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OIL SHALE PROGRAM TECHNOLOGY STATUS REPORT

Bob Mc

MORGANTOWN
ENERGY
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CENTER

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Oil Shale Program

Technology Status Report

October 1984

U.S. DEPARTMENT OF ENERGY
OFFICE OF FOSSIL ENERGY
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MORGANTOWN ENERGY TECHNOLOGY CENTER
TECHNOLOGY STATUS REPORT

Oil Shale Program

by

Extraction Projects Management Division
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Office of Fossil Energy
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EXECUTIVE SUMMARY

Oil shale research activities at the Anvil Points Facility (APF), located near Rifle, Colorado, began in the mid-1940's, and Government-sponsored research has been intermittent there since that time. The Bureau of Mines' gas combustion retorting technology was developed at the facility. In the mid-1960's the Bureau of Mines (which later became the Energy Research and Development Administration [ERDA] and the Department of Energy [DOE] built two small (10- and 150-ton) batch-type retorts near Laramie, Wyoming. These facilities were used to research in situ processing variables of oil shale. Variables such as active void volume, shale assay and size, and processing parameters have been studied. In the late 1970's, the U.S. Government sponsored four large in situ demonstration projects in Western Oil Shale: Occidental, Geokinetics, Inc. (GKI), Equity, and Talley-Frac.

At the present, approximately 24 major companies are at some level of effort in developing an oil shale industry. Major private companies, as well as Government-sponsored projects, are developing western and eastern shales. Some 22 major efforts are involved with western shales, and 7 are involved with eastern shales.

In FY 84, the Oil Shale Program was restructured to understand the oil shale conversion phenomena so that advanced concepts for the production of liquids from shale could be developed. The restructuring is a refocusing from process development to a more fundamental approach to research. The principal participants in the new program are: Laramie Project Office (LPO), Morgantown Energy Technology Center (METC), Los Alamos National Laboratory (LANL), Lawrence Berkeley Laboratory (LBL), Lawrence Livermore National Laboratory (LLNL), Pacific Northwest Laboratory (PNL), Sandia National Laboratory (SNL), Western Research Institute (WRI), and selected universities and private industry.

PROGRAM ACCOMPLISHMENTS

Control and responsibility for the APF was transferred to Naval Petroleum and Oil Shale Reserves (NPOSR) at the end of April. DOE continued as an informal advisor on the APF to NPOSR throughout the remainder of FY 84.

GKI conducted the simultaneous burn of two commercial-sized retorts for most of FY 84. More than 50,000 barrels of crude shale oil was produced and commercially marketed during that time. This successful demonstration of commercial operation of GKI's LOFRECO in situ oil shale retorting process was the final milestone of a long-term cooperative agreement with the DOE, and signaled the termination of the agreement.

Oil shale research at LBL has centered on process waters treatment. These efforts resulted in the development of techniques to determine nitrogenous compounds in wastewaters. Specifically, the direct quantifying of organic nitrogen, and the quantitation, identification, and estimation of complex mixtures of previously intractable nitrogen compounds found in oil shale process waters was accomplished.

The Los Alamos National Laboratory is conducting rock fragmentation research in oil shale. The research will be used to develop the blasting and fluid flow technologies required to prepare a rubble bed for a modified in situ retort. Work for FY 84 involved excavation and postshot analysis of three FY 83 experiments. Most important of these excavations and postshot analyses was the archeological mineback of the confined-volume experiment.

SNL analyzed the results of two blast tests in rich shale. Compared with similar blasts in lean shale conducted by LANL, it is apparent that lean shale is more brittle than rich shale, and fragments and rubble occur easier in leaner shale. In single hole blasts, stemming effects appear to be negligible. Results of these blast tests have been used to upgrade various numerical models that are used to describe rubble properties.

During the first quarter of FY 84, LLNL continued their investigations on the emissions of NO and SO_2 from the combustion of retorted oil shale.

The DOE Oil Shale Program was restructured in FY 84. METC activities were reoriented to investigate high heating rate retorting at a more generic level. Consequently, FY 84 marks the end of METC's emphasis on eastern and low-grade oil shales that used fluidized-bed hardware, such as the 2-inch diameter electrically heated fluidized-bed retort and the 9-inch diameter twin fluidized-bed retort/combustor. METC accomplishments are as follows:

- Solid state ^{13}C nuclear magnetic resonance techniques using crosspolarization and magic-angle spinning were applied to raw shales.
- Time-resolved, gated-decoupling pulse sequencing techniques were developed for liquid samples in the NR-80 IBM ^{14}C nuclear magnetic resonance spectrometer.
- Oils from Kentucky and Colorado oil shales retorted in N_2 were separated into class types (saturate, olefinic, aromatic, and polar) using column chromatography.
- A kinetic rate expression model that is based on a simplified reaction mechanism was developed. It is used to account for the pyrolysis kinetics of eastern oil shales.
- Fourier transform infrared technique (FTIR) was successfully interfaced to Pyroprobe and thermogravimetric analysis (TGA). It is used to obtain a faster data acquisition rate in the study of gases that are evolved during oil shale pyrolysis.

FUTURE YEAR RESEARCH PLAN

In the coming year, the Oil Shale Program will complete the transition to the new structure, which began in FY 84. The program's focus is to understand the oil shale conversion phenomena. Advanced concepts to produce liquids from shale can then be developed. The highest priority in both the technology base and environmental mitigation elements is to generate data that is needed to understand the conversion phenomena. The technology base elements will generate the data that will be used to develop the predictive capabilities for optimal environmental control.

The restructured program will be accomplished in two 5-year phases. The first phase is focused on data acquisition. The second phase is designed to use the data, through systems analysis and environmental control technology development, to design efficient, cost-effective, and environmentally acceptable conversion systems.

1.0 INTRODUCTION

Liquid fuel has been extracted from oil shale in various parts of the world since the early 19th century. A number of companies were processing oil shale in the United States in the mid-1800's, but the discovery of petroleum in 1859 virtually ended the oil shale industry in this country. During the 1920's, the high price of petroleum revived the interest in oil shale. Several pilot plants were constructed, including two by the U.S. Bureau of Mines. Shortly thereafter, large discoveries of petroleum caused the price to decline, and oil shale activity was again halted.

During World War II, the huge demand for liquid fuels prompted the Government to pass the Synthetic Liquid Fuels Act of April 5, 1944. After passage of that act, the Government increased its efforts to develop a feasible oil shale production process. After several years of operation, however, the Government terminated its demonstration-scale activities and limited its efforts to smaller scale work. When it became apparent in the 1970's that the ever-increasing demands for energy would soon require the development of all possible sources to stave off an energy crisis, interest in oil shale again increased and continues to do so.

Oil shale research activities at APF began in the mid-1940's, and Governmentsponsored research has been intermittent there since that time. The Bureau of Mines' gas combustion retorting technology was developed at that facility and was refined by subsequent private researchers. In the mid-1960's the Bureau of Mines (later ERDA and DOE) built two small (10- and 150-ton), batch-type retorts near Laramie, Wyoming, to research in situ processing variables of oil shale. Variables such as active void volume, shale assay and size, and processing parameters have been studied. In the late 1970's the U.S. Government sponsored four large in situ demonstration projects in Western Oil Shale: Occidental, GKI, Equity, and Talley-Frac.

At the present, approximately 24 major companies are at some level of effort in developing an oil shale industry. Major private companies, as well as Government-sponsored projects, are developing both western and eastern shales. Some 22 major efforts are involved with western shales and 7 with eastern shales.

2.0 PROGRAM DESCRIPTION

2.1 PROGRAM BACKGROUND

Several major *events* since FY 80 have led to the need for a major refocusing of the DOE Oil Shale Program. The events were:

- Formation of the Synthetic Fuels Corporation (SFC).
- Emphasis change of the DOE research effort from commercialization to long-range, high-risk research.
- Major reduction in world crude oil prices.
- Completion of several major DOE research and development efforts in FY 81, 82, and 83.

The formation of the SFC removed the need for DOE's direct support of commercialization projects and associated field demonstration efforts. The change in emphasis of DOE's efforts, reflecting the SFC role as well as the prospect of the development of several major commercialization projects, was initiated in FY 81 and led to the beginning of a major reassessment of the Oil Shale Program. This reassessment hardly began before the world crude prices fell and several major commercial oil shale projects were dropped (to date, only the Union Project has continued with first DOE then SFC support). This event clouded the issue because it exposed the true weakness of the competitiveness of oil shale-derived crude in the world market (i.e., even at $30/bbl it apparently cannot compete).

In addition to the events in the commercial marketplace, several major DOE R&D efforts begun in the mid-1970's were completed or brought to a decision-point stage in FY 82 and FY 83. These efforts have produced a wealth of technical data, exposed the weaknesses of many previous assumptions, and indicated new directions that must be taken for certain types of potential recovery methods. These research efforts were:

- The vertical modified in situ (VMIS) research efforts at LPO and LLNL.
- The Occidental cooperative agreement for field trials for the VMIS concept.
- The GKI cooperative agreement for field trials of the Overburden Lift/Horizontal Retorting Concept.

- The research associated with true in situ concepts, including the evaluation of the Rock Springs experiments.
- Investigation of major environmental consequences of abandoned in situretorts.
- Completion of the cooperative agreements with the Paraho and Superior Companies to design commercial-sized surface retorts.
- Completion of the evaluation of the APF Paraho pilot plant and semi-works surface retorting data, and the use of these data by LLNL to develop a retorting model for the direct-heated surface retorts.

2.2 FY 84 PROGRAM

In FY 84, the Oil Shale Program was restructured. Its goal was to understand the oil shale conversion phenomena so that advanced concepts could be developed to produce liquids from shale. In the Oil Shale Program, research that generates pedigree data essential to understanding the conversion phenomena is given the highest priority. The pedigree data for conversion phenomena will constitute the input to the private sector's decision-making processes leading to implementation of commercial processes. This research includes appropriate technology and environmental efforts to establish the data bases and predictive capability required to identify and mitigate potential problems.

The restructuring of the Oil Shale Program was a refocusing from process development to a more fundamental approach to research. The principal participants in the new program are the LPO, METC, LANL, LBL, LLNL, PNL, SNL, WRI, and selected universities and private industry.

3.0 PROGRAM ACCOMPLISHMENTS

3.1 ANVIL POINTS FACILITY

Objective

The goal of the program was to provide management support for oil shale research at the APF.

Discussion

DOE developed detailed plans for the decommissioning of the APF. On April 13, 1984, the nonpermanent shutdown of the APF was completed.

Control and responsibility for the APF was transferred to the NPOSR at the end of April. DOE continued to perform as an informal advisor on the APF to NPOSR throughout the remainder of FY 84.

3.2 GEOKINETICS, INC.

Objective

The program was focused on researching the GKI LOFRECO in situ retorting concept for recovering shale oil using a fire front moving in a horizontal direction.

Background

The GKI In Situ Oil Shale Project is a cooperative venture between GKI and the U.S. DOE. The project is being conducted at a field site, Kamp Kerogen, located 70 miles south of Vernal, Utah, on Section 2, Range 22 East, Township 14 South, Uintah County.

The process is a true in situ method for extracting oil from oil shale. The oil shale is fractured by explosives placed in blastholes that have been drilled from the surface. After a specific area has been fractured to create an in situ retort, air injection (air-in) wells are drilled at one end and offgas recovery (air-out) wells are drilled at the other. The oil shale is ignited at the air injection wells and air is continually injected to establish and maintain a burning front. The front is moved in a horizontal direction through the fractured rock. This heats the shale and drives out the shale oil, which drains to the bottom of the retort where it is recovered through oil production wells. As retorting progresses from the air-in to the air-out wells, the residual coke serves as the primary fuel source to sustain the moving burn front. The combustion gases from the offgas wells are treated and flared.

Discussion

During the third week of June, daily production from Retort 27 dropped to an average of 25.4 barrels, and continued to gradually decrease through the rest of the month. On June 29, the burn was terminated for Retort 27.

By the end of the year, Retort 27 was completely shut in and production operation had ceased. It had produced 32,563 barrels of crude shale oil. See Figure 1 for a production history of Retort 27.

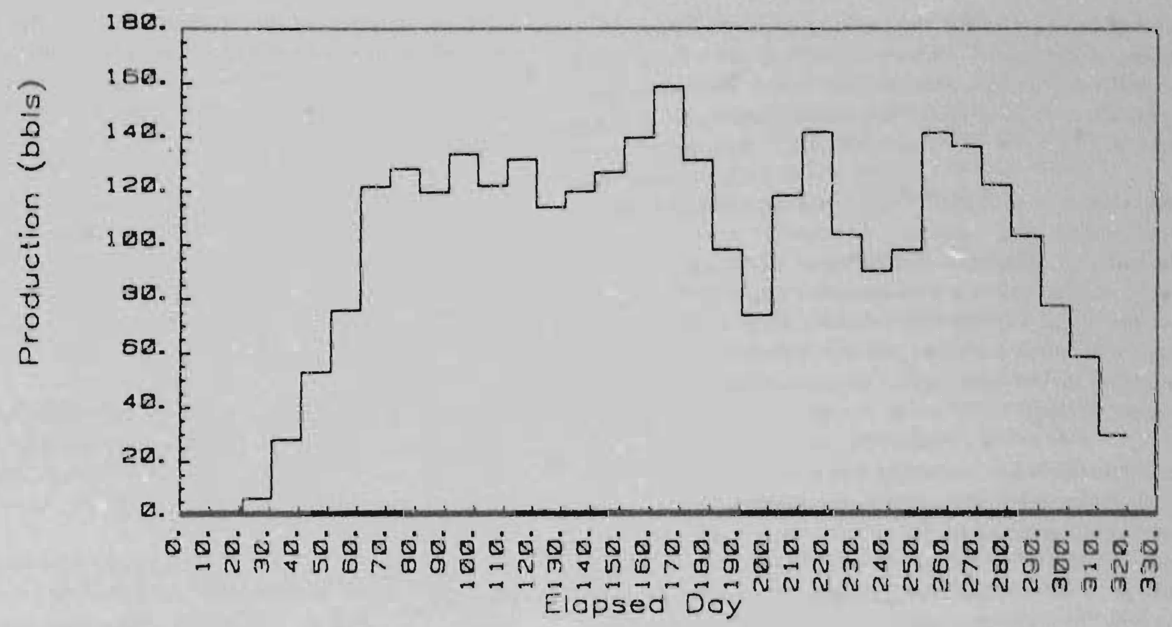

FIGURE 1. OIL PRODUCTION OF GKI RETORT NO. 27

Retort 28 was ignited on October 18, 1983, using the diesel ignition technique. Several advantages were realized, such as faster lighting times and wider ignition bands. The first oil-water emulsion was seen at Production Well 5 on October 31, 1983. Retort 28 continued to burn and produce simultaneously with Retort 27 through June 1984. The burn was terminated for Retort 28 on August 24, 1984. It had produced more than 28,750 barrels of crude shale oil by that time. The shale oil production history of Retort 28 is shown in Figure 2.

On January 23, 1984, preparations were made to begin the start-up of the offgas processing facility. The ammonia plant was started first. Ammonia is removed from the retort offgas in a simple absorption-stripping unit as it passes upward and counter-current to downward flowing water. The ammonia-free gas proceeds out the top of the absorber to either the afterburner or the ARI Technologies, Inc., Lo-Cat sulfur removal plant.

Start-up of the Lo-Cat Technologies, Inc., plant began January 29, 1984, and continued into February. Because of the low concentration of H_2S in the offgas stream, it was estimated that as many as 2 or 3 weeks would be required before sizeable quantities of elemental sulfur would be removed from the system. During this period, the sulfur melter circuit was remodeled. By the third week of February, the melter circuit had been tested and commissioned.

An engineering study of the ARI hydrogen sulfide plant and the ammonia plant began during start-up in early February and continued through March. The main objective of this continuing study was to maximize the removal efficiency of both units. The procedure included performing material and energy balances around the major pieces of equipment to determine the H_2S and NH_3 removal rates.

On March 29, 1984, the pressure drop on the gas side across the absorber tower in the ARI plant became so high that the gas ceased to flow. An inspection of the two packing beds in the absorber revealed that the lower bed was plugged with elemental sulfur.

The configuration of the plug in the bottom of the lower bed indicated the plugging occurred when the H_2S-rich gas entered the tower just below the lower packing bed and proceeded upward. The first significant contact between the H_2S in the offgas and the ARI solutions was in the bottom of the lower packing bed. The sulfide ions from the H_2S were instantly oxidized to elemental sulfur and began to fall. However, instead of falling through the packing and into the bottom of the tower, the sulfur was trapped by the pall rings and packing support trays, and eventually formed a plug. Repairs and cleanup were underway by the end of March.

Following tests in early May, a venturi scrubber was installed in the gas line between the ammonia and H_2S absorbers. The purpose of the scrubber (also called a precontactor) was to premix the offgas and Lo-Cat solution. This would remove as much sulfur as possible before the gas contacted the solution again in the absorber column packing.

Other methods for increasing gas flow through the plant included determining the maximum safe operating limits of the offgas blowers, and replacing valves in the gas system to decrease leakage to the bypass lines. By the end of June, gas flow through the plant had increased by 50 percent.

The ARI Lo-Cat process and solution were found to be very effective in removing H_2S from the retort offgas stream. Removal efficiencies of greater than 90 per cent were reported for H_2S. Removal efficiencies on the other sulfur species were not determined due to their very low concentrations in the LOFRECO process offgas. Low concentrations of these minor sulfur species should be typical of in situ direct combustion process offgases.

The Experimental and Range Division of the U.S. Forest Service began their fall reclamation tests on Retorts 24, 25, and 26 during October 1983. These tests included the planting of autumn vegetation to determine the optimum reclamation procedures on future retorts.

Shipments to the Crysen Refinery at Woodscross, Utah, were made throughout most of the year. The shale oil was blended with the refinery's No. 6 fuel oil cut without upgrading.

During March, GKI authorized North American Weather Consultants (NAWC) of Salt Lake City, Utah, to conduct an assessment of fugitive gaseous emissions that occur during the simultaneous operation of two in situ retorts.

