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PRESSURIZED FLUIDIZED-BED HYDRORETORTING OF EASTERN OIL SHALES

Progress Report for the Period July-September 1988

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EXECUTIVE SUMMARY

This report presents the work performed during the fourth program quarter from July 1 through September 30, 1988, under Department of Energy (DOE) Contract No. DE-AC21-87MC11089 for the project "Pressurized Fluidized-Bed Hydroretorting (PFH) of Eastern Oil Shales." The Institute of Gas Technology (IGT) is the prime contractor for the overall program. Six universities are working with IGT as subcontractors; their responsibilities and achievements in the program are discussed below in the appropriate tasks.

In Task 1 (PFH Scoping Studies), five tests were conducted in the batch PFH unit. All tests were conducted with -100+140 mesh shale at a fluidization velocity of 0.04 ft/s. The shale was preheated to 550°F and retorted at 1050°F for 30 minutes at 1000 psig in all five tests. Results from replicate batch PFH tests showed an average oil yield and organic carbon conversion to gas, oil, and residue of 16.0 gal/ton (GPT), 26.2%, 54.8%, and 19.0%, respectively. The standard deviation of the oil yield for the three replicate tests was 0.65 GPT. Standard deviations of organic carbon distributions to gas, oil and residue from the replicate tests were 3.1%, 2.7%, and 3.3%, respectively. Carbon balances for the three tests averaged 95%.

Results from a test conducted at a 10-minute shale retorting residence time compared to a 30-minute shale residence time showed no difference in total carbon conversion. Results from a test conducted to determine if oil mist is being recirculated and cracked to gas showed that recirculation of mist was not occurring.

Detailed chemical analysis of the feed shale and products from PFH tests showed that the shale used for the initial scoping tests had been severely weathered. Results of batch PFH tests with a "fresh" sample of Indiana New Albany shale showed oil yields of about 200% of Fischer Assay with no evidence of weathering. The "fresh" sample of Indiana New Albany shale will be used for the remainder of the test program for this task.

Modification and construction of the continuous PFH was completed this quarter. Shakedown and operation of the continuous unit is expected to commence next quarter.

In Subtask 3.2 (Electrostatic Desulfurization), the Illinois Institute of Technology (IIT) installed a new cyclone tribocharger, and began testing with

40 μm -size shale and pyrite particles. The quantity of charges developed on these particles was one order of magnitude higher than those developed by the honeycomb charger, however, no separation occurred during tests with the 40 μm -size shale. IIT determined the extent of liberation of pyrites as a function of particle size for ultrafine shale using a scanning electron microscope and an optical microscope for the size determinations. About 40% liberation of pyrite occurred at 40 μm -size particles. A 70% liberation of pyrite occurred at about 10 μm -size particles. Separation of pyrites from the Eastern shale was determined to be a function of the gas velocity.

In Subtask 3.3.1 (Microbial Desulfurization and Denitrification), Ohio State University (OSU) had the TEDXF spectrometer repaired, readjusted and tested for accuracy. OSU improved their sulfur analysis technique for shale samples. OSU also obtained an ion-selective ammonia probe that they are preparing to use in their denitrification studies next quarter. They are designing a continuous flow train and refining methods to trap and quantify ammonia.

In Subtask 3.3.2 (Microbial Process Development), a 500-gram sample of beneficiated shale was obtained from the University of Alabama for testing. Slurries containing 4 and 8 wt % beneficiated shale were prepared and settling characteristics were examined. A 1-liter bioreactor was constructed and inoculated with a 4 wt % slurry of beneficiated oil shale. The slurry was also inoculated with a microbial culture developed at IGT that is able to remove organic sulfur from sulfur compounds. Based on plate counts, the organisms are viable in the 4% oil shale slurry with marginal growth after 10 days. The growth of the organism in the oil shale will continue to be monitored.

In Subtask 3.5 (Restricted Pipe Discharge System [RPDS]), tests were initiated using two piping configurations. A "vertical downward" configuration and a "two-stage vertical downward" configuration were tested this quarter. Tests were conducted at system pressures of 150, 300 and 600 psig and at solids flow rates of 1500, 3000, and 6000 lb/h using -20+40 mesh shale in the "vertical downward" RPDS configuration. Pressure drops per unit length ($\Delta P/L$) were determined as a function of superficial gas velocities for three shale particle size consists, -1/4+80 mesh, and -20+40 mesh, and 40+80 mesh.

Two types of solids flow restrictions in the disengaging vessel were also tested.

The effects of pipe diameter, shale particle size, and one versus two-stage systems were tested. Results of these tests showed that the $\Delta P/L$ decreased dramatically as the diameter of the RPDS pipe is expanded from 2-inch to 3-inch. The data also show that the $\Delta P/L$ profiles do not change significantly as the particle size is changed. Results of the tests showed that the two-stage system was able to operate as smoothly as the single-stage system. The total gas flow out of the two disengaging vessels was not significantly different than the gas flow obtained earlier with the single-stage system.

The University of Alabama Mineral Resources Institute (MRI) is responsible for the work being conducted in Task 4 (Beneficiation Research). Under Subtask 4.1.1 (Ultrasonic Grinding), Dr. Chiang of the University of Pittsburgh is negotiating arrangements by which he will be able to schedule the work planned under this contract. Under Subtask 4.1.2 (Pressure-Cycling Comminution), concurrent with the move of the Principal Investigator to the University of Nevada (Reno) an agreement for the continuation of his activities was negotiated with the University of Nevada. A contract has been prepared between these Universities and forwarded through IGT for DOE approval. In Subtask 4.1.3 (Stirred Ball Mill Grinding), a 4-liter NETZSCH stirred ball mill was received and installed this quarter. During shakedown of the unit, it was discovered that the pump, supplied with the mill, was not satisfactory for handling -20 mesh feed to the mill. A substitute pump is being exchanged for the original pump. Under Subtask 4.2.1 (Column Flotation Tests), MRI conducted a series of tests in a 1-meter column cell operating in batch mode. The results show that the best separations are achieved at low air flow rates and at low frother concentrations. It was also concluded that the addition of sodium silicate had no effect on the separation. A second series of tests were performed in a 1.8 meter column cell (10.0 cm diameter). Initial results from the tests with the 1.8 meter column indicate that high kerogen recoveries were achieved, but the concentrates were of lower grade than achieved in the 1-meter column tests. In Subtask 4.2.2 (Air Sparged Cyclone), a 2-inch diameter air-sparged cyclone was received and installed this quarter. Tests will be conducted when sufficient feed material is

