijesinghe

Because a hydraulic fracture responds to the in situ properties of a large volume of rock, at least as large as itself, fracturing can be an attractive means of determining the in situ deformation moduli of a rock mass at different length scales. With this motivation, we developed a procedure based on a hybrid model to compute the crack-opening modulus from suitable bottomhole-pressure data for fracturing conditions that lead to fracture extension at constant height.

Laboratory experiments are being conducted in conjunction with the numerical modeling in order to provide diagnostic information on the interaction of hydraulic fractures with remote sand lenses. We use stressed blocks to simulate the propagation of a pressurized crack into

and through a gas-bearing sand lens. With constant fluid injection rates, features in the pressure-time history are related to physical events at the crack front, such as crack crossing, crack arrest, or crack offset.

The blocks are constructed of gypsum cement mixed with water (40 percent by weight). This material was used successfully to simulate a homogeneous rock medium in previous experimental programs of this type. The sand lenses are simulated by slabs of Berea sandstone embedded in the blocks. For the initial tests, the faces of the slabs were roughened to increase the shear strength of the interface so as to promote penetration of the hydraulic fracture. Later tests will investigate the effect of weaker interface bonding on the pressure-time signature. External stresses will be applied to all six sides of a block using a polyaxial test frame and unique hydraulic flat jacks. We have successfully tested the design to nearly 70 MPa and intend to patent it.

Another important part of the experimental program is the

development of methods for tracking a fracture. Both the monitoring of acoustic emissions and ultrasonic detection were investigated. These techniques had limited success in previous fracturing tests because sensors must be mounted externally, relatively far from the tip of the crack. Our experiments, however, have two advantages: (1) the direction of the crack can be fairly accurately predicted, and (2) sensors can be emplaced within the block. Thus, by positioning sensors near the expected crack plane, the location of the crack relative to a given sensor is less uncertain. Also, dispersion of the signal from material interfaces and boundaries has less influence on the interpretation. We investigated the feasibility of using a large number of inexpensive piezoelectric polymer (PVDF) sensors. Initial tests on short-rod specimens used in fracture-toughness measurements have demonstrated that they can detect acoustic emissions nearly as well as conventional ceramic transducers. In similar tests, we have demonstrated a more innovative detection scheme.

It consists of a planar array of PVDF receivers to monitor a single, externally mounted ultrasonic transmitter. A hydraulic fracture front can be located in both time and space as it crosses the sonic-ray path.

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Petroleum Geochemistry

Principal Investigators:

A. K. Burnham, R. L. Braun, and
J. J. Sweeney

Objectives

The use of chemical kinetic modeling of oil maturation in conjunction with other geological, geochemical, and geophysical techniques has the potential of greatly increasing the effectiveness of oil exploration, thereby reducing its costs. Our object is to develop a model of the conversion of various types of kerogen to oil and gas that is applicable to a wide range of heating rates, temperatures, and pressures. At the same time, it is desirable to develop more efficient ways of determining kinetic parameters from routine laboratory rapid-pyrolysis measurements as input to the model. The ultimate goal is to create detailed models of oil generation and compositional evolution in various parts of the world.

Accomplishments

Two years ago we demonstrated in the Uinta Basin, Utah, that detailed chemical models derived from laboratory experiments can be combined with thermal histories from geological models to predict the occurrence and composition of petroleum from lacustrine shales. However, most petroleum is generated from marine shales, and the higher oxygen and sulfur content in the organic matter (kerogen) of these shales causes the chemical kinetics to be more complex. Moreover, it is presently uncertain how different the chemical kinetics will be for different marine shales.

One implication of the chemical complexity is that global activation energies determined by simple laboratory experiments

cannot be used reliably to extrapolate the oil generation rate to geological thermal histories unless a formalism known as activation-energy distributions is used. We developed an easy-to-use computer program for determining these distributions from typical laboratory experiments, and it is now being distributed commercially. Two major oil companies are using it and more are presently acquiring it.

We used this program to analyze rapid-pyrolysis data from a Rock Eval II instrument, commonly used in the petroleum industry. We found substantial differences in the kinetic parameters from a variety of petroleum source rocks, which implies that there may be as much as a 50°C difference in the generation temperature from different source rocks undergoing the same

geological thermal history. Moreover, we found that these kinetic parameters disagreed with those from slower hydrous-pyrolysis experiments, which more closely simulate the natural generation process.

Through other types of laboratory experiments and modeling, we made major progress in understanding differences among oil-generation rates from various kinds of laboratory experiments. This understanding is important because we cannot hope to reliably extrapolate petroleum-generation rates to the vastly longer geological time scale if we do not understand quantitatively the differences between laboratory experiments of different time scales. Our modeling demonstrated that mass-transport resistance is more

important at the lower temperatures typical of hydrous pyrolysis and causes problems when one tries to deduce activation energies. However, we are still concerned that differences in natural generation temperatures may be smaller than those predicted using kinetic parameters from rapid micropyrolysis experiments (e.g., Rock Eval II) because of problems associated with temperature measurement and catalytic effects from minerals that are different from those in the natural environment. Therefore, determining how to best predict natural rates of petroleum generation will require further experimentation and modeling, including more detailed comparisons with geological data.

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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 volumeter 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 H₂, CO₂, CO, SO₂, NH₃, H₂S, and H₂O, 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). H₂, H₂S, H₂O, and NH₃ 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 SO₂ 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 CH_4 , O_2 , and Ar or 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 cm^3/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 , 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.

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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.

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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.

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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

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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 injection

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-km² 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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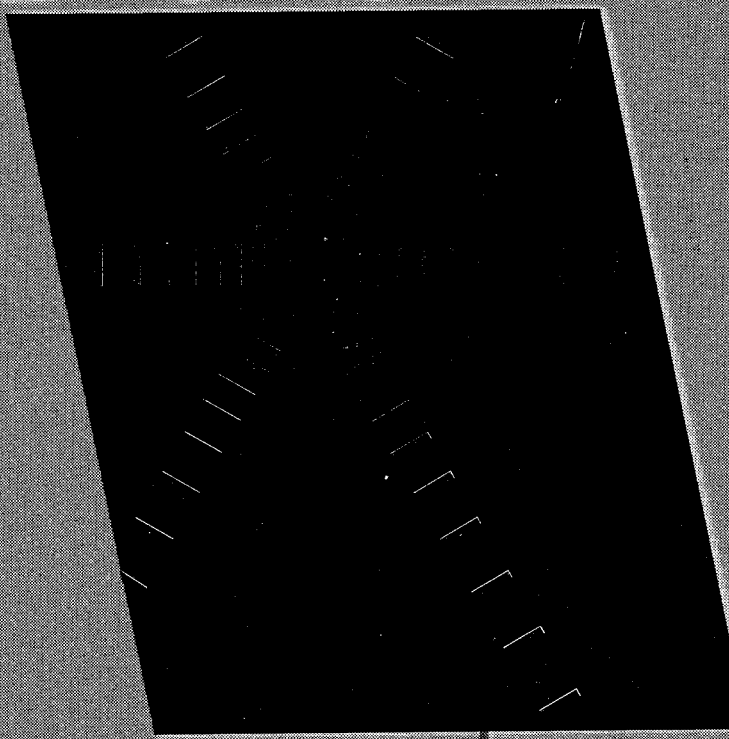
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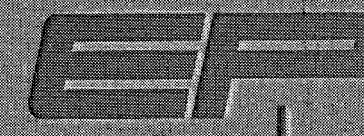
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UCRL 53859-87

Energy Program Annual Report



Lawrence Livermore
National Laboratory

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