The basic objective of this study was to use sulfur hexafluoride (SF_6), an inert gas, to "tag" the fugitive gaseous emissions in order to evaluate

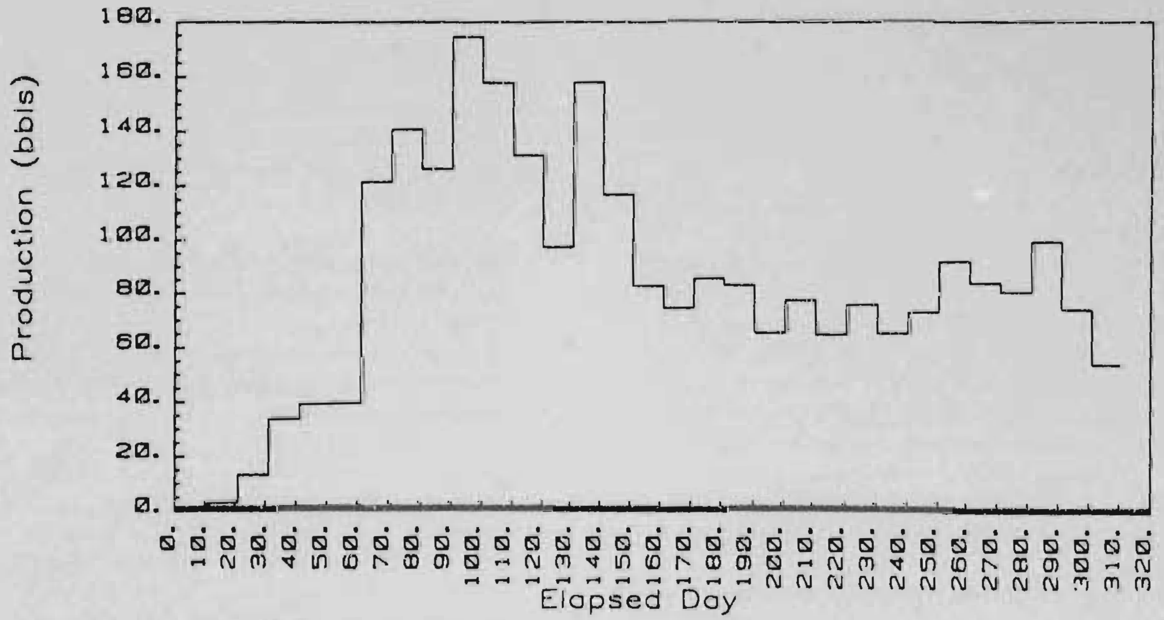

FIGURE 2. OIL PRODUCTION OF GKI RETORT NO. 28

fugitive hydrocarbon (HC) and carbon monoxide (CO) emissions. Known quantities of SF_6 were released from a level near the retort surface (fugitive emissions source) and ambient air samplers were located at selected sites, both upwind and downwind of the tracer release point. The upwind samplers provided data on natural background concentrations, and the eight downwind samplers measured the combined effects of the background and source-related impacts.

A groundwater tracer study was initiated in March. A contract was awarded to James L. Grant and Associates in Denver, Colorado, for the final study design and data analysis.

The purpose of the tracer study was to provide more definable data for permit compliance on the horizontal movement of groundwater, away from a rubblized retort. The study should better define groundwater behavior in the jointfracture media existing at the LOFRECO research site.

The compliance test for the Utah State Bureau of Air Quality approval order was begun on May 10, 1984. The preliminary results indicated that GKI was in compliance with the emissions limitations and removal efficiencies specified by the state.

During the second week of June, the York Research Consultants finished gathering data for the Utah Bureau of Air Quality compliance test.

3.3 LOS ALAMOS NATIONAL LABORATORY

Objectives

The program was initiated to (1) determine rock fragmentation characteristics at the AFP mine and perform blasting agent characterization, (2) provide mathematical simulation of retorting parameters to better understand the retorting processes and associated environmental concerns, and (3) characterize oil shale process effluents and possible environmental consequences of various oil shale processes.

Background

LANL is conducting rock fragmentation research in oil shale. This will help to develop the blasting and fluid flow technologies required to prepare a rubble bed for a modified in situ retort. This report details progress in the DOE/SNL/LANL Rock Fragmentation Program.

Work for FY 84 involved excavation and postshot analysis of three FY 83 experiments. See Table 1 and Figure 3 for descriptions and locations of these experiments. The most important of these was the archeological mineback of the confined-volume experiment, CV-1 (See Figure 4).

Rock fragmentation research at LANL is designed to provide the predictive capability required for developing a blasting scheme for a modified in situ (MIS) retort, and for evaluating the resulting rubble pile and its performance during retorting. This research is a combined program of laboratory and field experiments, and numerical simulations of fragmentation, tracer flow, and retorting.

About one-third of LANL's FY 84 funding went for completing the work at APF and removing equipment. About one-third was used for fracture and fluid flow model development and calculations, and the remainder for laboratory experiments in rock fracture and explosive characterization. These projected activities effectively moved the rock fragmentation effort from the field to the laboratory, and produced basic data needed for model development.

Discussion

In fracture modeling, the oil shale arbitrary lograngian-Eulerian (SHALE) code development continued. This development included the running of threedimensional problems and incorporating the effects of explosive gases on fracture and particle motion. This work was done in cooperation with the University of Minnesota. As a follow up to the First International Symposium of Rock Fragmentation by Blasting, in Lulea, Sweden, collaborative efforts have begun with the Changsha and Maanshan Research Institutes of Mining, Peoples Republic of China, with the exchange of technical reports on LANL fracture models and blasting data. This was the first step in an international cooperative effort to study the phenomena of the fragmentation process.

Retort calculations using the WAFEOS two-dimensional retorting model have shown good agreement with the experimental data obtained by the SNL laboratory retort experiment. The agreement of the calculations with observed temperatures and char zones was encouraging.

TABLE 1. DESCRIPTION AND LOCATIONS OF FY 83 EXPERIMENTS

Experiment	Purpose	Configuration	Results	Postshot Analysis
83-A	Stemming Performance for SB-1	2.5 m of 1175U	Stemming and Explosive Performed as Expected	None
83-B	Stemming Performance Similar to Test 83-A	2.5 m of 1175U	Stemming and Explosive Performed as Expected	None
83-C	Stemming Performance for Confined-Volume Test CV-1	1.5 m of 1175U	Stemming and Explosive Performed as Expected	Crater to be Excavated and Profiled, Rubble Screened, and Major Joints Mapped
83-D	Unstemmed Borehole in Lean Shale to Compare SB-1 and SB-2 to 83-C	2.5 m of 1175U	Explosive Performed as Expected	Crater to be Excavated, Screened, and Major Joints Mapped
CV-1	Confined Volume to Keep Oil Shale in Place During Fracture Process	1.1 m of 1175U	Blasting Mat Held Except in Central 3-m Diameter Section	Crater to be Excavated, 1/2 Rubble Screened, Three Cores Obtained, and Crater Mapped

Cooperative analysis of APF data with the University of Maryland continued, as well as the study of fracture propagation using plexiglas models and high-speed photography. This work included the study of crack propagation under confining in situ stresses, fracture pressurization as a result of explosive detonation, and the interaction of stress waves and crack propagation resulting from the adjacent detonations.

Excavation of the two stemming tests and the blasting mat experiment at APF was accomplished. Screening of the stemmed and unstemmed blasting experiments at the APF was completed in March.

Nine cratering tests were conducted at APF during 1983, four by SNL and five by LANL. Their purpose was first to study the performance of the stemming and its effect on rock breakage, and second, to investigate the role of the highpressure explosive product gases in blasting. All nine tests produced rubblefilled craters, but only five of the craters were excavated. The results of the tests with excavated craters are summarized in Table 2; the four tests not excavated are summarized in Table 3.

The SNL tests were performed in medium-grade shale. From the matched stemmed and unstemmed tests, SB-1 and SB-2, which produced nearly identical craters, it was concluded that the high-pressure explosive product gas plays no role in single-borehole tests in moderate-grade shale. These shallow craters look as if they resulted entirely from spall. The gas may have been important in throwing the broken rock, but apparently did not cause new fracturing.

The parts of the borehole where the explosive had been were easily accessible in the SB-1 and SB-2 craters, since the craters extend down to just above the top of the charge. The borehole walls there were highly fractured; pieces pulled from it crumbled under light pressure. The apparent enlargement of the boreholes resulted

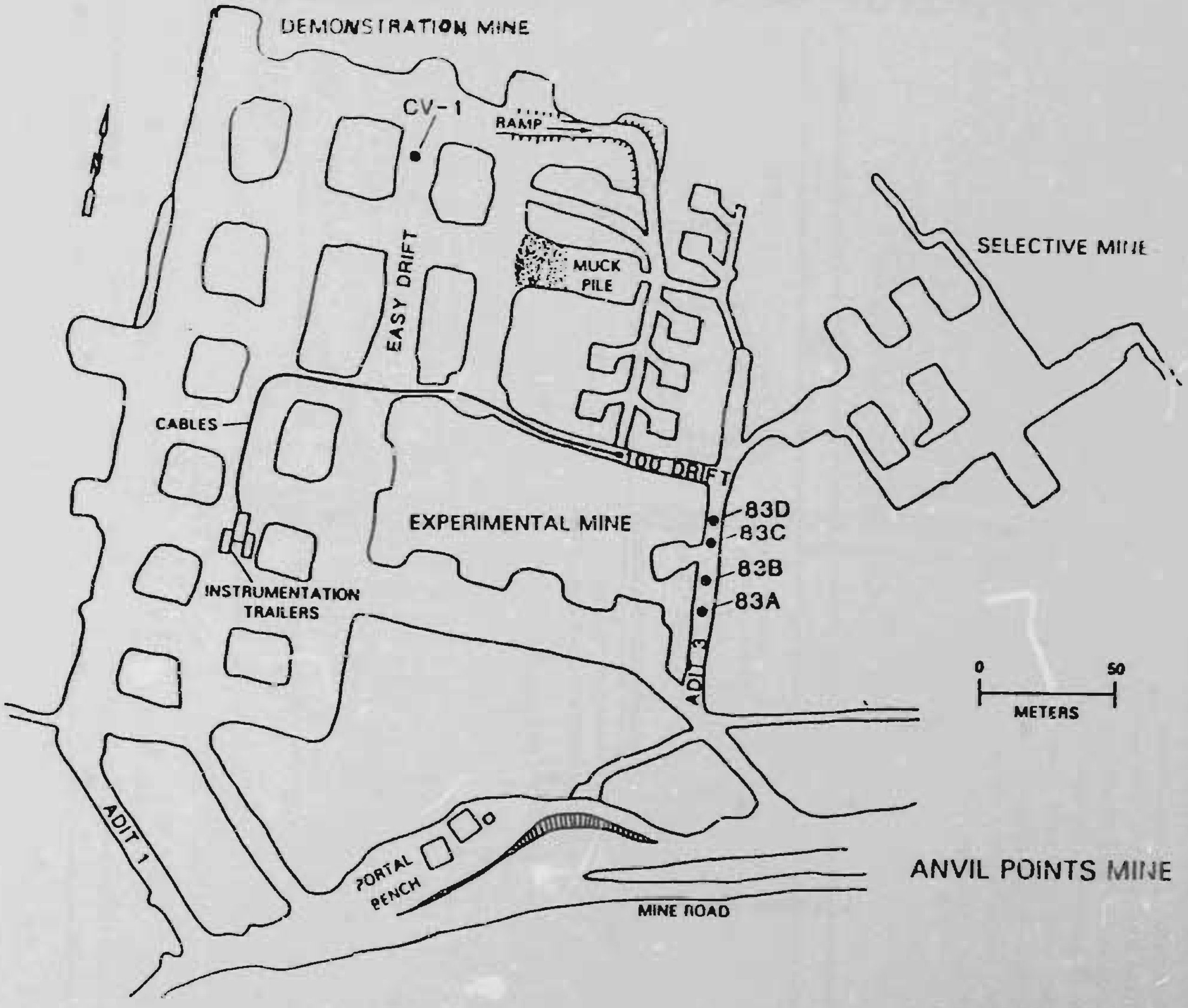

FIGURE 3. LOCATION OF LOS ALAMOS FIELD SITES

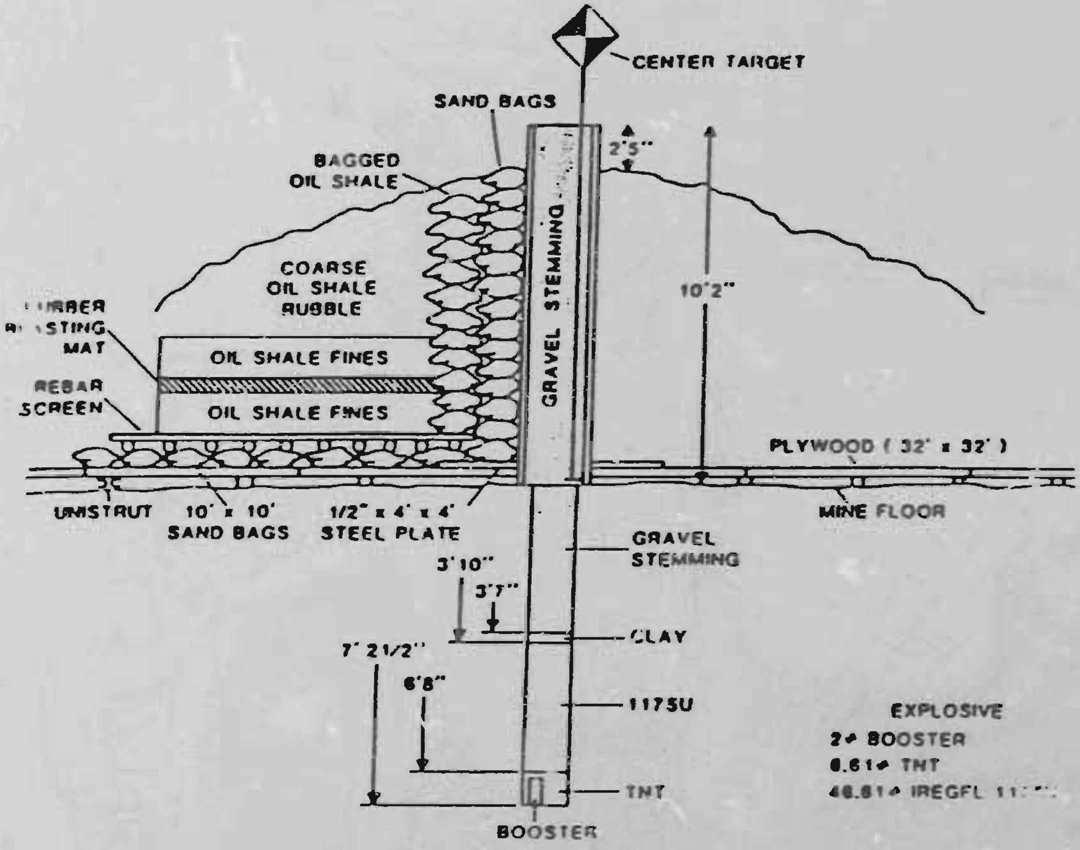

FIGURE 4. LOS ALAMOS CONFINED-VOLUME (BLASTING MAT) EXPERIMENT AT APF

from "scouring" of the fractured rock from the walls, rather than plastic deformation. The borehole was widest at the bottom where the booster was located.

Comparison of SNL tests with the LANL unstemmed test (lean shale) showed the unstemmed test in lean shale, 83-D, produced a cylindrical crater that pulled to the bottom of the charge. This is much deeper than the SB-1 and SB-2 craters in medium-grade shale. The pre-shot fracture calculations for these tests predicted rock breakage to just below the bottom of the charge. Therefore, among these experiments, the fracture calculations matched the 83-D crater. Experiment 83-D differed from SB-2 only in its location in Adit 3 where the oil shale is very lean. The difference between 83-D and SB-2 is clear evidence for a major grade effect in oil shale blasting.

Lean shale is different in two significant ways. First, it is more brittle than richer shale. Second, at least at the 83-D site, the rock has many prominent horizontal planes of weakness. It has been argued in the past that fragmentation occurs in two steps, where the stress wave causes fracture (crack growth), and then the gas causes the pieces to move, completing the fragmentation process. SHALE calculations, which currently

TABLE 2. EXCAVATED 1983 APF TESTS

Test	Lab	Purpose	Result
SB-1	SNL	Stemmed Test (Moderate-Grade Shale)	Shallow Crater to Near Top of Charge
SB-2	SNL	Unstemmed Test (Matched Pair with SB-1)	Shallow Crater to Near Top of Charge
83-C	LANL	Stemmed Test (Like CV-1, But in Lean Shale, and Without Rubble Pack)	Deep Cylindrical Crater to Bottom of Charge
83-D	LANL	Unstemmed Test (Like SB-2, But Lean Shale, Matched with 83-A, 83-B)	Deep Cylindrical Crater to Bottom of Charge
CV-1	LANL	"Confined Volume" (Stemmed, Moderate-Grade Shale, with Rubble Pack on Top)	Roughly Conical Crater to Below Bottom of Charge

TABLE 3. UNEXCAVATED 1983 APF TESTS

Test	Lab	Purpose	Result
ST-1	SNL	System Test Only	Rubble-Filled Crater
ST-2	SNL	System Test Only	Rubble-Filled Crater
83-A	LANL	Stemmed Test (Like SB-1, But Lean Shale, Fine Stemming)	Rubble-Filled Crater
83-B	LANL	Stemmed Test (Like SB-1, But Lean Shale, Coarse Stemming)	Rubble-Filled Crater

treat only brittle failure, should be more directly applicable in the lean shale. These calculations show fracture that extends at least as deep as the 83-D crater. The horizontal planes of weakness, some of which may have been open before the test, might then allow the gas to move quickly into the mass of fractured rock to produce tumbled rubble.

At SB-1 and SB-2, the richness of the shale apparently caused a ductile rather than brittle failure to occur near the charge, except along the borehole walls. Assuming the gas played a role at 83-D, the lack of brittle cracks near the charge in SB-1 and SB-2 prevented the gas from getting into the formation before it was vented out through the forming spall center. The ductile behavior of moderate- and high-grade oil shale under intense compressive loading must be taken into account in future calculations.

The stemming in the confined-volume test, CV-1, was effective enough to let gas enter fractures at least 0.3 m below the bottom of the charge, as indicated by the presence of soot stains when the broken rock was pulled apart. Soot stains could be found within about 1 m of the bottom of the charge, but not further out. The rubble pack emplaced above this test was intended to hold all the broken rock in place for detailed examination. It was successful, except in the center where the confinement was insufficient. Broken rock was observed lying in place. This required the removal of the rubble pack and considerable hand excavation and cleaning.

The broken rock in CV-1 clearly showed the effect of a pre-existing macroscopic joint structure. While there was a general increase in the fragment size with distance from the charge, significant local variations related to the joints were evident. Within about 1 m of the charge, there were large blocks that were essentially unbroken, while near the edge of the crater, there were blocks that had been shattered into small pieces. The joints varied widely in size and mean spacing through the test bed. The use of the term "joint" in this context may be misleading; the features being described are perhaps more properly called "macroscopic planes of weakness." A complete description of fragmentation will have to include these planes of weakness, including their influence in reflecting or scattering the stress waves generated by the explosive. Some of the fragmentation may not occur until the late stages of the blasting process, when the large blocks are set into motion and hit each other.

Solids characterization is vital to the assessment of health and environment consequences of oil shale processing. LANL is using several instrumental techniques for this characterization. This work focuses on determining (1) the trace element chemistry that occurs during shale oil extraction as a function of the fundamental process variables and (2) the environment of the material in the original matrix. This information is essential to understanding the environmental behavior of products, effluents, emissions and solid wastes from oil shale processing, and the potential for contaminant mobility and transport.

A set of carefully controlled heating experiments was conducted on a composite raw shale mineral material from Federal lease tract C-a shale core CE-709. This material was chosen for study because of its high pyrite content compared to other shales that have been characterized. These experiments were carried out to determine the influence of temperature and gas composition on product mineral assemblages, and major and trace element mobility behavior.

Another set of controlled heating experiments was carried out on a composite raw shale material from Federal lease tract C-b core 22x-1. Mineralogical characterization of the spent materials and standard leaching experiments were accomplished. Major elements (alkali and alkaline earth elements) behave similarly in all the materials that have been studied to date. The alkaline earths generally go through a region of maximum solubility from materials that have experienced temperatures in the vicinity of 825oC. In CO_2 atmospheres, this maximum solubility moves to higher temperatures, as would be expected, be causeof the inhibition of carbonate decompositions. Alkali metals show similar trends, except potassium, which shows increased solubility with increasing temperature in an air atmosphere. Several trace elements, including boron, molybdenum, and vanadium, exhibit increased mobilities from materials that have experienced temperatures in excess of 825°C. On the other hand, some trace constituents, including fluoride, show an inverse solubility trend with alkaline earths, suggesting that these experiments are addressing mobility and solution chemistry concerns.