obtained from the NETZSCH mill. In Subtask 4.2.3 (LICADO Process), initial test results indicate that it was difficult to upgrade the -200 mesh sample, however additional tests will be conducted with selective dispersants for the mineral matter to achieve improved results with this size sample. Tests with the 10 μ m oil shale sample showed that a partial upgrading of the sample was possible. A detailed test program will be carried out after receipt of new samples of oil shale from MRI. UP is also investigating the mechanisms of the LICADO process through surface and interfacial property measurements. A high-pressure apparatus equipped with the necessary optical and photographic accessories was utilized for contact angle measurements. Results showed that the average contact angle of water on polished samples of oil shale varied from 44° to 115°F at carbon dioxide pressures from atmospheric to 870 psig, respectively. This indicates that the oil shale surface is being rendered hydrophobic in the presence of CO₂ and that it is possible to effect a significant upgrading of the oil shale by the LICADO process.

In Subtask 4.3.2 (Tailings Disposal Studies), tailings produced in the beneficiation of Alabama shale were collected and tests were performed to determine the pozzolanic properties of the material, including measured setting time and strength over a prolonged curing time.

In Task 5 (Operation of PFH on Beneficiated Shale), the technique of pulsed-fluidization was investigated for beneficiated shale to determine if this technique would improve the quality and degree of fluidization of the shale at reasonable superficial gas velocities. Smooth fluidization and good solids mixing were obtained at gas velocities where gas channeling and only local fluidization were previously found with a continuous fluidizing gas flow. Plans are presently underway to fluidize beneficiated shale at elevated temperatures (approximately 500°F) to determine whether beneficiated shale can be fluidized with continuous gas flow without channeling in a high-temperature fluidized bed.

In Subtask 6.2 (Water Availability and Treatment Studies), Tennessee Technological Institute (TTU) essentially completed work on determining the locations and quantities of water flows in areas containing shale outcrops in Alabama, Indiana, Kentucky, Michigan, Ohio, and Tennessee. Sites were selected in each of the six states which could accommodate a commercial-scale PFH retorting facility. In Subtask 6.2.2 (Water Treatability), TTU conducted

batch biological experiments to determine the rates and degrees of removal of two substrates, propionitrile and acetone, individually, and in a mixture of the two.

In Subtask 6.3 (Heavy Metals Removal), the University of Michigan continued laboratory studies with samples of raw and hydroretorted shale to develop an understanding of the uncatalyzed dissolution kinetics.

In Subtask 6.4 (PFH System Analyses), modifications to the computer program that simulates a PFH process plant have been essentially completed. The modified computer program will be reviewed next quarter and additional inputs added when results from other tasks are available.

In Task 7 (Sample Procurement, Preparation and Characterization), samples of five Eastern oil shales have been collected, crushed to -1 inch, and stored under nitrogen in plastic-lined drums. Arrangements have been made to collect a sixth sample from the Chattanooga formation next quarter.

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INTRODUCTION

The Devonian oil shales of the Eastern United States are a significant domestic energy resource. The overall objective of the 3-year program, initiated in October 1987 by the U.S. DOE (Contract No. DE-AC21-87MC11089), is to perform the research necessary to develop the pressurized fluidized-bed hydroretorting (PFH) process for producing oil from Eastern oil shales. The program also incorporates research on technologies in areas such as raw shale preparation, beneficiation, product separation, and waste disposal that have the potential of improving the economics and/or environmental acceptability of recovering oil from oil shales using the PFH process. The program is divided into the following eight tasks:

- Task 1. PFH Scoping Studies
- Task 2. PFH Optimization Tests
- Task 3. Testing of Process Improvement Concepts
- Task 4. Beneficiation Research
- Task 5. Operation of PFH on Beneficiated Shale
- Task 6. Environmental Data and Mitigation Analyses
- Task 7. Sample Procurement, Preparation, and Characterization
- Task 8. Project Management and Reporting.

In order to accomplish all the program objectives, the Institute of Gas Technology (IGT), the prime contractor, is working with six other institutions; the University of Alabama/Mineral Resources Institute (MRI), Illinois Institute of Technology (IIT), the University of Michigan (UM), Ohio State University (OSU), Tennessee Technological University (TTU) and the University of Pittsburgh (UP).

This report presents the work performed during the fourth program quarter from July 1 through September 30, 1988.

ACHIEVEMENTS

Task 1. PFH Scoping Studies

The objective of this task is to determine the effects of process variables on product yields. The results of these tests will be used in Task 2 (PFH optimization tests). This task is divided into two subtasks: Batch Tests and Continuous Tests.

Discussion

Work during the reporting period was active in Subtask 1.1 (Batch Tests) and Subtask 1.2 (Continuous Tests). The objective of Subtask 1.1 is to construct and operate a laboratory-scale batch test unit to determine the effects of a number of independent variables that may affect the product yields of the PFH process.

The liquid collection system for the batch PFH was modified this quarter to improve liquid collection. The heat transfer area of the exchanger/condenser was increased and a demisting filter was added. Five successful tests were subsequently conducted in the batch PFH unit. All tests were conducted with -100+140 mesh shale at a fluidization velocity of 0.04 ft/s using a top feed position. The shale was preheated to 550°F and retorted at 1050°F for 30 minutes at 1000 psig in all the tests. Three of the tests were replicate tests conducted to determine the reproducibility of the data from the batch unit. A fourth test was conducted at a 10-minute shale retorting residence time to determine the effect of a shorter residence time on oil and gas yields. One test was conducted without the recycle feed gas compressor to determine if oil mist is being recirculated and cracked to gas.

