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Energy Program Annual Report

MASTER

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Contents

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.

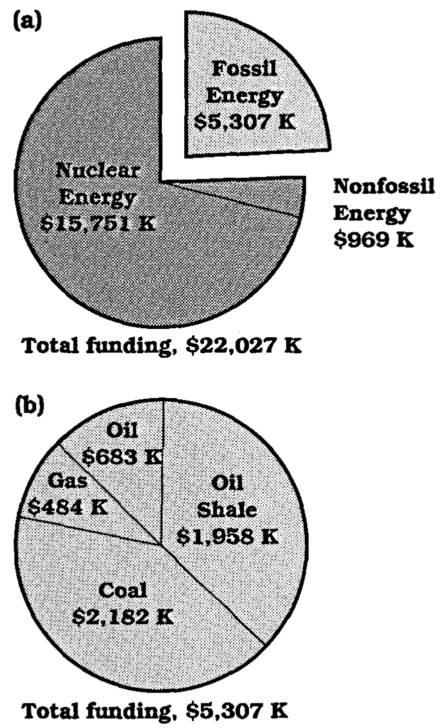
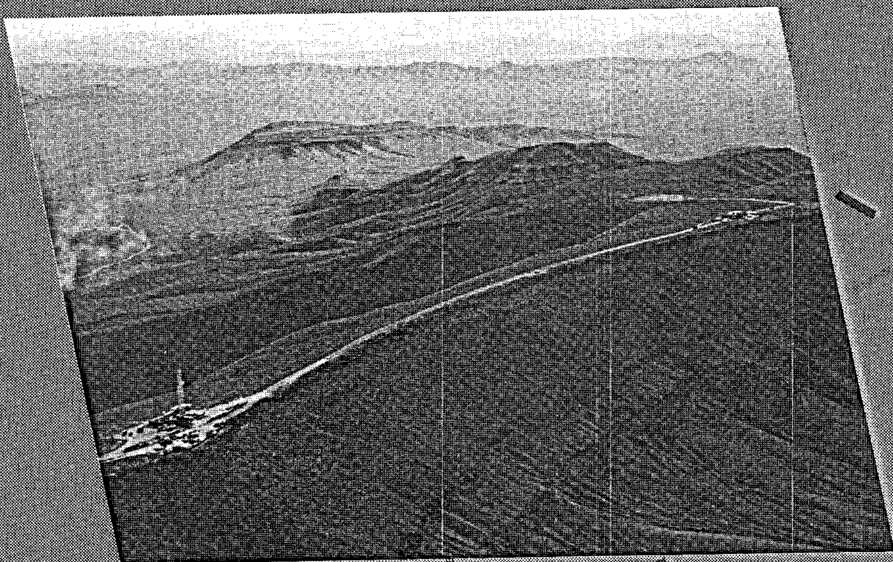


Figure 1. (a) DOE funding of LLNL's Energy Program for FY 1987. (b) Breakdown of DOE funding to Fossil Energy.



Nuclear waste repository site,
Yucca Mountain, Nevada.

Nuclear Energy

Nevada Nuclear Waste Storage

Program Leaders:
L. D. Ramspott and L. B. Ballou

Principal Investigators:
Waste Package Technical Leader: W. E. Glassley
Container Design Technical Leader: J. N. Kass
Release Rate Technical Leader: H. F. Shaw
Geochemical Modeling Technical Leader: R. D. Aines
Performance Assessment Technical Leader: W. J. O'Connell

Contributors:
C. J. Bruton, D. O. Emerson, K. J. Jackson, D. R. McCright, T. A. Nelson, D. U. Olness, V. M. Oversby, M. A. Revelli, R. J. Silva, A. Tompson, and D. G. Wilder

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 distribution 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 transport 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 submodels 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:
L. D. Ramspott, J. L. Yow, Jr., 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 utilizing 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.

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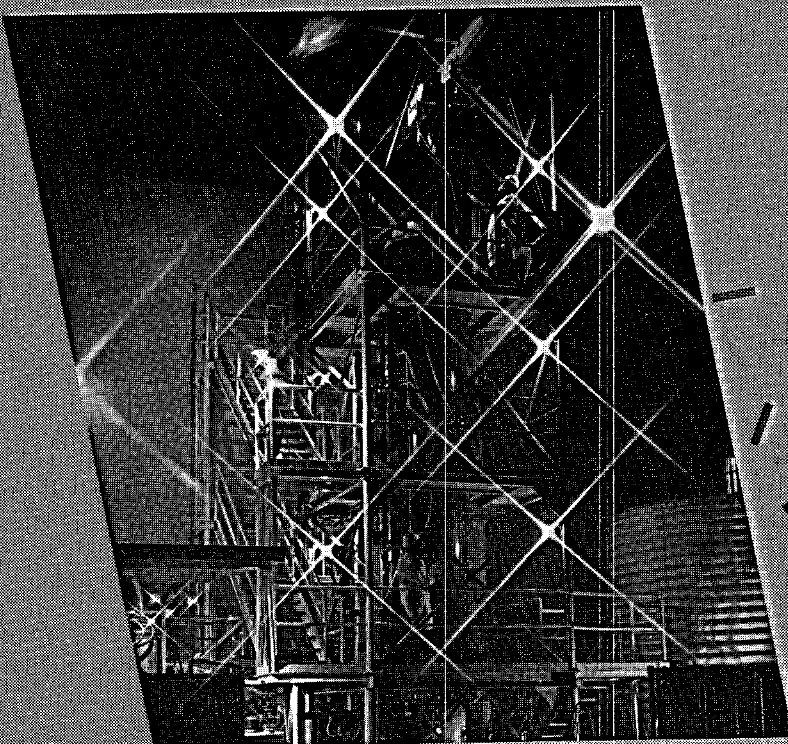

Cascading-bed Oil Shale Retort, Lawrence Livermore National Laboratory.

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 H_2S 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 adaption. 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 commerical-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:
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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 production, (2) technical consultation regarding construction and operation of the plant, and (3) development of an automated data-acquisition system. The latter task required several man-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:
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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 micromechanisms 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

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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.

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:
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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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