Leaching experiments with spent shales and high total dissolved solids (TDS) leaching media have been completed. Multistaged counterflow leaching of spent Colorado oil shale was conducted under anaerobic conditions. Dissolution of selected major and trace elements as well as several anionic species was analytically determined after each stage of 10 counterflow sets of experiments. The results indicate that the 1-week contact time for each stage achieved a remarkable degree of solution equilibrium, as determined by such key elements as molybdenum and lithium. Greater amounts of these and other trace elements were dissolved with each additional contact of "dirty" water with spent shale.

Advanced analytical techniques for characterization of oil shale solids continue to be investigated. Further evaluation of the electron microprobeautomated imaging analysis (EMX-AIA) continues to suggest the potential usefulness of this technique to characterize the oil shale matrix. Analysis of two mounted and polished portions of raw oil shale from the Federal lease tract C-a, operated by Rio Blanco Oil Shale Co., were analyzed using Tracor Northern's coal mineral analysis software on the Cameca electron microprobe. Better definition of the mineral phases present in the samples and better differentiation of agglomerates should be possible with application of these techniques. The combination of the EMX-AIA with data analysis by pattern recognition techniques is leading the characterization of these very complex mineral assemblages from semi-quantitative towards quantitative means. The LANL nuclear microprobe is being used to characterize the oil shale matrix. Other geologic samples influence the mobility and transport/attenuation of environmental contaminants.

A series of experiments has been conducted to test the usefulness of particleinduced X-ray emission (PIXE) to investigate trace element residences in the oil shale mineral assemblage. Elemental concentrations and detection limits for 36 elements were analyzed for raw and spent shale samples. On each shale sample a dark carbonaceous area and a light colored area were analyzed. Detection limits for the majority of elements range from 2 to 30 $\mu g/g$. This shows that the PIXE technique is a suitable method for a broad-spectrum trace element analysis in geologic samples.

Studies into shale/water interactions continued to probe the effects of process waters as a leaching medium. These studies focused on the effect that the shale type has on the composition of the water after contact is made with the shales.

Codisposal of solid wastes and low-quality aqueous effluents from oil shale operations is a disposal method being considered for these wastes. A preliminary experimental evaluation of this practice focused on the validation of analytical techniques for studying the chemistry that occurs when these wastes are mixed. Three shale types were contacted with a single retort water. This helped to evaluate the effect of shale type and surface area on the behavior of organics when in contact with solid shales, and the mobilization of inorganics within solid shales. Distilled water leachates from these shales were used as the base line case. The inorganic compositions of distilled water and retort water leachates were compared. The pH and conductivities of these leachates suggest that the ultimate composition of leachates from codisposal are dependent on both the shale type and the leaching medium. The concentrations of the trace elements suggest that they are mobilized by the retort water leaching medium. This mobilization probably is due to complexation by organic ligands or by increased solubility caused by the ionic strength of the leaching medium. The organic compositions of these leachates are dependent on the shale type. Because of the nature of the analytical methods, only about 5 percent by weight rather than by volume of the solvent extractable material was analyzed. However, previous work suggests that the material being analyzed contains the majority of the mutagenic compounds.

3.4 LAWRENCE BERKELEY LABORATORY

Objective

The program's focus was to develop various methods for biological treatment of process waters, and to determine volatilization during compaction from codisposed oil shale process wastes.

Background

A commercial-scale oil shale conversion industry will require tremendous quantities of water (about 2 to 4 barrels per barrel of oil) and will produce voluminous quantities of highly contaminated wastewaters (from 0.1 to 2.0 barrels per barrel of oil) and spent shale (about 1.4 tons per barrel of oil). Disposal of spent shale and the reuse and ultimate disposal of the wastewater streams may present technical and economic barriers to the development of a commercial oil shale industry. It is imperative that water management and solid waste disposal strategies evolve concurrently with retorting technology and commercial development.

Discussion

Steam stripping is the most often proposed means of removing ammonia and carbon dioxide from oil shale wastewaters; the removal of organic carbon generally is not an objective. Engineers rely on empirical correlations and research data to provide a rational basis for the design of pollution control equipment. Results from the steam stripping of both Oxy-6 gas condensate and a composite oil shale wastewater indicate that the steam stripping theory may not be applicable to the wide spectrum of oil shale wastewaters. For example, theory predicts that a 2.04-m column at 110°C should be sufficient to remove 99 percent of ammonia from most oil shale wastewaters. The results of studies indicate that a column of greater length is required to remove 99 percent of ammonia from most of these wastewaters. In contrast, these studies have shown that removal of carbon dioxide can easily be accomplished.

Experiments were conducted on Oxy-6 retort water at a G/L ratio of 0.20 and a temperature of 111.5°C. Under these conditions, the stripper removed 99.8 percent of the ammonia, 82.2 percent of the dissolved inorganic carbon (DIC), and 27.7 percent of the dissolved organic carbon (DOC).

The recovery of nitrogen from 17 organic compounds by the total Kjeldahl nitrogen (TKN) method was investigated. The compounds were chosen either because of (1) reported incomplete recovery by the TKN method, (2) less than full recovery by the combustion/chemiluminescence (C/CL) method, or (3) structural similarity to the resistant compounds. In contrast to the reported resistance of nicotinic acid to Kjeldahl digestion, 99 percent of the theoretical nitrogen was recovered from this compound. Similarly, pyridazine and cyanuric acid yielded greater than 90 percent of their theoretical nitrogen values. Compounds containing the pyrazole nucleus and tetrazole, however, yielded 15 to 79 percent of their theoretical nitrogen values; the recoveries by C/CL for these compounds were in the same range as the TKN recoveries. Imidazole and 2,5-dimethylthiadiazole yielded 100 percent of their theoretical nitrogen by the C/CL method, yet only 5 to 25 percent of their theoretical nitrogen was recovered by the TKN method. From these results, it is apparent that only a subset of the compounds refractory to acid Kjeldahl digestion is not amenable to combustion and chemiluminescent detection. This would indicate that the C/CL method would be the preferred method to quantify nitrogen in aqueous waste streams, such as oil shale wastewaters, that contain these refractory classes of compounds.

The evaluation of the TKN method for determining nitrogen in oil shale process waters was completed. The preliminary report is available as: Jones, B. M., G. J. Harris, and C. G. Daughton. "Applicability of Kjeldahl Analysis to the Quantification of Organic Nitrogen in Oil Shale Wastewaters." LBID-856.

A simple and rapid method has been developed and described for physically separating dissolved ammonia from organic nitrogen in complex wastewater samples, in particular oil shale process waters. This separation method has utility in directly quantifying organic nitrogen by nonspecific methods that ordinarily can only detect total nitrogen. The sample is buffered with a sodium carbonate solution to a pH of 10.5. This deprotonates the ammonium ion to dissolved ammonia gas. Many nitrogen heterocycles and aromatic and aliphatic A mines remain nonvolatile, however, because they either have vapor pressures lower than ammonia, high solubilities in the aqueous phases, or remain protonated. The sample is introduced into a tubular microporous polytetrafluoroethylene (Teflon) membrane. The ends of the tubing are sealed, and the membrane is immersed in a 1N sulfuric acid bath. The tubular membrane is extremely permeable to gases, but since it is hydrophobic, liquid water and associated nonvolatile solutes cannot permeate it. The diffusion of ammonia is driven by the concentration gradient that is maintained across the membrane by absorbing the permeated ammonia into the acid solution, where it is protonated to give ammonium ion. The method is analogous to dialysis, but differs in that osmosis of liquid water does not occur. The method is called Unosmotic Dissolved-Gas Dialysis. The dialyzed sample can then be analyzed for total nitrogen by a nonselective, rapid method such as C/CL. The result is a direct measure of nonvolatile nitrogen, which is an estimate of organic nitrogen if the sample contains sufficiently low concentrations of nonvolatile inorganic nitrogen and of volatile organic nitrogen.

Three fixed-film biological treatment (FFBT) columns, packed with glass beads, raw shale, or granular activated carbon (GAC), were each used to treat 40 liters of 50 percent Oxy-6 retort water medium during 8 months of operation. These columns removed 60 to 65 percent of the DOC when operated on an 11-day recycle mode at a hydraulic loading rate of 0.067 mL/min-cm^2 for a bed depth of 21 cm. These removals indicate that FFBT reactors can remove more DOC from Oxy-6 retort water than can batch cultures.

After 176 days of continuous operation, a FFBT column packed with GAC treated 76 liters of amended, spent Oxy-6 retort water. Of the 46.2 g of DOC applied to this column, 18.5 g were removed. Previous calculations indicated that the sorptive capacity of the GAC would be exceeded by the addition of 13.2 g of DOC. The amount of DOC removal exceeding the sorptive-saturation value can be attributed to biodegradation.

The removal of DOC from raw Oxy-6 retort water during 11-day batch biotreatment was compared with DOC removals from three FFBT columns operated on 11-day recycle mode with hydraulic loading rates of 0.061 mL/min/cm^2. Mean values for DOC removals were batch culture, 55 percent; glass beads column, 59 percent; raw shale column, 62 percent; and GAC column, 66 percent.

TOSCO Corporation hot solids process (HSP) and Lurgi spent shales had much lower sorptive capacities for the N-heterocycles. No reduction in concentration was detected when 23 g of Lurgi spent shale was shaken with 33 mL of aqueous solution, or when 35 g of HSP spent shale was shaken with 45 mL of aqueous solution. To determine if the three FFBT columns were capable of removing significantly more of the organic solutes of retort water than batch shake-flask cultures (typically a maximum of 53 percent of the DOC is mineralized by outgrown cultures), the data were analyzed by one-way analysis of variance (anova). Results of the anova showed a highly significant difference among the four biological treatments ($P < 0.001$). An a priori significance test showed that the FFBT columns removed significantly greater proportions of DOC than the batch cultures. Further significance testing (a posteriori) demonstrated that each FFBT column (glass beads, GAC, and raw shale) removed a significantly greater amount of DOC than the batch culture ($P < 0.05$). In addition, the GAC column removed significantly greater amounts of DOC than the glass-bead column ($P < 0.05$). Removals by the raw shale column were not statistically different from the removals by either the glass beads or GAC columns.

The above statistical analysis verifies that the biooxidation of organic solutes in Oxy-6 retort water can be enhanced by using a fixed-film of microorganisms instead of a homogeneous, aerated suspension (e.g., glass-bead column versus batch culture). In addition, DOC removals can be further enhanced when FFBT is combined with the physiochemical properties of a sorptive solid support (GAC column versus glass-bead column).

Successful biological treatment of oil shale wastewaters depends upon the biooxidation of aromatic nitrogen-containing compounds. To investigate possible causes of recalcitrance, the fate of selected nitrogenous heterocycles in both single- and mixed-substrate systems was followed; the latter was evaluated as a model of the more complex mixture in retort waters. The biodegradability of each of 26 N-heterocycles was evaluated in batch cultures with a defined medium containing the heterocycle as the sole source of carbon, nitrogen, and energy at a concentration of 100 mg/L. Of these N-heterocycles, 12 were biodegradable as determined by decreases in dissolved organic carbon and UV absorbance. After 3 months of incubation in individual enrichment cultures, the other 14 N-heterocycles were not biodegraded. A mixture of the 12 biodegradable compounds totaling 100 mg/L of substrate was mineralized in 1 week by pooled enrichment cultures. This mixture appeared to be significantly more resistant to biooxidation, however, when added to Oxy-6 retort water at 300 mg/L. This mixture may be suitable for further investigation of the mechanisms causing the recalcitrance of aromatic nitrogen-containing compounds in oil shale wastewaters.

Cleavage of the heterocyclic and aromatic rings was indicated by a decrease in UV absorbance. Only 2 to 6 days were required for cultures to acclimate to quinoline, pyridine, 2-methylpyridine, 3-methylpyridine, 2-ethylpyridine, 3-ethylpyridine, 2-hydroxypyridine, and 3-hydroxypyrindine. Each of these compounds was biodegraded in less than 2 weeks. Pyridine compounds substituted in the 4-position, or those that contained more than one ring substitution, were significantly more refractory than those substituted in either the 2- or 3-positions.

Even though acclimation times for 2,4-dimethylpyridine and 2,6-dimethylpyridine were about 1 week, 5 weeks were needed by the cultures to biodegrade the initial 100 mg/L of substrate. After 3 weeks of acclimation, enrichment cultures required an additional 3 weeks to biodegrade 2,4,6-trimethylpyridine and 2-methylpyrazine. After 3 months of incubation, none of the other 14 N-heterocycles was found to be biodegradable.

These results agreed with those reported in the literature. With the exceptions of 2,3,6-trimethylpyridine, cyanuric acid, and 4-methylpyridine, N-heterocycles previously reported to be biodegradable were also mineralized in the defined medium of this project. In addition, it is thought that this is the first report of the biodegradability of 3-methylpyridine, 3-ethylpyridine, and 2-methylpyrazine.

One of LBL's primary goals in the analysis of retort water headspace is to identify, and eventually quantitate, volatile components in retort water that may contribute to air emission problems in the codisposal of the water with spent shale. Aromatic mines and heterocyclic nitrogen compounds are of primary interest because of their malodorous and probably hazardous nature.

Volatilization of compounds from codisposed oil shale wastes is strongly influenced by partitioning of solutes among the solid, liquid, and gas phases. Experiments are in progress to determine the sorption of five nitrogen heterocycles on various spent shales at ambient and elevated temperatures. The compounds are pyridine, 2-ethylpyridine, 5-ethyl-2-methylpyridine, 4-ethyl-3-methylpyridine, and quinoline. Experiments have been done at ambient temperature with TOSCO HSP spent shale, Lurgi cyclone-collected spent shale, and L-60 spent shale from LLNL. The shale from LLNL was black and had not been burned to remove char, while the other two shales were gray and had been burned to remove char. L-60 spent shale had a high sorptive capacity for N-heterocycles. When 24 g of this spent shale (-12 + 20 mesh) was shaken at ambient temperature with 20 mL of aqueous solution that initially contained 250 mg/L total heterocycle concentration, all N-heterocycle concentrations were reduced to below the detection limit of a gas chromatograph with a flame ionization detector (GC-FID).

3.5 LAWRENCE LIVERMORE NATIONAL LABORATORY

Objective

This program seeked to provide laboratory studies of gas species, retorting parameters, and bed preparation needs for various retorting processes.

Background

LLNL has been working on oil shale retorting technology for approximately 10 years. The effort has included laboratory research on chemical reactions and kinetics, operation of retorts and retort components, and mathematical modeling of retorting processes and related phenomena. In the last several years, attention has been concentrated on surface retorting. The models developed have been very successful in evaluating retorting processes, in identifying and solving problems, and in the computer-aided design of process components and experiments.

Discussion

Oil is produced by heating oil shale in the absence of air. The material remaining, called retorted oil shale, is black and retains some carbon as char. The fuel value of the char amounts to approximately 20 percent of the fuel value of the oil. Because the char is remarkably reactive, various processes have been considered to utilize the heat from char combustion in retorted shale, and thereby improve the overall efficiency of oil production.

Retorted oil shale contains an exceptionally high concentration of nitrogen and also some sulfur. During the first quarter of FY 84, LLNL continued to investigate the emissions of NO and SO_2 from the combustion of retorted oil shale.

LLNL measured the amount and rate of NO release from the combustion of three retorted Green River oil shales. The emissions are of concern because they are equal to the limits allowed for coal combustion when compared on an equivalentenergy basis. Results suggest that the NO yield decreases with decreasing nitrogen and char concentrations.

The release of NO occurs after char combustion. Observation indicates that an 80 percent reduction in NO emissions can be accomplished by leaving 20 percent of the organic carbon unburned.

At temperatures above approximately 550°C, the reactions between SO_2 and carbon ate minerals to produce sulfates are fast compared to the oxidation reactions that produce SO_2 This fact is of interest in the use of oil shale to reduce SO_2 emissions from the fluidized-bed combustion of high-sulfur coals.

The combustion of retorted shale does not release SO_2 if the combustion temperature is sufficiently high ($> 525°C$) so that the reaction between SO_2 and dolomite is rapid. The net reaction may be a combination of the following two reactions:

$2FeS + 3.50_2 = Fe_2O_3 + 2SO_2$ (1) sulfide oxidation

$2SO_2 + O_2 + CaMg(CO_3) = CaSO_4 + 2CO_2$ (2) SO_2 capture

The rate of SO_2 capture by oxidized oil shale, and the relation between the fraction of carbonate reacted (sulfated) and the rate of reaction have been studied. Measurements were made of the decrease in SO_2 concentration in a gas (2 percent O_2, 0.1 percent SO_2, balance N_2) as it passed through a heated bed of granular oxidized oil shale. The rate is a complex function of bed temperature and the length of an experiment, suggesting that more than one reaction is taking place that removes O_2. This is confirmed by the fact that the rate of CO_2 release was less than the rate of consumption of SO_2.

It appears that iron oxide (Fe_2O_3) in the oxidized shale is also removing SO_2 and the reaction is:

$$Fe_2O_3 + 3SO_2 + 3/20_2 = Fe_2 (SO_4)_2ß.$$

Oil shale nitrogen is distributed in solid, liquid, and gaseous products of retorting. Increasing retorting temperatures or time increases the concentration of gaseous nitrogen species, probably ammonia, at the expense of nitrogen in the solid retorted shale. Under the same range of conditions, the nitrogen content of the oil remains nearly unchanged. Oxidation of retorted shale results in the release of NO. These NO emissions can be significantly reduced by stopping the oxidation of retorted shale before all the char is consumed.

The triple quadrupole mass spectrometer (TQMS) was used to analyze grab samples from the pyrolysis section of the solids-recycle retort system during retort runs R-2 and R-3. These grab samples were analyzed for H_2S, mercaptans, thiophenes, sulfides, disulfides, and carbonyl sulfide (COS).

In retort run R-2, H_2S was reduced from an expected 20,000 ppm (for Fischer Assay) to a few ppm, and methanethiol was reduced from 130 ppm to 5 ppm. In retort run R-3, the H_2S was roughly 25 times greater at 50 ppm than in R-2, but still represented a significant reduction in expected amounts of H_2S.

The conditions of the recycle retort runs allowed a much more complete mixing of solids and gases than did the lab experiments. There was, consequently, a more complete removal of the sulfur gases than was experienced in the laboratory-scale pyrolysis experiments; the trends predicted by the on-line, Fischer Assay-like apparatus held true, however. It had been predicted that the iron oxides found in the burned shale would react with H_2S and most trace sulfur containing gases, with the exception of the thiophenes. This is exactly what was seen from the retort pyrolysis gas samples run on TQMS.

Relatively simple, effective kinetic expressions have been derived for oil evolution during pyrolysis of Green River oil shale: single first-order for slow and moderate heating rates, and double first-order or single pseudo-nthorder for rapid isothermal pyrolysis. A number of workers have investigated how secondary reactions (as influenced by pyrolysis heating rates, temperatures, residence times, and pressure) can modify oil yield from that obtained for Fischer Assay conditions. They have found that the secondary reactions are very important, demonstrating that slow heating rates cause hetero-aromatic compounds in the oil to be converted to coke, and that excessively high temperatures cause aliphatic structures to crack to gases.

While the qualitative aspects of oil-yield loss and quantitative relationships for some circumstances have been established, there has been no mathematical formulation that can satisfactorily calculate the oil yield for any given oil shale heated under an arbitrary temperature-pressure-gas environment history.