The results from the replicate batch PFH tests showed an average oil yield and organic carbon conversion to gas, oil, and residue of 16.0 gal/ton (GPT), 26.2%, 54.8%, and 19.0%, respectively. The standard deviation of the oil yields for the three replicate tests was 0.65 GPT. Standard deviations of organic carbon distributions to gas, oil and residue from the replicate tests were 3.1%, 2.7%, and 3.3%, respectively. Carbon balances for the three tests averaged 95%.

Results from the test conducted at a 10-minute shale retorting residence time compared to a 30-minute shale residence time showed no difference in total carbon conversion. However, the conversion to liquid products was lower

and gas yield was higher than in the longer residence time test. Additional tests will be performed since the results are contrary to expectation.

Results from the test conducted to determine if oil mist is being recirculated and cracked to gas showed that recirculation of mist was not occurring.

High water yields and lower than expected oil yields from the batch PFH tests from the present feed shale sample (presumably an Indiana New Albany shale) prompted a comparison of this feed shale with three other shales tested in another program, including an Indiana New Albany and a Kentucky Sunbury shale. Fourier Transform Infrared (FTIR) spectroscopy was used to examine the differences between the feed shale used for tests in the batch PFH test program to date and four samples previously tested. Results of the FTIR analysis show that the shale presently being used does not match any of the four samples tested, including Indiana New Albany shale. Analysis of the present sample indicates that it may have undergone extensive weathering. A fresh sample of Indiana New Albany shale was received this quarter (Table 1) and one drum of material was crushed and prepared for testing in the batch PFH unit for the remainder of the test program for this task.

Table 1. ANALYSIS OF "FRESH" SAMPLE OF INDIANA
NEW ALBANY FEED SHALE

Moisture, wt %	3.02
Ultimate Analysis, wt % (dry basis)	
Ash	78.70
Organic Carbon	13.89
Mineral Carbon	0.09
Hydrogen	1.60
Sulfur	3.43
Nitrogen	0.59
Gross Calorific Value, Btu/lb	2787
Fischer Assay Oil Yield, GPT	13.7

Three batch tests were subsequently performed using the "fresh" sample of shale. Two tests were performed to determine the effect of using either sand or spent shale as the inert heat sink material in the reactor. The other test was made to prepare the spent shale to be used in the batch tests. Carbon

conversions and oil yields for the two tests conducted using sand and spent shale in the reactor were 84.3 and 82.6%, and 27.5 and 29.3 GPT, respectively. The two runs were conducted at 1000°F with a shale preheat temperature of approximately 600°F. A comparison of the results using sand and spent shale as a heat sink in the reactor indicates that the spent shale does not significantly affect the oil yield or carbon conversion when processed in the batch PFH unit. The differences in conversions and yields noted are within the experimental precision of the unit. The data obtained using sand in the batch PFH reactor should be scalable to the continuous PFH system. The oil yields obtained in the batch PFH unit for these tests were both 200% of Fischer Assay.

Modification and construction of the continuous PFH was completed this quarter. Shakedown and operation of the continuous unit is expected to commence next quarter.

Task 2. PFH Optimization Tests

The objective of this task is to obtain laboratory- and bench-scale data for optimizing the PFH process with six Eastern oil shales. This task is divided into four subtasks: Lab-Scale Batch Tests, Lab-Scale Continuous Tests, Bench-Scale Tests, and Data Analyses and Correlations.

Discussion

This task will be initiated during the second program year.

Task 3. Testing of Process Improvement Concepts

The objective of this task is to obtain data on novel process concepts that have the potential for improving the overall economics of PFH processing with Eastern oil shales. This task is divided into five subtasks corresponding to the five concepts being tested: In-Bed Sulfur Capture, Electrostatic Desulfurization, Microbial Desulfurization and Denitrification, Electroseparation of Shale Oil and Fines, and Restricted Pipe Discharge System (RPDS).

Discussion

Subtask 3.2. Electrostatic Desulfurization

The objective of this subtask is to remove pyritic sulfur from Eastern oil shales using an electrostatic process. This subtask is being conducted by the Illinois Institute of Technology (IIT). During the quarter, IIT installed

the new cyclone tribocharger, and began testing with 40 μm -size shale and pyrite particles. The charges developed on these particles were one order of magnitude higher than those developed by the honeycomb charger. Ten pounds of ultrafine ground (4 to 8 μm) shale were produced during the quarter and an electrostatic separation test in the existing sieve conveyor unit was attempted.

A series of tests with ultrafine shale were conducted in the sieve conveyor. The air/particle suspension was introduced into the conveyor after tribo-electrifying in the cyclone tribocharger. At an air velocity of 0.5 m/s, the solids all settled and passed through the positive electrode and no separation was achieved. An additional air stream was introduced after the cyclone tribocharger to increase the air velocities to up to 25 m/s. The results of tests conducted with the higher air velocity indicate better separation of the solids.

The ratio of the particles migrating toward either the positive or negative electrodes in the existing conveyor system was investigated as a function of inlet particle velocity at a constant applied potential of 18,000 volts. The results (Figure 1) show that the ratio of particles collected at the positive electrode to those at the negative electrode decreased from 12.5 to nearly 0 as the velocity was increased from 2 to 10 m/s.

Figure 1. THE EFFECT OF GAS VELOCITY ON THE RATIO OF PARTICLES MIGRATING TO THE POSITIVE ELECTRODE OR TO THE NEGATIVE ELECTRODE

IIT determined the extent of liberation of pyrites as a function of particle size for ultrafine shale using a scanning electron microscope (JOEL-JSM-35CF) and an optical microscope (Leitz Metallograph S-2000Y) for the size determination.