LLNL developed a mathematical model for pyrolysis of Green River oil shale from previous experiments on oil, water, and gas evolution, and oil cracking over a wide range of pyrolysis conditions. The model calculates the oil and gas product yields and the remaining shale composition as a function of time for a specified history of temperature, pressure, and gas environment. Reactions included are evolution of five gas species, oil, and water from kerogen, clay dehydration, oil coking, and cracking, and evolution of H_2 and CH_4 from char. Oil is treated in 11 boiling point fractions to treat the competition between oil coking and evaporation, and to evaluate the effect of oil cracking on the boiling point distribution of the oil.

When compared with experimental results, the yields agree very well, with a standard deviation of less than 2 percent of Fischer Assay. In agreement with previous observations, most of the yield loss at atmospheric pressure is due to oil coking. Both coking and cracking become greater at 27 atm because of longer liquid and gas residence times. Both oil liquid and oil vapor were allowed to crack, but most of the cracking was calculated to occur in the liquid, perhaps due to the greater mass concentration of the liquid oil compared with the oil vapor.

An apparent weakness of the model is the calculation of hydrogen evolution, particularly for rapid pyrolysis conditions. For isothermal fluidized-bed pyrolysis, it has been experimentally determined that hydrogen does not reach its maximum rate of release until most of the oil is evolved, suggesting that it is formed by a reaction intermediate. In contrast, the model calculates that the maximum rate of hydrogen evolution occurs during the initial stages of kerogen pyrolysis, even though a major source of hydrogen is oil coking. The problem emphasizes the importance of understanding the reactions of hydrogen for developing an improved general pyrolysis model.

A related problem is that the maximum possible oil yield is less than that attainable in high-pressure hydrogen. In the present model, the only way hydrogen can increase oil yield is by inhibiting oil coking. It appears necessary to include another mechanism in order to obtain higher yields in hydrogen than for flash pyrolysis. High-pressure hydrogen appears to inhibit the formation of additional aromatic carbon during pyrolysis. Under a wide range of other conditions, the total amount of aromatic carbon in the oil and carbonaceous residue is roughly constant and nearly twice that present in the raw shale. These measurements are important because the present model assumes that only part of the oil, roughly corresponding to the aromatic components, is susceptible to coking.

The computer model for the LLNL cascading-bed retort system was modified to include a surge bin for the shale passing from the pyrolyzer to the lift pipe. A major modification was also accomplished in the pyrolyzer model to allow particle-size-dependent velocities through the reactor. This is particularly important in simulating the LLNL two-stage fluidized-bed retort, in which the fines move more than a factor of two faster than the coarsest particles. Changes were also made in the lift-pipe model to allow certain parameters to be fixed for a given calculation (e.g., lift-pipe diameter, air flow rate). Previously, for exploratory studies, the model was allowed to determine optimum values of these parameters, rather than to use specified values. By March 1984, the complete model for the cascading-bed retort system was ready for application to the specific conditions of the LLNL experimental setup.

The LLNL moving-bed retort model was used to investigate the effects of changes in the hot-gas input rate for a hot-gas retort using external combustion. The Union B retort is one of this type. A base inlet-gas flow rate at 482°C was established, such that only 1 percent of the kerogen was unpyrolyzed in the outlet shale at 477°C. A 10 percent decrease in the gas flow rate caused the unpyrolyzed kerogen in the outlet shale to increase to 14 percent, a 20 percent decrease caused a 27 percent decrease. Furthermore, the outlet shale temperature decreased to 468° and 464°C, respectively. Thus, minor nonuniformities of the inlet-gas flux across the top of the shale could have pronounced effects on the degree of pyrolysis of the outlet shale, on the physical properties of the oil generated, and on the physical properties (especially cohesion) of the shale at the top of the retort. The calculations also illustrate that, even with a high inlet-gas flow rate, these same undesirable effects are necessarily present during start-up of the retort, if the hot-gas flow and the bed movement are simultaneously started in a retort loaded with raw shale at ambient tempera tures (i.e., no preheating of the shale bed before upward movement is started). If the shale bed is preheated (even for as short a period as 14 minutes) before upward movement is started, the outlet shale is fully retorted initially and decreases gradually to the steady-state value.

It would be advantageous to be able to use a higher inlet temperature, since the required flow rate of inlet gas would then be less, and the resulting pressure drop in the retort would also be less. The feasibility of doing this depends predominantly on the severity of oil cracking that would accompany the use of a higher inlet temperature.

LLNL analyzed the cracking of relatively low molecular weight oil vapor that might occur in the recycle gas from the time it is heated in the external combustor until it is again cooled by contacting shale (a total residence time of approximately 10 seconds including the time in the pressurized dome at the top of the retort).

It was shown that less than 10 percent of the oil vapor in the recycle gas will be cracked in 10 seconds, if the temperature of the recycle gas is kept below 550°C. This is probably acceptable, since it corresponds to a loss in total oil yield of only 1 percent of Fischer Assay. Allowing a drop in temperature of 25°C due to wall heat loss from the gas piping and retort dome, the maximum temperature of the inlet gas that finally contacts the top of the shale could then be 525°C without excessive loss from oil cracking.

The solids recycle retort system was assembled and start-up testing was begun in the first quarter of FY 84. The retort system is designed so that each component operates adiabatically. Electrical heaters on the surfaces of the vessels compensate for flow of heat through the insulation. The heaters are computer controlled so that the flow through the insulation and the heat provided are closely matched at each location.

In the solids recycle system, hot, burned shale serves as the heat source for pyrolysis of raw shale. In the LLNL equipment, mixing of the burned shale with the raw shale, and pyrolysis of the raw shale is accomplished in a densephase fluidized bed. Principal components in the recycle loop are the mixerpyrolyzer, surge tank, lift pipe, and combustor. All of these components and the interconnecting pipes are fabricated of stainless steel, are insulated, and have electrical heaters attached to the outer steel surface under the insulation.

In the first operation of the equipment, designated run R-1, the pyrolyzer was fluidized by preheated nitrogen. Lift gas and combustion gas were preheated air. Raw shale feed rate was 960 gm/min. The ratio of burned-to-raw shale entering the pyrolyzer was 3.8.

In subsequent runs, the fluidization gas was the pyrolysis gas from the discharge of the oil condensers. Since this gas has substantially lower viscosity than nitrogen, a high flow rate was used.

3.6 MORGANTOWN ENERGY TECHNOLOGY CENTER

Objectives

With restructuring of the Oil Shale Program during FY 84, the objective changed from developing a comprehensive data base for effective and efficient utilization of eastern and low-grade oil shale in an environmentally and economically acceptable manner, to performing focused research on oil shale, including shale properties and behavior under fast heat-up rate conditions, and characterization of process pollutants.

Background

In FY 84, the Oil Shale Program was restructured to focus the research on a fundamental understanding of the chemistry and physics of oil shale conversion. The restructured program required METC to reorient its activities from developing hardware to investigating high heating rate pyrolysis at a more generic level. Fluidized-bed retorting, by virtue of complex mass and heat transfer phenomena, does not lend itself easily to the elucidation of the chemical and physical phenomena involved in high heating rate pyrolysis. Consequently, fluidized-bed retorting research has been suspended in favor of developing new oil shale pyrolysis systems that lend themselves to more repeatable chemical and physical high heating rate phenomena elucidation, and are more readily supported by accompanying mechanistic models.

Discussion

The chemistry and physics of oil shale retorting do not permit the complete conversion of organic carbon to shale oil. A considerable amount of organic carbon is converted to carbon deposits that remain in the spent shale. Failure to use the spent shale carbon to provide energy represents a substantial loss in process economics.

To minimize thermal energy losses, it is advantageous to burn the spent shale promptly. One way to do this is to keep the combustion operation as close to the retorting operation as possible.

By virtue of the vigorous mixing inside a fluidized bed, there is excellent heat transfer between solid particles. The solid-to-wall heat transfer coefficient is also very high, about five to seven times that of a conventional steam-generation boiler.

A simple reactor was postulated that can burn the hot retorted spent shale and blend it with cold raw shale for efficient heat transfer. The gaseous products from combustion and retorting could be separated by a partitioning wall in the freeboard to prevent mutual contamination. Most solid handling problems would be eliminated or reduced if the solids transfer from retort to combustor could be achieved without an elaborate transportation scheme.

The twin fluidized-bed retort/combustor (TFBR/C) is such a reactor. The TFBR/C is divided into retorting and combustion sections by a partition with two interconnecting openings. These openings between the retorting and combustion chambers allow the spent shale to flow from retort to combustor, and the hot burned spent shale to flow from the combustor to the retort to mix with and retort the raw shale feed.

The TFBR/C is composed of three major parts: plenum chamber, bed region, and freeboard region. The interior of the twin bed, including the bottom of the plenum chamber, is covered with a layer of 2-inch thick castable refractory. The exterior of the twin bed is insulated to minimize heat loss. The interior of the twin bed is divided into two beds, the combustion and retort beds, by a partition plate.

To facilitate the supplying of different gases to each bed, the plenum chamber is also divided into two compartments. The plenum chamber under the combustor also serves as a precombustion mixer for air and propane. The combustion of propane will generate enough heat to preheat the twin bed. At the early stage of the test program, no attempt was made to delete the propane because the emphasis was directed toward oil yield improvement. At a later stage of the program, propane was used only for start-up until self-sustained combustion/ retort operation was achieved.

Product oil yields ranged from 60 to 70 percent of Fischer Assay. Selfsustained combustion/retort operation without the use of propane was demonstrated in five separate experimental runs with raw shale feed rates as low as 75 gm/min. This was also true when a binary mixture of nitrogen and steam was used as the fluidizing gas in the retort section. All the runs were conducted with a 20 x 42-mesh Colorado oil shale with feed rates from 75 to 112 gm/min.

Calculations show that the TFBR/C can be operated to achieve maximum use of combustion heat without depending on the heat transfer from direct solid-tosolid mixing. Apparently, for a small TFBR/C, the area for heat transmission between the combustion and retorting sections is sufficient to allow enough heat to be transferred from the combustion bed to the retort bed for retorting. For large bed operation, a special bed-to-bed heat transfer arrangement, such as heat pipes, may offer an ideal solution.

The ASPEN fluidized-bed retort (FBR) model for western shale consists of a retort section and a combustor section. The retort section has the kerogen pyrolysis reaction occurring in a stoichiometric reactor. The combustor section of the model consists of a heater block, two stoichiometric reactor models, and a chemical equilibrium reactor model.

This ASPEN model was exercised to duplicate studies on western shale. The western shale base case simulation calculated the solids recycle ratio (SRR) necessary to achieve a desired retort temperature of 950°F. The simulation predicts an SRR of 1.5, which was somewhat less than the originally published result, but nevertheless, a reasonable estimate.

The ASPEN FBR model was then modified for application to eastern shale by replacing the western shale properties with those for eastern shale. Major differences between eastern and western shale reside in the kerogen and mineral compositions. Eastern shale kerogen has a lower hydrogen-to-carbon ratio than western shale and also has more sulfur and oxygen. Eastern shale has little calcite or dolomite, while western shale has significant quantities of both of these minerals.

As a result of these differences, the eastern simulation produced different results. The eastern shale produced about 38 percent less light hydrocarbon gases. Since eastern shale has very few carbonate minerals, which decompose endothermally, the combustor reaches a higher temperature. The eastern shale combustor reaches a temperature of about 1,660°F compared to about 1,500°F for western shale. Accordingly, the solids recycle ratio for the eastern shale case is reduced to around 0.8.

The following pyrolysis mechanism was postulated for kerogen and natural bitumen decomposition in eastern oil shales:

$$\text{Natural Bitumen} \xrightarrow{K_1} \text{Oil} + \text{Gas} + \text{Carbon Residue}$$

$$\text{Kerogen} \xrightarrow{K_2} \text{Pyrolytic Bitumen} + \text{Gas} + \text{Oil}$$

$$\text{Pyrolytic Bitumen} \xrightarrow{K_3} \text{Gas} + \text{Oil} + \text{Carbon Residue}$$

Comparisons between the model prediction and the experimental data for weight loss versus temperature for Kentucky Sunbury shale were made and activation energies were determined.

In addition to the TGA, a pyroprobe was used to study higher heating rate phenomena. The pyroprobe achieves rapid heating rates over the range of 100 to a reported 20,000 K/S. The residence times can be varied from 2 to 20 seconds.

The TGA and the pyroprobe provide only the weight of the sample as a function of time or temperature and no information about the product gas composition. The FTIR technique gives a way of identifying the thermal decomposition products. Combining TGA or pyroprobe with FTIR provides information on the composition of gases evolved during oil shale pyrolysis and, consequently, kinetic data for the gases evolved.

For the eastern oil shales studied, the DTG peak areas over the 300° to 600°C temperature range were plotted against oil yield. The correlation observed between the differential thermal gravimetry (DTG) peak areas and Fischer Assay oil yield values are reasonably good, with a correlation coefficient of 0.91. Minerals such as pyrite (FeS_2), marcasite (FeS_2), and analcite ($NaAlSi_2O_6 \cdot H_2O$) show some thermal effect in this temperature range. The same is true for clay minerals such as kaolinite. The absence of the characteristic carbonate decomposition DTG peak in the eastern oil shales at the 700° to 800°C temperature region is indicative of the absence or very minor presence of carbonate minerals. This has been confirmed by X-ray diffraction.

Several heating rates were run for TGA decomposition kinetics. The extent of conversion versus temperature at various heating rates for Kentucky Sunbury shale was determined. With a heating rate of 5°C/min, a 20 percent conversion was affected at 407°C; with 20°C/min, a temperature of 433°C was required to achieve 20 percent conversion. This phenomenon is due to the fact that as heating rate is increased, the sample is exposed for a shorter time to a particular temperature. The rate maximum is also shifted toward higher temperature as heating rate is increased.

The oil shale samples (100/120 US mesh) were heated to 620°C in a continuous nitrogen gas flow at 100°, 200°, 500°, and 1,000°C/sec. The data indicate that percent decomposition increases with an increase in heating rate. These results suggest that higher heating rates may reduce the amount of coking of organic matter and, thus, significantly increase the oil shale devolatilization yields. Percent weight loss of Colorado shale is lower than that of Sunbury shale, even though Colorado shale provides greater yield in Fischer Assay.

Percent decomposition has also been studied as a function of residence time. Residence times for the runs were 2, 5, 10, and 20 seconds at 1,000°C/sec heating rate with 620°C final temperature. The results for 2, 5, and 10 seconds show that longer residence time is needed for devolatilizing Colorado shale than Kentucky shale. It is possible that Colorado shale, with large amounts of carbonate minerals, may require more heat for carbonate decomposition, thereby delaying organic decomposition.

The efficient extraction of shale oil involves effective retorting methods and oil collection techniques. Both of these distinct steps must be addressed by any well-conceived process for collecting oil from retorting.

Droplets formed after shale pyrolysis may be collected by a number of standard techniques, such as scrubbers, electrostatic precipitators, filters, etc. However, the efficiency of any collection technique depends on the size and concentration of the aerosol. Nucleation of the vapor phase on foreign particles and homogeneous nucleation are the two mechanisms of droplet growth.

A shale oil droplet generator was fabricated. The 2-inch inner diameter unit has a length of 23 inches. An extended length for the retort above the bed assists in decreasing entrainment of fines coming out of the unit. The bed material is composed of spent shale and has a static depth of ~ 4 inches, and a weight of ~ 200 grams.

The measurement of droplet size and concentration are accomplished with novel laser-based optical particle monitors. Light scattering by entrained aerosols has an angular dependence with droplet size, and an intensity dependence with concentration. The process stream in the test region has a calculated velocity of 20 cm/sec at a volumetric flow rate of 6 slpm, and will provide a proper residence time for droplet formation and growth of ~ 1 sec, based on plug flow of nitrogen at standard temperature and pressure. This test region can be modified so that several different residence times can be studied.

Shale oil is fundamentally different from petroleum because it contains saturate, olefin, and aromatic hydrocarbon compound types, while petroleum contains saturates and aromatics. Olefins, because they can polymerize, cause problems with the processing of shale oil. Olefins are also of interest because the amount, and perhaps the type, of olefins in shale oil is related to retorting conditions and, in turn, to the mechanism of decomposition.

Kentucky and Colorado shale oils were obtained from METC's 2-inch electrically heated fluidized-bed oil shale retort system. Alumina, activated silica, and silica coated with silver nitrate were used as the adsorbent material in the columns. Cyclohexane, toluene, chloroform, methanol, and heptane/toluene were used as solvents. Proton and carbon nuclear magnetic resonance (NMR), FTIR, and gas chromatography/mass spectrometry (GC/MS) were used to analyze the composition of the fractions.

The results of the class separation of Kentucky and Colorado shale oils indicate that the separation method developed is effective in separating whole shale oils into their component saturate, olefinic, aromatic, and polar fractions. Good reproducibility was obtained for the duplicate runs. The recovery of at least 90 percent of the starting material indicates that losses due to adsorbent retention and solvent removal are minimal, allowing this class separation to be used for the quantitative analysis of shale oils. Proton and carbon NMR data, along with FTIR analysis of the fractions, indicate that (1) the class overlap within each fraction is minimal and (2) valuable compositional parameters (i.e., aromatic alkyl chain length, olefinic and aromatic content) can be obtained and used to determine the chemical composition of the fractions.

Analysis of the mass balance data indicates that there exists a variability in shale oil composition with respect to the retorting conditions. The olefin concentrations appear to show the greatest variability with respect to the fluidizing gas composition. Both oil shales show a greater olefin concentration for oils retorted in 100 percent nitrogen, with the concentration decreasing when water is added to the fluidizing gas of the Kentucky shale.

Analysis of the Kentucky and Colorado shale oil class fractions by proton NMR revealed several trends in the chemical composition of the oils, irrespective of the fluidizing gas composition. The Colorado shale oils contained a greater proportion of hydrogen in polymethylene structures, approximately 39 percent as compared to ~ 30 percent for the Kentucky shale oil. This finding is supported by the carbon NMR data for the whole oils, which show the Colorado shale oils to be more aliphatic (~ 71 percent) than the Kentucky shale oils (~ 53 percent). This agrees with the accepted views that western shales are more highly aliphatic in character than eastern shales. The Kentucky shale oil had a higher concentration of aromatic hydrogen, approximately 13 percent, compared to ~ 7 percent for the Colorado shale oil.

Time-resolved gated decoupling NMR techniques, such as gated spin echo decoupling (GASPE), are being refined and used to differentiate between the protonated and nonprotonated carbon species in shale oils. Coupled with conventional NMR information on aromaticity, the added information can be used to measure aromatic ring condensation, methyl substituent condensation, and the degree of alkali and functional group substitution on aromatic structure.

The carbon NMR spectra of shale oils consists of broad resonance bands due to the variety of organic compounds present. Separation of the oil into class fractions improves the resolution; however, broad resonance bands are still present. Previously, the only information that could be derived was the aliphatic/aromatic ratio of the carbon atoms. Time-resolved gated decoupling NMR can be used to break down complex carbon spectra into subspectra containing resonances due to only one of the five following groups: (1) aromatic nonprotonated carbons, (2) aromatic methane carbons (CH), (3) aliphatic nonprotonated carbons, (4) aliphatic methylene carbons, and (5) aliphatic methane and methyl carbons (CH and CH_3).

Initial application of this technique to a Colorado light oil has shown the ability of the method to distinguish between protonated and nonprotonated carbons. Analysis of the nonprotonated carbon in the GASPE spectrum indicates that the nonprotonated carbons are ~ 70 percent aromatic. In contrast, the conventional proton-decoupled $_{13}$C NMR spectrum of the same oil had ~ 25 percent aromatic carbon as a fraction of the total carbon. Consequently, it can be concluded that the aromatic structures in this shale oil are polycyclic in nature and/or highly substituted. Since there is a considerable contribution of aliphatic material in the GASPE spectrum for unprotonated carbon, it is evident that some quarternary aliphatic carbon is present in shale oils from branching and cyclization of the aliphatic material. This accurate compositional information promises to provide correlations based on a fundamental understanding of the shale and its pyrolysis products.

The characteristics of rapid heat transfer and uniform temperature in a fluidized bed have been considered to be due primarily to the vigorous mixing of the solid particles. Data reported in the literature indicates that perfect or near-perfect mixing of solids takes place in fluidized beds when the solid is one of the reactants. However, good solid mixing might become a disadvantage because of the spread of the solid residence time distribution (SRTD), i.e., nonuniform solid residence time. To provide more uniform residence time, various mechanical devices have been investigated to obtain a baffle configuration that would be suitable for an oil shale retorting process.

Experiments on a fluidized-bed cold module were conducted in a 4-inch diameter cylindrical vessel which is 33 inches high and made of Lucite plastic material. Air was the fluidizing gas. Sand was used as fluidized solid, with a density of 2.7 g/cm^3 and a size range of 20 to 50 mesh. The tracer used in the experiments was potassium permanganate crystals (^{a}p = 2.6 g/cm^3), sieved to the same size fraction as the sand.

After a steady-state flow of solids and gas had been established, the step input signal tracer (the concentration of tracer was about 0.5 percent) was added and, simultaneously, the solids leaving the bed were collected into sample bottles over timed intervals. The tracer concentration in the effluent was found by extracting the color.

Based on the experimental results, the following preliminary conclusions can be drawn:

- Comparison of SRTD data in a free-bubbling bed and in the compartmented beds with different types of baffles indicated that a tube tray with about 10 percent free area can be used to improve the pattern of solid mixing.
- An increase in solid-feed rate will make the baffles effective. However, the average residence time of solids in the bed would decrease with the increased solid-feed rate. To keep the minimum residence time necessary for oil shale retorting, the height of the bed can be increased, which also helps to achieve plug flow. However, the proper ranges of these parameters, including gas and solids flow rates as well as the bed height, have not yet been explored. Experiments on the effects of these parameters on solid mixing are currently being conducted in the 4-inch diameter cold module.

3.7 PACIFIC NORTHWEST LABORATORY

Objectives

This program was focused to determine the distribution of arsenic (As), cadmium (Cd), mercury (Hg), and selenium (Se) among product streams during oil shale retorting and to identify the chemical forms present, as well as the mechanisms responsible for their formation.

Background

Because of their volatile nature, a significant fraction of these elements is released from the raw oil shale matrix during retorting, and subsequently migrates to the product shale oil, retort water, or offgas streams. Thus, depending on the form(s) of the chemicals in each product stream, these elements may be mobilized into the environment unless removed from the streams before disposal.

For each of the aforementioned elements, the objectives of this study are to (1) determine the distribution coefficients for each product stream; (2) identify the chemical forms in retort water, offgas, and shale oil with particular emphasis on inorganic or organometallic species known or suspected of being carcinogenic or toxic; (3) investigate the mechanism(s) responsible for mobilizing toxic, or labile chemical forms identified in Item (2) into each product stream; and (4) determine the effect of retorting rate, maximum retorting temperature, and retorting atmosphere on Items (1) and (3) above.

Discussion

This work required fabricating and testing a retort furnace assembly to generate product streams for analysis. Techniques and procedures were adapted or developed for the extraction and determination of the metals of interest and/or their compounds.

The first successful full-scale retort run was carried out during the early part of January. The test involved retorting 6 kg of oil shale to a maximum temperature of 500°C using a 1°C/min heating rate. Three oil fractions were collected corresponding to the heavy, medium, and light distillates. Important operational parameters (input N_2 gas flow; total outlet gas flow; shale bed temperatures at the top, middle, and base of the retort vessel; and outlet gas temperatures) were monitored throughout this retort run with the data collection system.

The sensitivity of the proposed analytical techniques was tested to determine their suitability on oil shale retort samples. This work included the determination of cadmium by prompt gamma neutron activation analysis, mercury and selenium by instrumental neutron activation analysis, and arsenic by X-ray fluorescence in the raw shale, spent shale, retort water, and shale oil.

Preliminary "micro-retort" experiments were carried out in an inert N_2 atmosphere using 2 to 10 grams of shale, a shale heating rate of approximately 200°C/min to a maximum temperature of 1,000°C, and a N_2 sweep gas flow rate of 0.4 L/min. The objectives of these experiments were to (1) evaluate the performance of the Zeeman Atomic Absorption system (ZAA) for on-line measurement of total As in the offgas stream during retort runs, and (2) obtain an initial estimate of the As volatilization profile as a function of retorting temperature. Prior knowledge of this As volatilization profile will allow optimization of total As measurements, using ZAA, and As speciation measurements using GC-Microwave Plasma Detector (GC-MPD) during future high-temperature (1,000°C) retort runs, using the 6 kg PNL retort.

Spent shale samples from retort run PNL-1 (N_2 sweep gas, 1°C/min heating rate, and maximum temperature of 500°) were heated in the "mini-retort." This apparatus consisted of a 6-mm ID quartz tube or a 12-mm 305 stainless steel tube heated with nichrome wire. Nitrogen gas flowed through the shale as the shale was heated from 25° to 1,100°C/min The nitrogen sweep gas laden with arsenic then passed directly into the ZAA carbon tube atomization furnace (2,800°C). The As temperature profile was obtained for 10 runs with PNL-1 spent shale, and two runs with LBL-3 spent shale. LBL retort run 3 was conducted under identical retort conditions as PNL retort run 1, except that Colony shale was used rather than APF shale. All runs showed bimodal As emission profiles that peaked at 500° to 600°C and 950° to 1,050°C. The maximum concentrations observed at the low- and high-temperature peaks were approximately 8 and 6 ppm, respectively. These results suggest the possibility of two forms of As in the shale. A second interesting result was that As began to evolve into the carrier gas stream at 200°C. However, the apparent volatilization of As at this low temperature may be an artifact of the slow response time of the thermocouple that was used to measure the shale temperature.

The second run of the PNL 6-kg retort was successfully completed during June 1984. The objectives of retort run PNL-2 were to measure the concentration of Hg in the offgas by ZAA, to determine the composition of the offgas, and to identify and quantify which organomercury species were present in the offgas. The oil shale was heated at 1°C/min to a maximum temperature of 500°C with a N_2 sweep gas flowing at 1.8 L/min. During peak mercury emission in the offgas, as indicated by the ZAA, numerous samples were taken to determine the organomercury species in the offgas. This included using Tenax and Carbosieve-G as an absorption media, and cryotrapping followed by silver and gold traps as backups to the cryotraps. All important retorting parameters (i.e., flow rates, shale temperatures, Zeeman signal, etc.) were monitored by the data acquisition system throughout the retort run. Preliminary review of the data collected indicated that retort run PNL-2 met all the intended objectives. The Zeeman functioned was designed to indicate mercury concentration in the offgas. All problems initially observed in retort run PNL-1 were corrected. The most impressive result from retort run PNL-2 was the identification of dimethyl-, diethyl-, and di-n-propyl-mercury, and the tentative identification of methylethylmercury in the offgas.

3.8 SANDIA NATIONAL LABORATORY

Objectives

This program was initiated to (1) test various parameters of oil shale retorting processes; (2) determine rock fragmentation characteristics; and (3) perform blasting agent characterizations.

Background

During 9 years of involvement in the DOE program, SNL has been pursuing a goal of developing the technology to improve the overall efficiency of shale oil recovery processes. In particular, SNL activities have focused on in situ shale oil recovery processes. The objective of these activities has been to acquire the ability to prescribe an efficient process for in situ recovery of a given oil shale resource.

Recent field experiments have demonstrated that the yield from an in situ retort is largely controlled by the characteristics of the rubble bed produced during the bed preparation step. This realization has shown that there is a need to develop a predictive capability for the fragmentation step in the process of constructing an in situ retort. In addition, it is important that criteria for the blast results be developed that are based on a thorough understanding of retort yield as a function of bed characteristics. The influence of permeability structure on retort yield must be clearly defined.

At the present time, the SNL program addresses the two interrelated areas of bed preparation and characterization and retort processing.

A joint DOE/LETC, LANL, SNL Rock Fragmentation Working Group was formed in mid-1981 to coordinate DOE-sponsored bed preparation studies. In mid-1982, following reviews of previous and ongoing work in VMIS rock fragmentation, a joint LANL, SNL Rock Fragmentation Experimental Program Plan was generated. Emphasis of this plan was placed on experiments to specifically address questions related to the accomplishment of a prescriptive design capability, i.e., that the field program encompass both pragmatic and theoretical aspects of VMIS blast design. Further, the experiments would be conducted primarily for data acquisition for correlation with numerical modeling. The field experiments were conducted at the APF mine to maintain continuity between past work and possible future mini-retort fracturing and retorting experiments.

The experimental program was initiated in early 1983. Stemming tests and one confined test were conducted by LANL during June 1983. Stemmed and unstemmed single borehole cratering tests were conducted by SNL during June 1983. Two additional tests were also conducted by SNL. They provided two complete performances of the field test firing and data acquisition systems prior to the execution of the heavily instrumented cratering tests.

Discussion

Excavation of rubble from the cratering tests that were performed during the summer of 1983 began on December 12, 1983. Excavation of rubble from the two instrumented tests, SB-1 and SB-2, was completed on December 23. Excavation of rubble from two stemming tests conducted by LANL, 83-C and 83-D, was completed on January 11. Screening of the rubble began January 30 and was completed on February 29.

Both SB-1 and SB-2 craters were shallower than expected. Neither crater was more than 2 meters deep; the craters did not reach the top of the explosive column. Formation of the crater walls appears to have been dominated by bedding planes and vertical joints. As a result, both craters are asymmetric.

The porosity of the post-test rubble piles was calculated from the elevation surveys conducted before and after excavation. The volume of the SB-1 crater was 43.4 cubic meters, the volume of the SB-1 rubble was 73.1 cubic meters, and the porosity was 40.6 percent. The volume of the SB-2 crater was 40.8 cubic meters, the volume of the SB-2 rubble was 66.2 cubic meters, and the porosity was 38.4 percent. On this basis, both the stemmed and the unstemmed tests seem similar despite the asymmetry that each displayed. The volume of rock involved in the SB-2 test, however, was slightly less than the volume of rock involved in the SB-1 test. Since the difference is less than 10 percent, it does not necessarily indicate any difference in cratering effectiveness of the two tests. This amount of difference could be due simply to a slight difference in local geology.

Another way of comparing SB-1 and SB-2 is to compare profiles obtained from the elevation surveys. These profiles were obtained by averaging all of the elevation readings at various radial distances. Despite apparent differences, the two tests show similar average profiles of crater depth.

It had been expected that the stemmed and the unstemmed tests would be different because of the reduced gas pressure effect, but the results demonstrated that the reduction of gas pressure had little or no effect on these single borehole tests.

As noted above, LANL tests 83-C, stemmed, and 83-D, unstemmed, were also excavated. Test 83-C had 1.5 m of explosive and 1.5 m of stemming, compared to the 2.5 m of explosive and 2.5 of stemming in test SB-1; test 83-D had essentially the same geometry as test SB-2, 2.5 m of explosive and 2.5 m of burden. These tests were conducted in lean shale in the floor of Adit 3. Test 83-C was between tests 83-B and 83-D; blastwell spacing for the test series was 6.7 m.

The craters are significantly deeper than those for tests SB-1 and SB-2. The 83-C crater depth was to the bottom of the 3 m blastwell; the 83-D crater depth was approximately 3.8 m.

The greater "pull" of tests 83-C and 83-D can be attributed to two factors. First, these tests were two of a series of four blasts at 6.7 m spacing. Some "preconditioning " of the rock due to the prior tests may have occurred. Second, shale grade in the Fred (analcimized tuff) bed beneath the floor of Adit 3 is about 5 to 10 gpt, compared to the 20 to 30 gpt in the C and D beds where tests SB-1 and SB-2 were conducted.

The crater excavation and rubble screening clearly showed (1) only negligible differences in fragmentation extent or particle size distribution between stemmed and unstemmed tests in the same shale grade, and (2) substantial differences in both fragmentation extent and particle size distribution between a brittle lean (5 gpt) shale and a moderate (25 gpt) shale

The numerical modeling effort at SNL has been directed toward developing a model that will correctly describe rubble properties when given a set of blasting conditions. This depends on the development of the late time motion codes BLOCKS and BUMP. These codes require as their initial input a specification of the rock as it is constituted after the fracturing is complete from the explosive detonation. Specifically, it is necessary to describe the extent of fracturing and the fragment size distribution. SNL has begun to use an explicit, two-dimensional finite-element code, DYNA2D, to provide this description.

In February, DYNA2D was used to model the SB-1 test configuration. The explosive behavior was approximated using the measured detonation velocity and density to estimate detonation pressure. Properties used were otherwise those of amonium nitrate fuel oil (ANFO) to substitute for the real explosive, IRECO 1175U, which is presently only crudely characterized. The simulations were performed using two different representations of the rock. In the first case, the rock was assumed to be homogeneous and isotropic with respect to properties. The layers were chosen to correspond to grade variations based on the analysis of a core taken near the test area. These layered calculations are not entirely rigorous since only density, Poisson's ratio, and Young's modulus were varied for the different grade regions. Other parameters inherent in the damage model, such as the relationship between fracture stress and strain rate, were held constant at values for 20 gpt shale. Nevertheless, the layered calculations provide a better approximation of the actual media. DYNA2D was used to predict the extent of damaged rock for both of these cases.

The region of damaged rock in the layered model relates to the layering. In the low grade regions, damage is more extensive. Also, a larger region of rock is damaged in the homogeneous model. This indicates that there is less rockbreaking energy in the layered model. This apparent loss of energy is due to dispersion of the explosive shock waves at layer boundaries. In the actual blast, there are many more layers and the layer interfaces are less distinct. This would cause a continuous dispersion of the energy that could not be modeled with DYNA2D.

Recently, The BUMP computer code has sustained a number of modifications designed to increase stability and decrease running time. In addition, practical modifications, such as addition of a restart option, have been added and modeling of the SB-1 experiment has begun.

Two changes in BUMP have made the calculation of the collision sequence more accurate, and have produced a stable time step for an initially packed body of fragments that is blown apart by large forces (as during an explosion). These changes are in the integration algorithm and in the functional form of acceleration allowed to superpose smooth linear functions in time.

BUMP can model the extremely short-term, high-acceleration phase of the blast and the long-term settling of the rock fragments in a single stable calculation. It is currently the only motion code that can be used to model the complete blasting process within a reasonable computer running time, and is thus the only code that can be used for parameter studies. However, some problems remain to be solved before BUMP will yield easily interpreted and meaningful results.

Eleven cores were extracted at APF during March for use in assessing the cratering tests that were conducted in the summer of FY 85. Three slant (45°) cores were obtained beneath the craters of each of the two instrumented cratering tests. One vertical core was extracted at a 9 m radius for fracturing assessment and for material property tests.

Three vertical cores were obtained for LANL within the crater of their blastmat test; one additional core was also obtained at a 9 m radius from this test. This work completed SNL field experimental activities at APF.

Examination of the cores from these holes has shown that the damage caused by the blast extends beyond the rock that is included in the crater region. Also, it is obvious from first inspection that the degree of damage depends upon the layering; a damaged layer might be between two intact layers.

The core was logged with special emphasis on describing the extent of damage observed along the core length. The layers of damage can be traced from one hole to another. The extent of damage was quantified by counting the number of complete fractures. For additional documentation, the core was photographed to show each portion of the core in detail.

Several recent field experiments have shown local yield losses well in excess of that predicted by state-of-the-art, one-dimensional retort models. Examination of data from those retorts, particularly thermal data showing nonuniform progress of the retorting front, has lead us to believe that rubble-bed nonuniformities (permeability contrasts) were causing not only the expected sweep inefficiencies, but also much higher-than-expected local yield losses.

Previous one-dimensional modeling and pilot retorting studies are not adequate to predict these phenomena because the permeability contrast effects are inherently multi-dimensional. Even uncoupled, parallel one-dimensional simulations are inadequate, since the observed yield losses result from the coupled transport of mass and energy between regions of differing permeabilities. Hence, SNL initiated multi-dimensional pilot retorting and modeling programs to isolate and quantify these effects.

Several 100-kg retorting experiments, with variations in permeability contrast from run to run, have demonstrated conclusively that local oil yield losses can be introduced or worsened solely by rubble bed nonuniformities and resulting nonuniform flow through the retort. The primary mechanisms causing this increased yield loss are (1) overlap of retorting and combustion fronts in the vicinity of the permeability contrasts (causing product migration to hot, oxygen-rich environments, with resulting oil cracking and combustion); and (2) slow heating rates in low-permeability zones, resulting in increased oil coking.

These mechanisms are very similar to those causing low yield in large oil shale blocks. In fact, to the extent that a block is simply a region of very low permeability (or vice versa), the two processes are the same.

Results from the two-dimensional retort model that was developed to simulate these conditions have been compared to the experimental results to isolate the various mechanisms causing the increased losses, and to validate the model. Agreement between model calculations and experimental observations has been excellent. Model calculations of full-scale in situ retorts will be done in the future.

Based on these studies, it appeared reasonable to attribute much of the yield loss observed in recent field experiments (beyond those losses predicted by one-dimensional studies) to this permeability contrast mechanism. Reductions in permeability contrasts in field retorts can then be expected to improve local oil yield as well as sweep efficiency.

SNL also examined a number of control strategies to try to limit losses caused by permeability contrasts. However, the unlikely (or at best uncertain) effectiveness of variations in process control parameters (gas flow rate and composition, and location of gas injection and withdrawal points) limits the likelihood of significant improvements in this area.

The primary means of improving local yield (as well as sweep efficiency) within in situ retorts is, then, improvement in initial bed uniformity. Research in bed preparation and blasting techniques is necessary to improve the fundamental understanding of rock fragmentation and rock motion phenomena. This understanding will lead to a prescriptive capability for creating uniformly permeable retorts to maximize oil yield.

3.9 VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

Objective

The program's objective is to provide a data base on the sorption-desorption capacity of oil shale materials for selected organic and inorganic species in aqueous media.

Background

In solid waste management, sorption and desorption of organic and inorganic species on spent shale and soil are important to the identification and mitigation of environmental impacts. Factors affecting adsorption include physical characteristics, particle size, temperature, hydrogen ion concentration, dilution, synergism, and molecular weight of adsorbate.

Discussion

Early in FY 84, sorption experiments with inorganic ions were performed by shaking raw APF shale with distilled water for 168 hours. It was found that pH decreased, and the following values increased: conductivity; redox potential; and concentrations of fluoride, sulfate, and potassium. Concentrations of arsenic, cadmium, and iron tended to remain constant.

To better simulate actual field situations, a series of continuous-flow columns were built. The continuous-flow systems work very well and the results being obtained are reproducible. Each elution experiment is replicated three times, and is performed by pumping about 70 to 80 pore volumes of DI water through a column of shale. The 8 to 30-mesh particles of four different shales are being used in the column trials.