The number of particles greater than 40 μm indicated about 40% liberation of pyrites at these particle sizes. Figure 2 shows the effect of particle size on the liberation of shale pyrite.

Figure 2. PERCENT MINERALS LIBERATED AS A FUNCTION OF PARTICLE SIZE

Pyrites in finely ground shale appeared to oxidize in air. A color change was observed visually. Chemical analyses of freshly ground and weathered shale (ground particles exposed to air for several weeks) showed that the pyritic sulfur contents of these samples were 4.31 and 3.38 wt %, respectively. This suggests that samples have to be stored under an inert atmosphere.

Two tests were conducted with the 40- μm Indiana New Albany shale in the electrostatic conveyor system. The inlet gas velocities were varied for these runs. Poor separation occurred, possibly due to recirculation of air in the conical section beneath the perforated electrode. Recirculating air carries particles with it through the holes in the electrode. The electrode was subsequently modified to prevent the shale particles from being dragged into the holes in the electrode.

Surface charge measurements were made for 5- μm particles of Indiana New Albany shale and chemically pure pyrites as a function of inlet gas velocities using a Faraday cage. These data are shown in Figure 3. The surface charge of both shale and pyrites increases with velocity as expected. However, the rate of increase of charge for pyrites is much higher than that for shale. This results in a crossover of charges of pyrites and shale at the system operating conditions. This crossover occurs at a gas velocity of around 5.8 m/s.

Figure 3. EFFECT OF GAS VELOCITY ON THE SURFACE CHARGE OF SHALE AND PYRITE

Two tests were made in the modified conveyor system. The formation of a particle layer at the negative electrode was observed. The thickness of this layer was observed to increase with time. This layer was carefully removed

from the electrode and analyzed for organic carbon and for pyritic sulfur. This sample was found to have 20.5% carbon compared with the feed composition of 12.3% carbon. Pyrites were found also to migrate toward the negative electrode. A second stage may be required for separation of pyrites from beneficiated shale.

Subtask 3.3. Microbial Desulfurization and Denitrification

The overall objective of this subtask is to achieve microbial removal of organic sulfur and nitrogen from oil shales. Work on Subtask 3.3.1 (Culture Development) is being conducted by Ohio State University (OSU). The objective of this subtask is to develop microbial cultures for the biological removal of organic nitrogen and sulfur from Eastern oil shale.

During the quarter, OSU had the TEDXF spectrometer repaired. Two electronic boards for the computer that had failed, were ordered, received, and installed. The spectrometer was readjusted and tested for accuracy and precision.

OSU improved their sulfur analysis technique for shale samples. The basic protocol is to 1) analyze each individual sample in the TEDXF spectrometer 3 times under identical analytical parameters, 2) expose the shale to various experimental conditions, and then collect and dry the sample, and 3) analyze each sample again in the TEDXF spectrometer.

OSU has also obtained an ion-selective ammonia probe that they are preparing to use in their denitrification studies next quarter. They are designing a continuous flow train and refining methods to trap and quantify ammonia, based on information gained from experiments with Proteus vulgaris growing in urea broth. The system is being readied to initiate small-scale experiments utilizing shale as the inoculum and substrate.

The objective of Subtask 3.3.2 (Microbial Process Development), is to determine the effects of process conditions and inocula from Subtask 3.3.1 on the efficiencies and rates of organic nitrogen and sulfur removal from Eastern oil shale.

During the quarter, 500 grams of beneficiated oil shale were obtained from the University of Alabama. The sample was analyzed for the following physical characteristics: bulk density, particle density, true density and particle size distribution. Also, a chemical ultimate analysis was performed.

The results of these analyses are reported in Table 2. The average particle size (D_p) of the sample was determined by standard (dry) sieve analysis to be 646 microns. Slurries containing 4 and 8 wt % beneficiated Alabama oil shale were prepared and the settling characteristics of these slurries were examined. Batch settling tests without agitation were performed and analyzed based on the method by Kynch.* The change in height of the clarification zone, which is the interface between the settled oil shale layer and clear liquid was monitored with time. The heights of the clarification zone versus time for the 4% and 8% oil shale slurries are presented in Figure 4. The figure suggests that initially the movement of the clarification zone was faster for the 4% slurry than the 8%. This may be due to less resistance encountered by the 4% slurry because there are fewer shale particles in the same cross-sectional area. The values of the settling velocities and concentrations of the slurry at the clarification zone were determined from these plots and the settling curves were constructed (Figure 5). As the concentration of the shale in the clarification zone for the 4% slurry approached that of the 8% slurry, the settling curves become similar for both concentrations. Further experiments are required to understand the settling characteristics of the beneficiated shale.

Also during the quarter, a 1-liter bioreactor was constructed and inoculated with a 4% slurry of beneficiated oil shale. The mixing and air flow rate in the bioreactor can be controlled. The air flow rate was maintained at about 80 ml/min, which is the maximum flow rate the system can handle without excessive liquid loss. The oil shale slurry was being well mixed with no settling at approximately 250 rpm; therefore, this rate was maintained.

The slurry was also inoculated with IGTS7, a microbial culture developed at IGT that is able to remove organic sulfur from sulfur compounds, such as dibenzothiophene, typical of those present in coal. This culture grows at a neutral pH. Therefore, the oil shale slurry was adjusted from a pH of 3 to a neutral pH using a phosphate buffer (final pH 6.8) and inoculated. Microbial growth was monitored. Based on plate counts, the organisms are viable in the 4% oil shale slurry with marginal growth after 10 days.

* Introduction to Chemical Engineering, Badger and Banchero, Eds, pp. 650-657, 1955.

Table 2. PHYSICAL CHARACTERISTICS OF ALABAMA OIL SHALE
AND ULTIMATE CHEMICAL ANALYSIS

Density	
Bulk, lb/ft ³	38.4
Particle, g/ml	0.71
True, g/ml	1.80
Average Particle Size,* μm	646
Ultimate Analysis, % (dry basis)	
Carbon	34.29
Hydrogen	3.18
Nitrogen	1.55
Sulfur	8.36

* $D_p = \sum x_i d_i$. Standard (dry) sieve analysis.