To standardize data, three utility computer programs have been developed: Interpolate (INTER), Convert (CONVRT), and Extinction Calculation (ESCALC). INTER interpolates evenly spaced points from data that may be unevenly spaced. Currently, this is being used to interpolate the digitized UV spectrophotometric scans in the 184 to 360 nm range at 1 nm intervals. This results in standard format data of one transmittance or absorbance value at every whole number wavelength from 184 to 360 nm, a total of 177 points per curve. The interpolation is very faithful to the actual digitized points and reproduces the digitized curve accurately.

CONVRT is used to convert the 177-point curves obtained either from the INTER program or generated otherwise. The conversion can be from transmittance to absorbance or vise versa.

ESCALC calculates the extinction coefficients given the molecular weight of a compound, and either transmittance or absorbance values. It also averages the extinction coefficients for up to five curves extinction coefficients for the pure compound solutions.

3.10 WESTERN RESEARCH INSTITUTE

Objectives

Work on this program was conducted to (1) characterize the chemical and physical properties of raw and spent shales, (2) characterize oil shale process waters, and (3) characterize raw oil shale properties to better understand rock fragmentation processes.

Background

On March 19, 1983, the U.S. DOE and the University of Wyoming entered into a cooperative agreement, effective April 1, 1983. The University of Wyoming, through the formation of a nonprofit corporation known as the University of Wyoming Research Corporation (UWYRC), took responsibility for operation of what was previously LETC, a federally owned and operated facility. WRI was subsequently formed as an affiliate of UWYRC to conduct the research wi thin the cooperative agreement and to pursue related research with other organizations.

To address the objectives of the DOE Oil Shale Program, WRI has divided its research into four activities: physical/chemical properties, in situ processes and rock fragmentation, novel concepts, and environmental research. The physical/chemical properties activity provides a basic understanding of the reaction chemistry and transport processes in retorting systems. In situ processes and rock fragmentation focus on the development of analytical methods for predicting oil yield losses in rubble beds. The novel concept activity addresses innovating ideas that have not been explored but may lead to improvements in oil shale conversion, product recovery, or mitigation of environmental impact. Environmental research is aimed at identifying and understanding the origin of possible pollutants. From this understanding, methods will be tested and evaluated to control pollution to within acceptable levels.

Discussion

Modifications to the LLNL one-dimensional retorting model are improving the predictive capabilities in comparison to laboratory retorting tests. A change to the code for calculating temperature distribution and shrinking core behavior in rectangular shale particles predicts about 5 percent less oil production than corresponding predictions for spherical particles. This new code is intended to help evaluate the experimental results from low void retorting tests.

A new experimental configuration has been devised to extend the range of temperatures for measuring the kinetics of kerogen decomposition at isothermal conditions. The new experimental configuration is based on using a fluid-bed bath to heat the oil shale sample, which is enclosed in a small diameter, thin-walled tube.

A new apparatus has been assembled to measure the cooling and cracking rates at isothermal conditions over a temperature range of 300° to 1,100°F. In this experimental procedure, cold shale oil is injected into a hot rubble bed where the volatile fraction evaporates and is swept out the top of the rubble bed, while the remaining liquid drains through the rubble. The residence time for cracking of the shale oil vapor is controlled by the sweep gas rate, and the residence time for coking of the nonvolatile liquid is varied by adjusting the shale oil injection rate.

Oil yields in five previous 10-ton retorting tests with nonuniform flow distributions correlate well with the degree of flow nonuniformities. The Blake-Kozeny equation has been used to represent the relative variations in flow velocities for the different bed geometries. The highest oil yields are obtained with the most uniform rubble beds.

Work was undertaken to define the trace element horizons over the oil shale resource areas and to correlate these data with existing information on Fischer Assay oil yield and mineralogical profiles. The selection of three cores from Wyoming completed the effort to identify the samples necessary for this task.

Work on characterization of the organic material in raw process waters was accomplished. A method for profiling the amphoteric compounds in synfuels process waters that have been fractionated by an environmentally mimetic procedure was completed.

Approaches to treat oil shale retort waters include (1) alternative pretreatment methods for various retort waters, (2) development of activated carbon adsorption parameters in batch and continuous flow modes for raw and pretreated water, and (3) the preliminary screening of reverse osmosis operating conditions for ultimate retort water disposal.

A project was completed to determine if pretreatment of select oil shale retort waters by contact with spent shale enhanced activated carbon adsorption. The results indicate that the spent shale did not adsorb any organic materials extracted by methylene chloride.

Samples of raw and moderate temperature retorted Green River oil shale were analyzed by X-ray diffraction. Raw samples were composed of the normal Green River minerals suite (western oil shale) listed in decreasing order of abundance: dolomite (Ca,Mg,Fe) $(CO_3)_2$, quartz (SiO_2), albite $(NaAlSi_3O_8)$, orthoclase $(KAlSi_3O_8)$, calcite $(CaCO_3)$, analcime $(Na,Ca)AlSi_2O_2$, with trace amounts < 1 percent of pyrite (FeS_2) and clay minerals. The heat-altered samples were Green River samples that had been subjected to temperatures sufficient to mostly decompose the carbonate minerals and produce silicates. Minerals identified were raw western oil shale minerals plus peraclase (Mg,Fe)O, augite $(Ca,Mg,Fe,Al)Si_2O_6$, akermanite—gehlentie $Ca_2(Mg,Fe)Si_2O_7-Mg_2(Ca,FeSi_2O_7)$ and monticellite—merwinite $(CaMgSiO_4-Ca_3Mg(SiO_4)_2)$. The silicification products are the normal products that are predicted by the high-temperature (i.e., > 550°C) retorting of Green River oil shale.

Samples examined for the Total Resource Energy Extraction (TREE^{sm}) project produced some very interesting results. TREE^{sm} low void experiments were run under conditions that are not normally encountered in nature; hence, some of the mineral products were unusual. Oil shale was retorted along with the injection of a sulfur product gas. The resultant mineral assemblage reflected this sulfur in the formation of previously nonexisting sulfur mineral forms. Most significant of these were pyrrhotite $(Fe_{1-x}S)$. Several family species alterations of $FE_{1-x}S$ were encountered, including greigite (Fe_7S_8) anhydrite $(CaSO_4,H_2O)$ and oldhamite (CaS). Oldhamite is not a characteristic earth mineral, but has previously been found only in meteoric matter.

3.11 ULTRASYSTEMS, INC.

Objective

This program seeked to investigate the acid drainage potential of eastern oil shales.

Discussion

Late in the second quarter of FY 84, the investigation of the leaching behavior of a spent shale from the Institute of Gas Technology (IGT, New Albany shale) was terminated. No net acid production was observed after 223 days exposure, which is not surprising in view of the carbonate and potential ferrous sulfide contents of the sample.

Leaching studies carried out on a mixture (1:1) of raw and spent New Albany shale samples (to simulate the redeposition of spent shales with low-grade raw shale) failed to result in acid production after over 237 days exposure.

3.12 UNIVERSITY OF CALIFORNIA, BERKELEY

Objective

This program was implemented to obtain rate expressions for the interdependent physical processes of shale oil mist formation, deposition, and drainage that can be incorporated into comprehensive models to improve oil shale retort design, operation, and control.

Discussion

A final report for this work, performed under DOE Contract No. AS20-80LC-10350, was received. Some of the major technical findings are summarized here.

Mist deposition and pressure drops were measured from oil-loaded granular beds covering a wide range of experimental conditions. Mist drop size varied from 0.15 to 4.7 μm. Gas velocity varied from 2 to 100 mm/sec, and the percentage of voids occupied by oil varied from 0 percent to 76 percent. Decreases in efficiency were most pronounced where large drops were combined with low velocities. Here, sedimentation is the dominant capture mechanism. Decreases of as much as four-fold have been measured. Measurements have been successfully correlated to permit prediction of deposition efficiency under similar circumstances. Size distribution was measured of shale oil mists that have been formed from vapors during flow through an initially cold bed of shale rock. The oil used was retorted by GKI on December 2, 1978. The average drop size decreases from about 1.3 μm at a cooling rate of 87°K/sec to about 0.3 μm. These sizes are significantly smaller than measurements made using a straight tube condenser, but they showed the same trends with cooling rates and vapor concentration. Loss of larger droplets by sedimentation onto the rock surface appears to account for these differences.

3.13 UNIVERSITY OF WYOMING

Objective

This program's goal was to determine the technical feasibility of radio frequency (RF) retorting of oil shale through an investigation of the basic principles involved in RF retorting.

Background

Thermal conversion of oil shales in situ require rubbling of the shale to allow efficient heat conduction and convection and flow paths for the shale oil. Experimental work indicates the possibility of unrubbled oil shale conversion through the use of RF heating. As the shale heats the porosity increases, permitting recovery of the shale oil. This study is designed to investigate the basic principles of RF retorting of oil shale.

The University of Wyoming is actively engaged in the third year of a 3-year contract for theoretical and experimental studies related to the physics of oil shales. To achieve the stated objective, it is necessary to investigate the basic principles involved in RF retorting, specifically:

- The nature of propagation of electromagnetic waves in oil shales.
- The absorption properties of electromagnetic waves in oil shale materials.
- The heating rates that can be achieved by RF methods.
- The electromagnetic power requirements as a function of time, temperature, and volume of oil shale samples.
- The mechanisms for oil flow as the oil shales are heated by RF methods.

This work involves theoretical and experimental studies concerning the thermal and electrical properties of oil shales. The contract has three phases:

Phase 1 — Evaluation of physical properties such as shale structure (mineralogy, etc.), reaction rates (kerogen and mineral decomposition), and mechanical, thermal, and electrical properties. From these physical properties, models will be developed for heat flow in the heterogeneous oil shales, and for inclusion of dielectric constant effect.

Phase 2 — Experiments suggested from Phase 1 will be performed.

Phase 3 — A basic understanding will be attained of physical mechanisms based on properties of oil shales. Recommendations will be made concerning technical feasibility of RF retorting of oil shales.

As a follow-up to the theoretical (modeling) effort at the University of Wyoming, WRI will design a laboratory experiment for testing RF heating of large blocks of oil shale. These tests are needed to measure the oil coking losses, and to evaluate alternative antenna configurations for RF retorting.

Discussion

The problem of volumetric heating of oil shales by electromagnetic methods has been studied theoretically. This study included both a detailed examination of heat conduction in composite media, and the development of a numerical model to describe the heating process.

The effects of layering on heat conduction in oil shale materials was studied theoretically. A new solution to a heat conduction equation in heterogeneous materials was developed that included both the effects of inclusions and contact resistance. The solution was presented in terms of the associated Green function and numerical results were obtained. In addition, a new solution to the heat conduction equation was presented for materials that consist of constituents whose thermal properties vary in a discontinuous manner. This solution was also presented in terms of a Green function. An interaction technique was developed to solve the related eigenfunction problem. Numerical results were exhibited for heat flow in layered materials.

A two-dimensional numerical model that describes electromagnetic heating of oil shales was developed. The model includes equations for temperature, pressure, saturations, chemical reactions, mass conservation, and source terms. The gases are all assumed to form one bulk species and the oil is assumed to remain in liquid form. The chemical reactions include pyrolysis of kerogen and char, release of bound water, coking, and decomposition of carbonates. Porosity and permeability are dynamic functions of the organic materials. Calibration of the model was accomplished by comparing the model results with experimental data obtained by the Illinois Institute of Technology Research Institute (IITRI). Nonlinear relationships for viscosity, thermal properties, and source terms were used as inputs to the model. A finite difference approximation to the differential equations was derived and solved using Newton's iteration technique. For the cases studied, the solutions are quite stable.

Objectives

The objectives of this program were to (1) develop theoretical fracture mechanics tools that are applicable to transversely isotropic materials such as sedimentary rock (more particularly oil shale); and (2) develop a fracture mechanics test procedure that can be conveniently used for rock specimens.

Background

Basic to the understanding and planning of in situ fragmentation and ex-situ mining of oil shale are the mechanical properties of the shale. This research is an extension of a research project entitled "Mechanical Properties of Oil Shale," originally funded in February 1977, by the ERDA Fossil Energy Program, through its Division of Oil, Gas, and Shale Technology, under Contract No. EF-77-S-04-3954. Later, the project was extended to 1983 to include physical characterization of selected oil shale. During the past 6 years, a program was established that developed an efficient methodology for standardized and simplified mechanical testing of western oil shale. The experiments include precise, representative, and duplicable sample preparation; uniaxial static compression testing; "modified" split cylinder testing; uniaxial creep and relaxation testing under extended periods of time; dynamic testing with varying strain rates; fatigue resistance; and three-dimensional constitutive relationships. The variables investigated include organic volume, mineral contents, stratigraphy, strain rates, and stress levels.

Numerical modeling and rubblization experiments have been performed by various investigators. Surface uplift blasting has been successful for shallow formations; it also provides opportunities to investigate high strain-rate rock mechanics. Rock rubblization experiments, including the propagation of stress waves, were described. Time-explicit, finite-difference numerical analyses were applied to evaluate the stimulation treatment in the multiple fracturing of well bore, and to study explosively induced fractures in void generation.

However, as far as the fracture mechanics are concerned, the fundamental explosive rock breakage mechanisms are still not understood, which has necessitated extensive reliance on very costly empirical approaches. Fracture mechanics of oil shale have been based on conventional fracture mechanics that use notched samples and assume the material to be isotropic and elastic. Oil shale is a layer material that is more accurately characterized as transversely isotropic; it behaves nonlinearly due to stress dependency. Furthermore, the notches upon which cracks initiate are extremely sensitive to the location of the bedding planes (layers). Consequently, a more promising fracture mechanism should involve the average behavior of a section of oil shale (for example a 2-inch thick specimen sampled by oil yield), instead of the breaking strength of a particular layer.

Discussion

A critical review of the state-of-the-art of fracture mechanics on layered rocks has been completed. Recommendations are made for innovative and promising methods for oil shale fracture mechanics., Numerical and analytical studies of mixed-mode fracture mechanics of oil shale are being investigated. Transversely isotropic properties of oil shale are input using isoparametric finite elements with singular elements at the crack tip. The model is a plate with a center edge crack, whose angle with the edge varies to study the effect of mixed-mode fracture under various conditions. The cracked body is represented geometrically by four finite element grids with the notch at 30, 45, 60, and 90°.

Once a numerical solution is found using the finite element method, it is necessary to be able to estimate the crack tip stress intensity factors using the established crack tip relations. This study uses a direct method in which the displacement field is used to find the stress intensity factors.

The conic-section simulation analysis is a method to determine stress intensity factors when using the finite element analysis. The method involves the mapping of the nodal displacements into a single elliptical function. It has been shown that a relatively coarse mesh could be used to obtain reasonably accurate results.

The conic-section method was checked using the displacement method and an isotropic material since solutions are available for comparison. Four transversely isotropic materials were analyzed, and the effect of the angle change on the stress intensity factors was studied. The materials analyzed include Green River Formation oil shale with an organic volume of 30 percent and a stress level of 21 percent.

Verification runs on steel were made to check the validity of the analysis in this study using the 45° and 90° meshes. The values obtained check favorably with results published by the Society for Experimental Stress Analysis (SESA). Comparison between the displacement method and the conic-section simulation method yields results for all angles of cracks agreeing closely in both methods.

Precracked disks of oil shale cored perpendicular to bedding planes are being analysed numerically. Fracture toughnesses are determined by (1) strain energy method, and (2) elliptic simulation method.

3.14 BATTELLE-COLUMBUS LABORATORIES

Objective

The program was focused to develop the multi-solids, fluidized-bed combustion (MSFBC) oil shale retort concept.

Background

In 1974, Battelle initiated an internally funded program to develop innovative technology to satisfy the need for a high-performance combustion system that would enable expanded use of solid fuels of all types, while meeting emission standards. The MSFBC process resulted from this development effort. This process features an entrained bed of small or light particles (typically sand or limestone) and a permanently fluidized dense bed, both in the combustor. The entrained bed acts as the heat carrier, in addition to contributing to the excellent quality of fluidization achieved in the MSFBC. The MSFBC has demonstrated high-combustion efficiencies, wide flexibility in fuel feed rate, and an ability to process a wide range of fuel types and particle sizes. The high degree of mixing and heat transfer, fast heat-up rate, and high throughputs were thought to be beneficial for the retorting of oil shale.

Discussion

In this concept (see Figure 5) oil shale is fed to a MSFB retort where kerogen is pyrolized to produce gas and oil vapor. A recirculating stream of spent shale is the entrained phase and supplies the heat required for retorting. The retorted shale is elutriated from the retort column, captured in a cyclone, and fed to a fluidized-bed combustor where the residual carbon in the retorted shale is burned to reheat the recirculating entrained phase. Mixtures of steam and nitrogen were the fluidizing media. Key operating parameters of retorting temperature, shale particle size, residence time, throughput, and use of steam on oil yield of eastern oil shales were determined.

The system's ability to process large shale particles was demonstrated in a preliminary cold model investigation funded by Battelle. In the first series of tests, the ability to operate a conventional fluidized bed was compared to that of a MSFB retort. Operation of the 6-inch diameter cold model was limited to particle sizes of less than ½ inch in diameter when operated in a conventional fluidized-bed mode, even while superimposing an entrained phase similar to that obtained in a "fast-fluidized bed." However, with the addition of a third material acting as the dense-phase medium, shale particles as large as 2.5 inches in diameter could be fluidized in a well-mixed, stable system.

To achieve this condition, both the dense bed and the entrained phase had to be present. This synergistic effect between dense-phase material and entrained phase permits the MSFB to achieve stable operations over a wide range of conditions.

The preliminary cold model experiments demonstrated that stable conditions could be achieved with a superficial gas velocity as low as 16 ft/sec and an entrained phase recirculation rate as low as 3,800 lb/hr-ft2, based on the cross-sectional area of the reactor. The maximum value for velocity was 24 ft/sec. The maximum value for entrained-phase recirculation rate was 12,000 lb/hr-ft2. These limits resulted from physical constraints of the model.

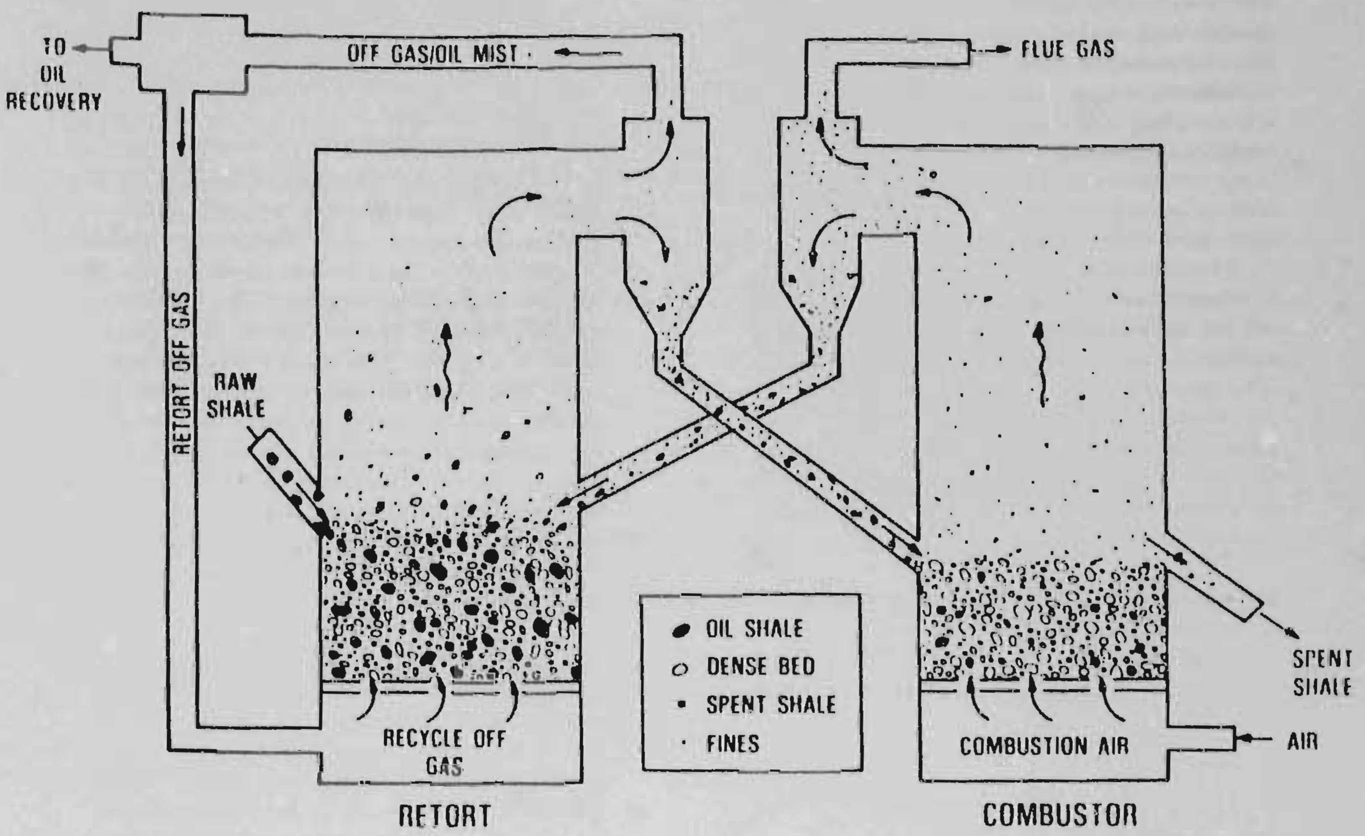

FIGURE 5. BATTELLE MULTI-SOLID FLUIDIZED-BED OIL SHALE RETORTING CONCEPT

Fine particles are typically easily processed in a fluidized bed, as long as they have sufficient residence time to complete the desired conversion before being elutriated from the bed. One might expect that the residence time of fines would be extremely short in a fluidized bed that is operated with a superficial gas velocity of 20 ft/sec or more. However, the presence of the dense bed in the MSFB inhibits fines elutriation and substantially increases residence time, as illustrated in Figure 6. This increased residence time, along with the extremely high heat and mass transfer rates obtained in the turbulent fluidized bed, was sufficient to obtain a high conversion efficiency.

To minimize equipment costs associated with this program, the experiments were conducted in a process research unit (PRU) originally designed and currently operated to develop a forest residue gasifier (FRG) similar to the MSFB oil shale retort. The PRU was designed as a flexible system capable of integrated operation of the retort/combustor system. For all but the last test, the system consisted of a 6-inch I.D. retort coupled to a 40-inch I.D. combustor. The last test was conducted with a 10-inch I.D. retort. The retort and all connecting piping are constructed without refractory linings to reduce costs and time required to reach steady-state operation. The PRU combustor is refractory-lined and is oversized to ensure that the retort, which receives all its heat from the circulating entrained-solids phase, can be maintained at a sufficient temperature. Natural gas is added to the combustor as needed to help balance the large heat losses inherent in a small-scale system.

The retort can be operated at temperatures to 1,600oF and pressures to 5 psig. A linear gas velocity of 20 ft/sec was selected for the design bases, giving a gas residence time of about 1 second in the 20-foot long reactor. Entrained sand, retorted shale, and spent shale were separated from the product gas and vapors in a disengager, and were returned to the combustor. The retorted shale was burned in the combustor to heat the sand and spent shale, which was recirculated to the retort to supply heat. The combustor is a conventional fluidized bed designed to operate at temperatures to 1,900°F.

Due to the difficulties encountered in operating a satisfactory product condenser/collection system, all oil yield data were obtained from analysis of the product gas and vapor stream. Product collection by a total product condenser was not sufficient due to the low concentration of hydrocarbon vapors in the product vapor and gas stream. Since nitrogen was used to simulate recycle product gas, the product vapor was significantly diluted by a noncondensible gas. As a result, the dew point for the hydrocarbon vapors was unusually low.

The experimental results indicating enhanced yields by the use of steam to fluidize the retort are fairly consistent with results obtained by others working in fluidized-bed oil shale retort-

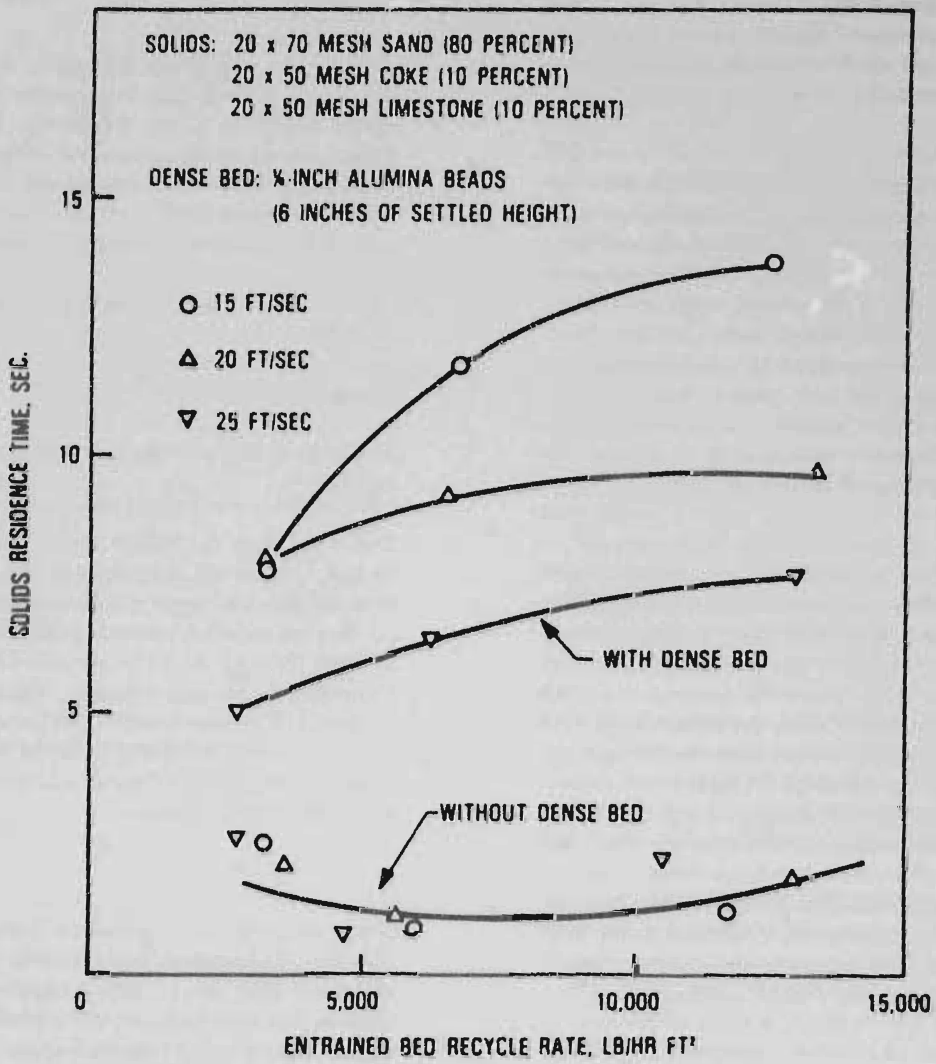

FIGURE 6. EFFECT OF ENTRAINED-BED RECYCLE RATE AND DENSE BED ON SOLIDS RESIDENCE TIME

ing. Yields to 162 percent of Fischer Assay (54.6 percent carbon conversion to oil) were obtained with steam, while yields were at or below Fischer Assay when nitrogen was used to fluidize the retort. The low oil yield obtained with nitrogen was surprising since other investigators have found moderate yield enhancement in fluidized-bed retorting due to the rapid heating rate obtained.

A limited number of tests were run to determine the effect of shale particle size. In these tests, three different size distributions of the feed were used. These size distributions were 100 percent minus ¼ inch, ¾ inch x 1/4 inch, and 100 percent minus ¾ inch. Due the manner in which the shale fractures, the larger pieces (up to about 10 percent of the feed in the latter case), had one dimension equal to or slightly greater than 1 inch. Again, no discernible difference in yields or the system's ability to handle the feedstock were observed.

Cold model experiments indicated that the MSFB retort can process shale particles up to 2.5 inches in diameter. The synergistic effect of the dense bed and the superimposed entrained phase results in a stable fluidized bed, even with the presence of these very large shale particles. For comparison, a few cold model tests were conducted without the dense bed. Under these conditions, the maximum shale particle size that could be used, even with a recirculating entrained phase, was limited to about ½ inch.

Throughputs in excess of 3,300 lb/hr-ft2 were achieved. The relative insensitivity of feed rate on retort performance indicates that shale residence time does not significantly vary as a direct function of throughput. In the MSFB retort, shale residence time is more a function of particle size than throughput. Small particles always have a fairly short residence time because they are entrained in the fluidizing gas. Fortunately, these small particles pyrolyze rapidly. Large particles that cannot be entrained remain in the dense bed region until they are retorted, by which time they break down sufficiently to be elutriated. Tests indicate that the larger particles remain in the bed for as long as 20 minutes; however, at no time did the solids inventory cause an operational upset.

An economic analysis indicated the cost of crude shale oil would be approximately $37.00/bbl compared to a cost of $50.00/bbl for a similar-sized Paraho plant (1983 dollars).

3.15 GULF RESEARCH AND DEVELOPMENT COMPANY

Objective

This program's objective was to develop an understanding of the fundamentals of a solvent hydrogen donor process. The process would be used to convert kerogen in eastern U.S. shales to useful products. Other program objectives were to determine the effect of donor content on conversion, changes in kerogen and products with conversion conditions, and the fate of the donor solvent including material balances with losses through isomerization, adduction reaction, and physical retention in the rock matrix.

Discussion

Two specific samples of shale were suggested for use in this project. The first sample was supplied by the Kentucky Center for Energy Research. This shale sample is designated "Hilpat shale." It was obtained from a freshly mined 25-foot (vertical) face in Fleming County, Kentucky, and is part of the Cleveland member of Ohio shale.

The second sample of eastern U.S. shale was obtained from Battelle-Columbus Laboratories. It is designated "Indiana shale," and was mined and originally obtained from Phillips Petroleum.

Available analyses of the shale samples are given in Table 4.

Two samples of the Hilpat shale, one being untreated 150 μm x 0 material and the other being material that had been subjected to prior chemical demineralization treatment, were beneficiated by froth flotation in a Denver cell. Concentrates containing 60 percent organic carbon were produced. The beneficiation results are shown in Figure 7. The froth/floated fraction was further concentrated by hydrofluoric acid/hydrochloric acid (HF/HCl) treatment.

Complete elemental analyses for various samples of treated Hilpat shale are shown in Table 5. Elemental analyses are shown for the "as-received," acid demineralized, froth/floated, and froth/floated plus acid demineralized samples of Hilpat shale. Also shown in Table 5 are the calculated atomic H/C ratios for the various samples.

TABLE 4. SHALE SAMPLES

Shale Designation	Eastern U.S. Shale (Hilpat Sample) Cleveland Member Ohio Shale Fleming Cty., KY		Eastern U.S. Shale (Indiana) Phillips Petroleum Sample	
Analysis, Wt%				
Moisture	2.6-2.9		1.5	
Carbon (HF Basis)	12.2		12.0	
Hydrogen	1.3		—	
Nitrogen	0.4		—	
Sulfur	2.2		—	
Fischer Assay				
Oil Yield (g/t)	10.1[1]		11.8[2]	
H_2O Yield (g/t)	10.0		6.9	
Oil Gravity: 60/60	0.9443		0.9504	
Gas from Fischer Assay	**Mol %**	**Wt %**	**Mol %**	**Wt %**
Hydrogen	30.4	2.8	25.3	2.0
CO	3.4	4.3	2.4	2.7
CO_2	6.6	13.2	11.3	19.7
H_2S	21.3	33.4	31.1	41.9
C_1	21.0	15.5	14.6	9.3
$C_2=$	1.7	2.2	1.8	2.0
C_2	7.5	10.3	5.4	6.4
$C_3=$	2.3	4.5	2.2	3.7
C_3	2.8	5.7	2.4	4.1
C_4's	2.4	6.3	2.8	6.3
C_5's	0.6	1.8	0.7	1.9
	100.0	100.0	100.0	100.0
Yield (g/100 g Shale)	—	1.61	—	3.46

Notes:

[1] This specific shale sample contained 11.87 percent total carbon and 0.11 percent carbonate carbon. The Fischer Assay residue contained 7.79 percent total carbon.

[2] This shale sample contained 12.44 percent total carbon and 0.44 percent carbonate carbon. The FA residue contained 8.32 percent total carbon.

These results demonstrate the relative merits of the different methods for concentrating the organics in eastern oil shale. Acid demineralizing alone results in a 20 percent (absolute) decrease in mineral matter with no apparent inclusion of chlorine or fluorine from the mineral acids used. A sample of more concentrated organic material can be generated by froth/flotation. Froth/flotation resulted in a decrease of the mineral matter to nearly 52 weight percent. Interestingly, sulfur-bearing material seems to be lost by froth/flotation, but not by acid demineralizing. Pyrites with specific gravities of about five are liberated, presumably, and sink during the froth/flotation. The HF and HCl used in the acid demineralizing would not be expected to dissolve pyrites.

The most concentrated organic-containing kerogen was obtained by first froth/floating the Hilpat shale and then acid demineralizing the recovered floated material. Bitumen that might have coated some mineral matter of the froth/floated shale was removed by Soxhlet extraction prior to treatment with mineral acids. The resulting kerogen concentrate from the combined treatment contained about 55 percent organic matter. Despite efforts to remove metastable fluorosilicates, the combined-treatment concentrate contained about 7 weight percent fluorine.

The results shown in Table 5 also confirm prior literature findings that the organic material in eastern oil shale is more coal-like than the kerogen found in Green River oil shale. Typical eastern kerogen H/C values (Table 5) are about 1.1. Green River kerogen H/C values are typically 1.4 to 1.6. Hence, eastern kerogen contains much less hydrogen per organic carbon atom. The elemental analysis data and previously obtained solid carbon-^{13}NMR data (along with similar data in the literature) supports the contention that eastern oil shale kerogen is much more aromatic than Green River kerogen.

Saponification of the acid treated concentrate led to the conclusion that less than 1 percent of the organic matter in this kerogen sample exists as saponifiable ester.

Trifluoroperoxyacetic acid (TFPA) oxidation of the froth/floated acid demineralized concentrate was used to retain alkyl groups and burn away aromatics. Products are presently being identified and quantified by GC/MS techniques.

Reductive alkylation of HCl/HF extracted Hilpat shale using hexamethylphosphorictriamide (HMPA) showed that this kerogen is more like coal than western oil shale kerogen, and that toluene solubility was increased to 3 percent by weight of the organic matter. This was an order of magnitude higher conversion than was observed with Green River kerogen. $_1$H-NMR analysis of these Hilpat toluene solubles reveals the extract to be primarily aliphatic.

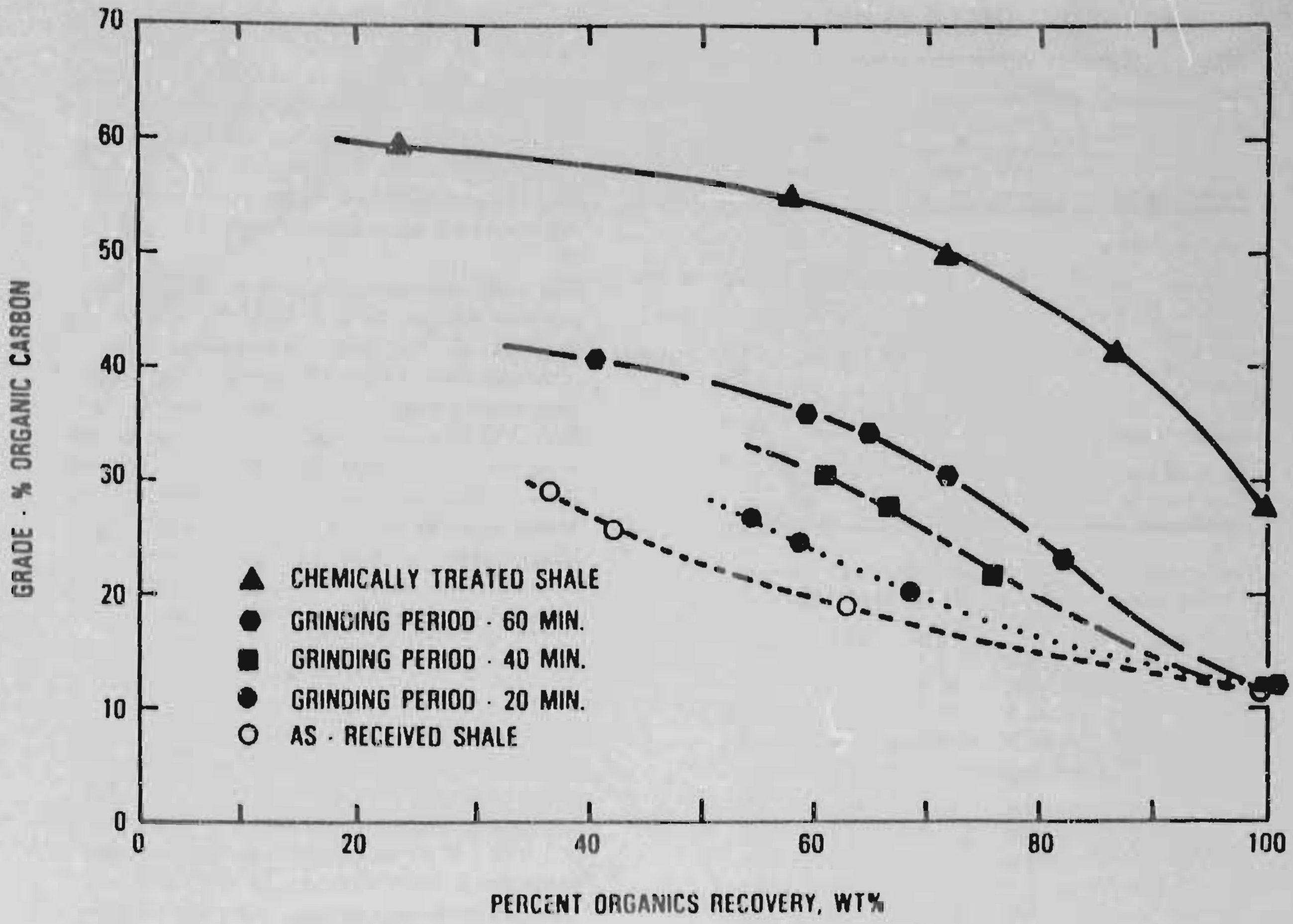

FIGURE 7. HILPAT BENEFICATION RESULTS: GRADE AND RECOVERY CURVES

Hydrogen donor runs have been made in a microreactor with Hilpat, Indiana, and western shales to observe the importance of using donor solvents in achieving high conversion levels. Experiments were also done to observe changes in the donor solvent. These experiments were used to observe the extent of solvent cracking and isomerization, and to measure the extent of chemical attachment (adduction) of the solvent with itself and shale-derived products.