Figure 4. EFFECT OF SLURRY CONCENTRATION ON THE CLARIFICATION ZONE HEIGHT DURING SETTLING TESTS CONDUCTED WITH BENEFICIATED SHALE

Figure 5. EFFECT OF SLURRY CONCENTRATION ON SETTLING VELOCITY

The growth of the organisms in the oil shale will continue to be monitored. At the end of 1 month of incubation, the shale will be removed and analyzed for nitrogen and/or sulfur content. In the present oil shale slurry, hydrocarbons serve as the carbon source for IGTS7 metabolism. IGTS7 can also readily use glucose as a carbon source. With glucose present as a carbon source, IGTS7 can utilize the sulfur in a wide range of model organic sulfur compounds. Therefore, glucose will be added as an auxiliary carbon source.

Subtask 3.5. Restricted Pipe Discharge System (RPDS)

Objective

The objective of this subtask is to determine the feasibility of using the RPDS for discharging spent shale from a pressurized fluidized-bed shale retort.

Equipment Description and Operation

A flow sheet of one RPDS configuration used in the test program is shown in Figure 6. This configuration was called the "vertical downward" configuration and its dimensions are shown in Figure 7. The pressure vessel was approximately 9 feet 6 inches high and 36 inches in diameter and was capable of operating at pressures of up to 650 psig. The feed vessel was equipped with a 60-degree-angle internal cone to facilitate solids removal at the bottom. The gas-solids disengaging vessel was 3 feet 6 1/2 inches high and 18 inches in diameter.

During a test, the sample solids were initially charged to the pressure vessel. Solids flowed out of this vessel through a section composed of 2-inch- followed by 3-inch-diameter pipe, and then into the 18-inch-diameter disengaging vessel. A packed bed of solids was maintained in the disengaging vessel. This packed bed acted as a solids flow restriction at the end of the pipe. A 3-inch-diameter slide valve located below the disengaging vessel, was used to control the solids flow rate in the system.

The solids flowed through the slide valve into a 2-inch-diameter pneumatic conveying line and then into a 4-foot-diameter solids receiver vessel. The receiver vessel was used to store the solids discharged from the disengaging vessel during a test, and was maintained at atmospheric pressure. Following a test, the feed vessel was depressurized, and the 3-inch-diameter

Figure 6. SCHEMATIC DRAWING OF VERTICAL DOWNWARD RPDS TEST UNIT

Figure 7. VERTICAL DOWNWARD RPDS TEST UNIT DIMENSIONS

ball valve located between the receiver and the pressure vessel was opened to allow the solids to flow into the pressure vessel.

Solids flow rates in the system were determined by diverting and collecting the solids in a container over a measured time interval, and then weighing the solids. This was accomplished by using the two ball valves located below the 3-inch slide valve.

Nitrogen gas was used as the motive gas and was added to the system near the top of the pressure vessel. A back-pressure regulator was used to maintain a constant pressure in the pressure vessel. Gas from the disengaging vessel was discharged from the system at atmospheric pressure through a rotameter.

Pressure taps were located along the entire flow path. The taps were connected to differential-pressure transmitters to obtain pressure drops between various points in the system. These differential pressures were recorded in all tests.

A second piping configuration was also investigated in the RPDS tests. Its configuration and dimensions are shown in Figures 8 and 9, respectively. This was basically a "two-stage vertical downward" configuration in which system gas was removed not only at near atmospheric pressure, but also simultaneously at a higher pressure. This configuration was called the "two-stage" configuration.

A third piping configuration presently under construction that will be tested in the RPDS program is shown in Figure 10. This configuration is called the "vertical transfer" configuration. In this configuration, solids first flow downward out of the pressure vessel into a short, vertical section of 2-inch-diameter pipe, and then into a horizontal section of 2-inch-diameter pipe. The solids then flow upward through a long vertical section of 2-inch-diameter pipe. Following this section, the solids pass through a horizontal section of 2-inch-diameter pipe, and then through a vertical downflow 3-inch-diameter pipe section back into the disengaging vessel. The 3-inch-diameter slide valve located below the disengaging vessel will control the solids flow rate in the system.

Figure 8. SCHEMATIC DRAWING OF TWO-STAGE RPDS TEST UNIT

Figure 9. TWO-STAGE RPDS TEST UNIT DIMENSIONS

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Figure 10. SCHEMATIC DRAWING OF VERTICAL TRANSFER TEST UNIT

Experimental Procedure

In a typical test, the shale test material is loaded into the 3-foot-diameter pressure vessel. The 3-inch-diameter slide valve and the 3-inch-diameter ball valve are closed. The 2-inch-diameter ball valve below the pressure vessel is then opened, and the unit is pressurized. During pressurization, the solids flow through the pressure-reduction discharge piping and into the gas-solid disengaging vessel. The flow of solids ceases when a packed bed of solids is established in the disengaging vessel. After reaching the desired system pressure, the steady-state pressure drops between various sections of the pressure-reduction piping, the gas flow out of the disengaging vessel and other system parameters are recorded with no solids flow in the unit. The desired air flows in the 2-inch-diameter pneumatic conveying line are then set. The conveying line velocity is set at approximately 30 to 35 ft/s. Solids flow is then started by opening the 3-inch-diameter slide valve. The position of the slide valve is adjusted until the desired solids flow rate is achieved. Measurement of the solids flow rate is accomplished by diverting and collecting the solids over a short period of time. At each solids flow rate, pressure drops, exit gas flows out of the disengaging vessel, and other system parameters are recorded. At the end of the test, the system is depressurized.