The experiments were performed at temperatures to 450°C and reaction times between 0 (allowing 2.5 minutes for heating) and 30 minutes. The experiments were carried out with equal weights of shale and solvent. Unless specified, the experiments were conducted using a nitrogen atmosphere at 0.3 MPa(50 psig) pressure.

With Hilpat shale, donor solvents fell in the following decreasing order of effectiveness, based on carbon conversion:

- Octahydrophenanthrene
- Dimethyltetralin
- Tetralin
- Tetrahydroquinoline (THQ)
- Decaline
- Mesitylene

At reaction conditions of 450°C (842°F) and 30-minute residence time, up to 70 percent of the Hilpat shale was converted to liquid and gaseous products using octahydrophenanthrene. On a car-

TABLE 5. ELEMENTAL ANALYSES OF VARIOUSLY TREATED HILPAT SHALE SAMPLES

	Elemental Analysis, Wt %*								
Sample	C	H	N	S	O**	CL	F	Ash	H/C
Hilpat Shale, As Received	11.61	1.59	0.42	2.23	4.66	0.05	0.72	80.18	1.41
Hilpat Shale, Acid Demineralized	27.51	2.41	0.83	4.88	5.03	~0	.40	63.09	1.05
Froth/Floated Hilpat Shale	34.75	3.43	1.01	2.95	4.89	0.00	0.75	52.64	1.17
Froth/Floated and Acid Demineralized Hilpat Shale	37.89	3.46	1.08	2.85	7.38	0.00	7.07	45.17	1.08

* Elemental analyses were performed by either Galbraith Laboratories, Knoxville, Tennessee, or Microanalysis, Inc., Wilmington, Delaware.

** Directly determined oxygen by a modified Unterzarcher Method.

bon basis, this is equivalent to 2.0 times Fischer Assay. At the same reaction conditions, an 83.7 percent carbon conversion level was observed for the Indiana shale. This is 2.4 times the Fischer Assay conversion level.

Four extraction runs with Hilpat shale were made using a cascade reactor system. In this system, a solvent/shale slurry was injected into a preheated reactor. With the solvent tetralin at reaction conditions of 400°C and 30 minutes, this shale underwent a carbon conversion of ~ 40 percent (1.2 x FA). With increased conditions to 410°C and 60 minutes, carbon conversions of ~ 53 percent (1.6 x FA) were observed. Even in the latter case, low hydrocarbon gas yields occurred (0.4 gm/100 gm shale).

Initial experiments with an Indiana shale in both the cascade and microautoclave reactors have resulted in high conversion levels. At 450°C in tetralin, carbon conversion (toluene solubles) levels to 75 percent were observed. With the non-donor solvent decalin, conversion levels approached 50 percent. This is in contrast to a Fischer Assay carbon conversion level of 34 percent for this shale.

To provide a comparison with the above experiments with eastern shale, a series of runs were made at 400°C using western shale and the solvents tetralin or mesitylene. From the results, it appears that the solvent is playing a different role in the conversion of the two shales.

Specifically, mesitylene (MST) was a better solvent at 400°C for the western shale, or, perhaps, some tetralin was depositing on the shale in the form ofcoke, thereby resulting in a decrease of apparent conversion.

It has been demonstrated that the extent of shale conversion is strongly dependent upon donor capacity; solvent losses through adduction are acceptable for hydrocarbon solvents but excessive for nitrogen-containing solvents; hydroaromatic solvent losses through isomerization and cracking are reasonable at about 2 percent per pass. Initial results of the analysis of the oils from shales indicate a composition about equally distributed between aromatics, hydroaromatics, and combined alkenes and alkanes. Detailed product characterization is underway.

3.16 ROCKWELL INTERNATIONAL

Objectives

The goals of this program are to (1) conduct the testing, data reduction, and chemical analysis necessary to determine the performance of eastern oil shale in a flash hydropyrolysis (FHP) reactor; (2) select operating conditions suited to high yields of shale oil; and (3) perform a conceptual analysis and economic assessment of the process.

Background

The Energy Systems Group of Rockwell International is investigating the application of its FHP technology to the hydro-retorting of eastern oil shale. This technology can maximize the production of high-value liquid and gaseous products from eastern oil shale by reacting pulverized shale with hot hydrogen in the reactor. Since 1975, Rockwell International has been developing, under U.S. Department of Energy sponsorship, FHP of carbonaceous feedstocks.

In FHP, the oil shale is reacted with heated hydrogen at moderately elevated pressures (500 to 1,000 psig) in a compact, entrained-flow reactor to produce a selected high-quality product slate. Very short residence times and low reactor temperatures (i.e., high severity) favor hydrocracking of liquids and maximum production of gaseous products. Shale particle heat-up rates are extremely rapid (~ 50,000°F/s), and devolatilization of the kerogen occurs in milliseconds.

The residue (spent shale) retains all of the shale's ash content and any unreacted carbon. It is separated from the hydrocarbon products while they are still in the vapor phase and is recovered as a dry, free-flowing granular solid for disposal or further processing.

Discussion

The feedstock used during the reactor testing was a Cleveland Member of the Ohio shale obtained from the University of Kentucky's Institute for Mining and Minerals Research (IMMR), Lexington, Kentucky. The raw shale was pulverized to approximately 70 percent through 200 mesh.

Selection of the planned reactor test conditions was based primarily on analyses that use Rockwell's generalized kinetic analysis program, in conjunction with supporting experimental data from FHP testing with coal, heavy residual oils, and shale oil at Rockwell. The work of other investigators in the field of eastern oil shale conversion was also reviewed. Results of the test condition selection analysis indicated that:

- The reactor temperature range of interest was approximately 1,000 to 1,400° F.
- The residence time range of interest was 30 to 500 ms.
- The sensitivity to reactor pressure was low.

A minimum reactor temperature of about 1,000oF is required to obtain significant devolatilization of the oil shale, while temperatures much above 1,400°F will probably produce excessive liquid fragmentation and, hence, result in high gas production. A minimum residence time of $\cong$ 30 ms was calculated to be necessary for heat-up and devolatilization of the oil shale. It was also estimated that residence times of > 500 ms would result in excessive liquid fragmentation.

All six of the tests were conducted at a normal reactor pressure of 1,000 psig and a nominal oil shale flow rate of ¾ ton/h. The reactor used for the first three tests provided a nominal residence time of 200 ms; the reactor used for the last three tests provided 75 ms.

Increasing the reactor temperature from approximately 1,100 to 1,400°F increases overall carbon conversion and conversion to gas, and decreases conversion to liquids. The overall conversion varies from 61.4 percent to 70.0 percent, and appears to reach a plateau at ~ 70 percent. Carbon conversion to gas varies from 7.1 to 28.6 percent, while conversion to liquids varies from 55.5 to 41.2 percent. The effect of residence time on reactor performance is less significant than that of temperature in the residence time range that was investigated. Overall, carbon conversions to gas increase at longer residence times, while the corresponding carbon conversion to liquid decreases. Shale oil production decreases with increasing reactor severity, ranging in quantity from approximately 19.0 to 13.5 gallons of raw liquid produced per ton of oil shale.

Along with the hydrocarbon liquids, carbonaceous gases are formed in the reactor. The methane concentration in the gas ranges from about 35 to 50 mole percent and decreases with increasing reactor severity. The total C_2, C_3, and C_4 hydrocarbons account for about 50 mole percent of the gas over the entire range studied.

In general, hydrogen consumption increases linearly with reactor severity, a trend that is consistent with previously observed Rockwell coal liquefaction test data.

Analysis of the data obtained during the test series resulted in the selection of an operating point that is suitable for producing high yields of shale oil, high-value olefin by-products, and a portion of the plant fuel gas requirements.

Based on the selected operating point, a commercial plant conceptual design was developed. This plant was designed to produce 50,000 bbl/day of partially hydrotreated shale oil that was suitable for use as refinery feedstock for final processing. The plant uses commercially proven processes and equipment for all plant subsystems, other than the FHP reactor system.

Nominal reactor conditions are 1,000 psig, 1,200°F, and 75-ms residence time. The yield of upgraded product oil is approximately 21-gal/ton of dry shale.

Approximately 11 percent of the carbon in the shale is converted into C_2-C_4 paraffin and olefin compounds. Although fuel gas is needed for several plant systems, the high value of olefins as a plant by-product (~ $10/million Btu) makes them less desirable to use as sources of fuel. Therefore, it was decided to recover ethylene and propylene from the gas as a saleable by-product, and to incorporate a steam cracking plant into the process flow sheet to convert C_2-C_4 paraffins to olefins. Hydrogen produced during the cracking process also helps to reduce plant requirements for makeup hydrogen. Plant fuel requirements are met by supplementing internally produced fuel gases with purchased methane, as required.

The plant is designed to process ~ 4,150 ton/h of dry eastern oil shale into a high-quality oil feedstock for a petroleum refinery. The plant produces 50,000 bbl/day of hydrotreated oil. Saleable by-products include ethylene (857 tons/day), propylene (460 tons/day), anhydrous ammonia (187 tons/day), and sulfur (1,016 tons/day).

The shale is dried to 2 percent maximum moisture content, and is conveyed to crushers that reduce the size to ½ inch maximum. The crushed shale is then sent to ball mills to further reduce the size to 70 percent through 200 mesh. Shale is continuously dense-phase fed with a small amount of hydrogen at ~ 1,000 psig into the reactor, where it is uniformly mixed with 1,500°F hydrogen. The heat content of the hydrogen is sufficient to pyrolyze the oil shale and raise the products to a 1,200°F reactor exit temperature. Residence time in the reactor is 75 ms, during which ~ 67 percent of the carbon in the shale is converted to liquid and gaseous products.

The total plant investment was estimated at $1,994 million in first quarter 1983 dollars. This figure includes project contingency. The total capital requirement, including allowance for funds used during construction, start-up costs, working capital, etc., is $2,515 million. Net annual operating cost is $275 million after inclusion of by-product credits. The calculated average product selling price is $35.20 per barrel.

4.0 FUTURE YEAR RESEARCH PLANS

The FY 85 Oil Shale Program will complete the transition to the new structure that began in FY 84. The program is structured to derive the understanding of the oil shale conversion phenomena so that advanced concepts to produce liquids from shale can be developed. The highest priority in both the technology base and environmental mitigation elements is to generate the data essential to understand the conversion phenomena. The technology base element will generate the data and develop the predictive capabilities of optimal environmental control.

The restructured program will be accomplished in 10 years, and will be performed in two 5-year phases. The first phase is designed to acquire the best possible data. The second phase is designed to utilize the data through systems analysis and environmental control technology development to result in design of efficient, cost-effective, and environmentally acceptable conversion systems. The major activities to be initiated in FY 85 are as follows.

- The detailed 5-year plan for the chemical/physical properties and behavior of oil shales activity will be completed in early FY 85. Implementation of the plan will begin. WRI has been assigned the lead role in developing the plan. LPO/METC will establish a reference "Shale Bank" for use by all the participants. A contract will be awarded for the acquisition, preparation, and storage (in 5- and 55-gallon containers), of at least 10 reference shales. The reference shale will consist of at least five eastern and at least five western shales. By the end of FY 85 the bank will be established. Preparation of the first pair of reference shales for use in FY 86 will be underway.

- The detailed 5-year research plan for the surface processes — fast heat-up rate activity will be completed by METC in early FY 85. METC will design, construct, and begin operation of reference retorts needed to understand the chemistry and physics of the conversion phenomena at fast heating rates. METC will initiate development of a mechanistic model for fast heat-up rate conversion of oil shale.

- The detailed 5-year research plan for the surface processes — slow heat-up rate activity will be completed by LLNL in early FY 85. LLNL will design, construct, and begin operation of reference retorts that are needed to understand the chemistry and physics of the conversion phenomena at slow heating rates. LLNL will use its existing models as predictive tools for the laboratory experiments. Considerable experimental data exists for various slow heat-up rate processes. These data, albeit of various quality, represent a large data base. LLNL will complete a reference data book incorporating all the knowledge existing for slow heat-up rate processes based on the existing experimental data. LLNL will also complete a modeling and evaluation of the hydroretorting process.

- The detailed 5-year research plan for the in situ effort in the in situ processes and rock fragmentation activity will be completed by WRI in early FY 85. WRI will continue its efforts to understand the phenomena involved in in situ conversion through use of its facilities, especially the low void retort and the recently installed large block retort. The large block retort, capable of retorting a single block of shale with dimensions of 2 x 2 x 6 feet, can be used to simulate horizontal in situ conversion processes.

- The detailed 5-year research plan for the rock fragmentation effort in the in situ processes and rock fragmentation activity will be completed by SNL in early FY 85. LANL will complete its evaluation of the consortium tests, and SNL and LANL will complete their evaluations of the APF tests. SNL will negotiate for acquisition of a new field site and will begin site development for tests in FY 86. Site development is contingent upon acquisition of the site in FY 85. Exxon is interested in DOE use of the Colony mine, and will make its decision on the maintenance of the mine in early FY 85. If Exxon decides to keep the mine open, SNL could complete negotiations and begin site development in mid-FY 85.

- In the technology data base activity, METC will initiate the data inventory in FY 85. METC will identify the data sets and format required to computerize the oil shale technology data base. All program participants will begin transfer of the data to METC for compilation and analysis. METC/LPO will contract WRI to provide the LETC data base.

- METC/LPO will co-sponsor the 18th Oil Shale Symposium/First Western Synfuels Conference as an example of technology transfer to the private sector.

- METC, with the support of LANL, will initiate development of process evaluation in the systems analysis activity. The ASPEN code will be the primary tool for description and analysis of complete oil shale systems from extraction to production. As the activity progresses, ASPEN will be used to identify research needs and data gaps, and will be used to direct the research within the program.

- In the novel concepts activity, METC/LPO will solicit research from private industry. A novel concept is one with potential for significantly improving resource recovery through process efficiency, economics, or environmental acceptability. An example would be development of a high throughput, hydroretorting process for eastern shale. The awards, targeted for late FY 85, will allow for process development, rather than fundamental studies.

- METC/LPO will award a contract for modeling and laboratory experimental work utilizing volumetric heating by RF. IITRI and Texaco have completed RF field tests, but no predictive modeling capability was available. This 3-year contract will result in a predictive model for future laboratory and field testing of the concept.

- The detailed 5-year research plan for the siting methodology activity will be completed by LANL in FY 85. LANL will initiate modeling and laboratory efforts. The initial focus will be on air dispersion and transport modeling on a regional basis (e.g., the Piceance Basin), and on the correlation of resources and existing processes for plant siting in the Piceance Basin. The new activity is designed to provide a system of models that describes the regional impacts of various schemes for siting commercial plants. The models and data generated will result in the capability to predict technological environmental effects and identification of the type and amount of control technology required at a specific site for a specific process. Such capability will be useful to government, industry, and regulatory agencies in future decisions and policies.
- In the environmental data base activity, METC will initiate the data inventory in FY 85. METC will identify the data sets and format required for computerization of the oil shale environmental data base. LANL, LBL, LLNL, PNL, and WRI through a METC/LPO contract, will begin transfer of the data to METC for compilation and analysis.
- The detailed 5-year research plan for the environmental research — process gas/air will be completed in early FY 85 by WRI. In mid-FY 85, when year 3 of the DOE-WRI cooperative agreement begins, WRI will refocus its efforts to characterization of gaseous effluent streams. METC and LLNL will characterize the gaseous effluents from their respective reference retorts. LBL will complete the characterization of gaseous effluents relating to codisposal, and PNL will complete the speciation studies of gaseous effluents. The LANL effort will relate directly to siting methodology.
- The detailed 5-year research plan for the environmental research — water activity will be completed by WRI in early FY 85. In mid-FY 35, when year 3 of the DOE-WRI cooperative agreement begins, WRI will refocus its efforts to characterization of aqueous effluent streams. METC and LLNL will characterize the aqueous effluents from their respective reference retorts. LBL will complete the wastewater treatment study. PNL will complete the speciation studies of aqueous effluents.
- The detailed, 5-year, laboratory-scale research plan for the environmental research — solid waste activity will be completed by WRI in early FY 85. In mid-FY 85, when year 3 of the DOE-WRI cooperative agreement begins, WRI will refocus its efforts to characterization of solid effluent streams. METC and LLNL will characterize the solid effluents from their respective retorts. PNL will complete the speciation studies of solid effluents. In late FY 85, Associated Western Universities (AWU) and Waterways Experimental Station (WES) will complete the detailed engineering-scale research plan for solid waste disposal.
- The detailed 5-year research plan for the environmental research — retort abandonment activity will be completed by WRI in early FY 85. In mid-FY 85, when year 3 of the DOE-WRI cooperative agreement begins, WRI will refocus its efforts to address the retort abandonment issues identified in the research plan.
- METC/LPO will co-sponsor the Fifth International Conference "Chemistry for Protection of Environment." This transfer of technology will be for the international community and the private sector.

5.0 LIST OF ACRONYMS

APF	Anvil Points Facility
AWU	Associated Western Universities
C/CL	combustion/chemiluminescence
COS	carbonyl sulfide
DI	deionized water
DIC	dissolved inorganic carbon
DOC	dissolved organic carbon
DOE	Department of Energy
DTG	differential thermal gravimetry
ERDA	Energy Research and Development Administration
FBR	fluidized-bed retort
FFBT	fixed film biological treatment
FHP	flash hydropyrolysis
FRG	forest residue gasifier
FTIR	Fourier transform infrared
GAC	granular activated carbon
GASPE	gated spin echo decoupling
GC/FID	gas chromatograph with a flame ionization detector
GC/MPD	gas chromatograph/microwave plasma detector
GKI	Geokinetics, Inc.
HF/HCl	hydrofluoric acid/hydrochloric acid
HMPA	hexamethylphorictriamide
HSP	hot solids process
IGT	Institute of Gas Technology
IITRI	Illinois Institute of Technology Research Institute
IMMR	Institute for Mining and Minerals Research

LANL	Los Alamos National Laboratory
LBL	Lawrence Berkeley Laboratory
LETC	Laramie Energy Technology Center
LLNL	Lawrence Livermore National Laboratory
LPO	Laramie Project Office
METC	Morgantown Energy Technology Center
MIS	modified in situ
MSFB	multi-solids fluidized-bed
MST	mesitylene
NAWC	North American Weather Consultants
NPOSR	Naval Petroleum and Oil Shale Reserves
PIXE	particle-induced X-ray emission
PNL	Pacific Northwest Laboratory
PRU	Process research unit
RF	radio frequency
SESA	Society for Experimental Stress Analysis
SFC	Synthetic Fuels Corporation
SHALE	oil shale arbitrary lograngian-Eulerian
SNL	Sandia National Laboratory
SRR	solids recycle ratio
SRTD	solid residence time distribution
TDS	total dissolved solids
TFBR/C	twin fluidized-bed retort/combustor
TFPA	trifluoroperoxyacetic acid
TGA	thermogravimetric analyzer
TKN	total Kjeldahl nitrogen
TQMS	triple quadrupole mass spectrometer
TREE	total resource energy extraction

UWYRC	University of Wyoming Research Corporation
VMIS	vertical modified in situ
VPI	Virginia Polytechnic Institute
WES	Waterways Experiment Station
WRI	Western Research Institute
ZAA	Zeeman atomic absorption

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