The operating procedure is basically the same for the "vertical downward" and the "vertical transfer" configurations. For the two-stage system, gas is discharged from the Stage 1 and Stage 2 disengaging vessels simultaneously. The pressure in Stage 1 is set at the desired constant value by setting the backpressure regulator in the gas outlet line from the Stage 1 pressure vessel. All system pressure drops and gas flows from the Stage 1 and the Stage 2 disengaging vessels are also recorded.

Materials

Three different size consists of shale material were used in this investigation. The size range and the physical characteristics of each of these materials are given in Table 3. Minimum (U_{mf}) and complete (U_{cf}) fluidization velocities were experimentally determined for each of these solids in a 2-inch-diameter Plexiglas fluidization column. The fluidization curves for these shale materials are shown in Figures 11, 12, and 13.

Table 3. PHYSICAL CHARACTERISTICS OF SOLIDS TESTED

Screen Size, U.S.S. Mesh	Shale Sample		
	-14+30	-20+40	-40+80
	-Weight % Retained on Screen--		
+ 10	--	--	--
-10 + 12	0.4	--	--
-12 + 14	0.6	--	--
-14 + 16	--	--	--
-16 + 18	2.7	--	--
-18 + 20	9.7	0.2	--
-20 + 30	53.7	18.7	--
-30 + 35	--	45.9	2.9
-35 + 40	26.3	5.6	0.1
-40 + 50	--	24.8	18.6
-50 + 60	6.3	2.9	18.4
-60 + 80	--	1.1	43.5
-80 + 100	0.1	0.8	--
-100 + 120	--	--	15.3
-120 + 140	0.2	--	--
-140 + 170	--	--	0.5
-170 + 270	--	--	0.2
-270 + 400	--	--	0.5
Total	100.0	100.0	100.0
Average Particle Size, D_p , μm	621	471	224

Particle Density = 128.6 lb/ft³
 Bulk Density = 74.5 lb/ft³

$$* D_p = \frac{1}{\sum x_i / d_{p_i}}$$

Figure 11. FLUIDIZATION CURVE FOR -14+20 MESH SHALE

Figure 12. FLUIDIZATION CURVE FOR -20+40 MESH SHALE

Figure 13. FLUIDIZATION CURVE FOR -40+80 MESH SHALE

Results and Discussion

Solids Flow Restriction Inside the Disengaging Vessel

Two different types of solids flow restriction were tested using the "vertical downward" RPDS configuration. The purpose of the test was to determine the type of restriction that could provide the best type of solids flow restriction inside the disengaging vessel. Tests were conducted at system pressures of 150 and 300 psig, and at solids flow rates of 1500, 3000, and 6000 lb/h using -20+40 mesh shale.

A drawing of the first solids flow restriction tested is shown in Figure 14. It consists of four gas-solid separation cylinders inserted into the disengaging vessel. Each cylinder was made of a continuous wire screen, which allowed gas, but not solids, to pass through it. The gas-solid separation cylinders were spaced at 90 degrees around the vessel and concentric to the solids feed line into the vessel. During operation, the entire vessel was almost completely filled with the test solids.

Several tests were conducted with this configuration. In all of the tests, the system operated very smoothly. The pressure reading inside the disengaging vessel was steady in all tests. The solids flow in the system was stable and easily controlled.

A second type of solids flow restriction in the disengaging vessel was also tested. The second flow restriction (Figure 15) was simply a packed bed of solids maintained in the bottom of the disengaging vessel. The advantage of this type of restriction was that it is extremely simple, just a bed of solids in a small vessel. Several tests were then conducted using the same solids material used with the first configuration. Results of the tests showed that this type of restriction was able to perform satisfactorily only at a relatively low system pressure (150 psig). At a pressure of 300 psig and high solids flow rate (6000 lb/h), the gas flow (40.6 scfm) out of the disengaging vessel was large enough to cause local fluidization of the solids near the end of the 3-inch-diameter RPDS pipe. When this occurred, the restriction to solids flow was destroyed, resulting in uncontrollable flow of the solids. This flow restriction was, therefore, considered to be unacceptable.

Figure 14. SCHEMATIC DRAWING OF DISENGAGING VESSEL
WITH SCREEN BARRIER RESTRICTION

Figure 15. SCHEMATIC DRAWING OF DISENGAGING VESSEL AND SOLIDS FLOW RESTRICTION WITHOUT SCREEN BARRIER RESTRICTION

Effects of System Pressure and Solids Flow Rate

The effects of system pressure and solids flow rate on the operation of the RPDS were determined by testing at three different nominal pressures (150, 300, and 600 psig) and three different solids flow rates (1500, 3000, and 6000 lb/h) using the "vertical downward" RPDS configuration. In each test, the gas rate out of the disengaging vessel, the pressure profile, and the pressure drop per unit length profile over the length of the pressure reduction pipe were determined.

In general, the RPDS operated very smoothly. Figure 16 shows the effect of system pressure on the total gas flow out of the disengaging vessel for the three different solids flow rates tested. This figure shows that the amount of gas flowing out of the disengaging vessel increases with increasing system pressure. This result was expected, because in order to generate the additional pressure drop required at high pressures, gas velocity in the RPDS pipe had to increase. The gas flow from the disengaging vessel was also found to be almost linearly proportional to system pressure.

Increasing the solids flow rate from 1500 to 6000 lb/h was found to increase the gas flow from the disengaging vessel only slightly. This was because the gas velocity was much greater than the particle velocity inside the depressurization pipe. A typical gas velocity near the end of the 3-inch-diameter depressurization pipe at a solids flow of 1500 lb/h was calculated to be 14 ft/s at a system pressure of 300 psig, compared to a solids velocity of 0.11 ft/s at the same location. Therefore, even when the solids velocity was increased four times to 0.44 ft/s (equivalent to a solids flow rate of 6000 lb/h), the gas velocity would only need to increase to 14.33 ft/s [$14 \text{ ft/s} + (0.44 \text{ ft/s} - 0.11 \text{ ft/s})$] in order to maintain the same gas-solids relative velocity and generate the same pressure drop. This represented only a 2.4% increase in the gas flow.

Pressure profiles, for the tests conducted at three different pressures and at a solids flow rate of 3000 lb/h, are shown in Figure 17 for the "vertical downward" RPDS configuration. The pressure drop per unit length ($\Delta P/L$) profiles for these same tests are shown in Figure 18. These profiles were typical of those obtained in all of the tests conducted with the "vertical downward" configuration.

Figure 16. GAS FLOW FROM DISENGAGING VESSEL AS A FUNCTION OF PRESSURE

In general, the $\Delta P/L$ in the RPDS pressure reduction pipe was found to be higher in the 2-inch pipe than in the 3-inch pipe. This is because both the relative gas-solids velocity and the gas density in the 2-inch pipe were higher than those in the 3-inch pipe. The relationship between $\Delta P/L$, relative gas-solids velocity (V_r), and gas density (ρ_g) for gas flow through a packed bed of solids is given by the Ergun equation:

$$\frac{\Delta P}{L} = \frac{150\mu (1-\epsilon)^2 V_r}{g_c (\phi \cdot D_p \cdot \epsilon)^2} + \frac{1.75 (1-\epsilon) \cdot \rho_g \cdot V_r^2}{g_c \cdot (\phi \cdot D_p \cdot \epsilon)} \quad (1)$$

where —

D_p = average particle diameter, ft
 $\Delta P/L$ = pressure drop per unit length, psi/ft
 μ = viscosity of gas, lb/s-ft
 ϵ = voidage
 g_c = gravitational acceleration, 32.2 ft/s²
 ϕ = particle sphericity
 ρ_g = gas density, lb/ft³

This equation shows that $\Delta P/L$ in a pipe is proportional to the relative gas-solids velocity.

Figure 18 also shows that $\Delta P/L$ decreased dramatically as the diameter of the RPDS pipe was expanded from 2-inch to 3-inch. This was mainly due to the large drop in the gas velocity in the RPDS depressurization pipe. Pressure drop per unit length was found to increase along the length of the 2-inch and the 3-inch RPDS pipe. This result was expected because as the pressure decreased along the pipe, the gas would expand, increasing the absolute gas velocity and the relative gas-solids velocity.

Pressure profiles along the RPDS pipe are presented in Figure 19 for the tests conducted at three different solids flow rates. The pressure distribution along the pressure reduction pipe was hardly affected by the solids flow rate.

Effect of Particle Size

Tests to determine the effect of particle size on the operation of the RPDS were also conducted in the "vertical downward" configuration. Tests with all three materials were made at nominal system pressures of 150, 300, and 600 psig.

Figure 18. PRESSURE-DROP PROFILES ALONG THE DEPRESSURIZATION PIPE AS A FUNCTION OF SYSTEM PRESSURE

Figure 17. PRESSURE PROFILES ALONG THE DEPRESSURIZATION PIPE AS A FUNCTION OF SYSTEM PRESSURE

Figure 19. PRESSURE PROFILES ALONG THE DEPRESSURIZATION PIPE AS A FUNCTION OF SOLIDS FLOW RATE

A plot of the gas flow rate from the disengaging vessel versus the particle size is shown in Figure 20 for the three pressures tested. At a solids flow rate of 3000 lb/h, this figure shows that the amount of gas flow out of the disengaging vessel increased with increasing particle size. This is in agreement with the trend predicted by applying the Ergun equation to the RPDS standpipe. During the tests, it was also observed that the unit was noisiest when operating with small material (224 μm) at a system pressure of 600 psig. This could be due to the fact that solids flow in the RPDS depressurization pipe was in stick-slip flow at these conditions.

As shown in Figure 21, solids flow rate was found to have a minimal effect on the gas flow from the disengaging vessel for all the three particle sizes tested. This result was expected because for a given particle size, the flow of gas relative to the solids creates the pressure drop in the system. Because the gas velocity was found to be approximately an order of magnitude greater than the solid velocity inside the pipe, changing the solids flow rate from 1500 to 6000 lb/h would be expected to have little or no effect on the overall gas requirement to generate the necessary pressure drop in the system.

The pressure drop distribution along the RPDS pipe is also presented in Figure 22 for the three different shale particle sizes tested. Figure 22 indicates that the $\Delta P/L$ profiles did not change significantly as the particle size was changed.

Two-Stage Configuration

The RPDS was also modified to investigate the operability of a two-stage system (Figure 8). One of the potential benefits of the two-stage system is that a portion of the gas in the pressure reduction line can be bled off at a higher pressure than atmospheric. This high-pressure gas could then be used for other purposes if desired.

Three tests were conducted with this configuration using the -20+40 mesh shale material. These tests were carried out at ambient temperature and a system pressure of 300 psig. Three different solids flow rates (1500, 3000, and 6000 lb/h) were tested while the Stage 1 disengaging vessel was maintained at a pressure of 80 psig, and the Stage 2 disengaging vessel at a pressure slightly above atmospheric.

Figure 20. EFFECT OF PARTICLE SIZE ON GAS FLOW FROM DISENGAGING VESSEL

Figure 21. GAS FLOW FROM DISENGAGING VESSEL VERSUS SOLIDS FLOW RATE AS A FUNCTION OF PARTICLE SIZE

Figure 22. EFFECT OF PARTICLE SIZE ON THE PRESSURE DROP DISTRIBUTION

The results of the tests showed that the two-stage system was able to operate as smoothly as the single stage. Analysis of the data also showed that the total gas flow out of the two disengaging vessels was not significantly different than the gas flow obtained earlier with the single-stage system, i.e. 42.4, 43.9, and 41.9 scfm for the two-stage versus 43.0, 41.5, and 44.6 scfm for the single-stage system at solids flow rates of 1500, 3000, and 6000 lb/h, respectively.

Task 4. Beneficiation Research

The objective of this task is to test several novel and advanced grinding and beneficiation concepts, which have shown promising results with coal, for processing Eastern oil shales. This task is divided into three subtasks: Grinding Studies, Kerogen/Mineral Separation, and Waste Treatment and Disposal Studies.

Discussion

This task is being carried out by the Mineral Research Institute (MRI) of the University of Alabama. One task of this part of the program is being conducted by the University of Pittsburgh (UP) as a subcontractor to MRI. The activities undertaken during the quarter are described below:

Subtask 4.1. Grinding Studies

Subtask 4.1.1. Ultrasonic Grinding

This subtask was originally subcontracted to Energy and Minerals Research Company. Upon the bankruptcy of that company, the equipment required to perform the research was returned to DOE/PETC. Dr. Chiang of the UP has confirmed that the equipment is complete and operational in the PETC laboratory. He is currently negotiating arrangements by which he will be able to schedule the work planned under this contract. When those arrangements are complete the subcontract between University of Alabama and UP will be expanded to include the ultrasonic grinding research.

Subtask 4.1.2. Pressure-Cycling Comminution

Concurrent with the move of the Principal Investigator to the University of Nevada (Reno) an agreement for the continuation of his activities was negotiated with the University of Nevada. A contract has been prepared between the Universities of Alabama and Nevada and has been forwarded through

IGT for DOE approval. Further activities are delayed until final approval of the contract.

Subtask 4.1.3. Stirred Ball Mill Grinding

A 4-liter NETZSCH continuous stirred ball mill was received and installed this quarter. Several delays have been encountered in putting the mill into operation. Standard power in the MRI laboratory (208V) was stepped up to 230V to permit grinding power measurements with the watt meter integral to the NETZSCH mill. A dedicated high pressure air line is being installed to permit simultaneous operation of the stirred ball mill and the air sparged cyclone (Subtask 4.2.2). It was discovered in a shake down trial that the pump supplied with the mill was not satisfactory for handling the relatively coarse feed (-20 mesh) to the mill. A substitute pump is being exchanged for the pump supplied by the manufacturer.

Subtask 4.1.4. Grinding Circuit Optimization

This subtask will be initiated during the second program year.

Subtask 4.2. Kerogen/Mineral Matter Separation

Subtask 4.2.1. Column Flotation

Three series of column flotation tests were performed during the quarter. The first series of tests consisted of a 2 level, 5 factor factorially designed experiment. The tests were performed in a 1-meter column cell (7.6 diam.) operating in batch mode. The results of the experiment are presented in Table 4. The coded factor levels used in the experiment are defined in Table 5. The results show that the best separations are achieved at low air flow rates and at low frother concentrations. It was also concluded that sodium silicate additions had no effect on the separation.

Two individual tests reported in July indicated that concentrates with kerogen contents with Fischer Assay (FA) oil yields of 45.1 GPT and 39.1 GPT could be realized with recoveries of 73.4% and 95.2%, respectively.

A second series of tests were performed in a 1.8 meter column cell (10.0 cm diam.) as a factorially designed experiment. The factor levels were based on results from the previous experiments. The tests were again done in batch mode, however, an attempt was made to simulate continuous operation by maintaining a constant level of the pulp-froth interface (i.e. constant hold

Table 4. RANDOM FACTORIAL EXPERIMENTAL DESIGN TEST SERIES
FOR THE COLUMN FLOTATION OF ALABAMA OIL SHALE

Air Sparger Pore Size	Solids, %	Air Flow Rate	Frother	Sodium Silicate	Coefficient Separation (Carbon)	Carbon Grade, wt %	Carbon Recovery, %	Oil Yield, gal/ton
-1	-1	-1	-1	-1	0.58	45.72	73.8	39.0
-1	-1	-1	-1	+1	0.88	42.08	88.9	95.7
-1	-1	-1	+1	-1	0.63	34.88	94.3	29.0
-1	-1	-1	+1	+1	0.85	43.73	83.3	37.2
-1	-1	+1	-1	-1	0.29	19.76	97.1	15.5
-1	-1	+1	-1	+1	0.23	18.55	98.3	14.4
-1	-1	+1	+1	-1	0.34	20.65	97.0	16.3
-1	-1	+1	+1	+1	0.29	19.61	97.1	15.4
-1	+1	-1	-1	-1	0.61	33.49	93.0	27.9
-1	+1	-1	-1	+1	0.35	42.74	46.0	38.3
-1	+1	-1	+1	-1	0.57	31.65	90.3	25.3
-1	+1	-1	+1	+1	0.56	30.32	92.7	25.1
-1	+1	+1	-1	-1	0.28	19.57	97.1	15.4
-1	+1	+1	-1	+1	0.24	18.92	96.1	14.8
-1	+1	+1	+1	-1	0.26	18.85	97.7	14.7
-1	+1	+1	+1	+1	0.21	18.34	96.1	14.3
+1	-1	-1	-1	-1	0.62	38.97	84.7	32.9
+1	-1	-1	-1	+1	0.58	39.67	79.0	33.5
+1	-1	-1	+1	-1	0.80	41.45	82.1	35.1
+1	-1	-1	+1	+1	0.59	42.34	78.5	35.9
+1	-1	+1	-1	-1	0.50	27.35	94.7	22.4
+1	-1	+1	-1	+1	0.48	24.78	94.8	20.1
+1	-1	+1	+1	-1	0.40	23.08	95.7	18.5
+1	-1	+1	+1	+1	0.37	22.08	95.7	17.5
+1	+1	-1	-1	-1	0.48	46.40	60.1	39.5
+1	+1	-1	-1	+1	0.43	38.90	59.6	32.8
+1	+1	-1	+1	-1	0.58	36.93	83.7	31.0
+1	+1	-1	+1	+1	0.58	38.49	81.8	32.5
+1	+1	+1	-1	-1	0.39	22.80	95.8	18.1
+1	+1	+1	-1	+1	0.37	22.13	95.6	17.7
+1	+1	+1	+1	-1	0.32	20.67	95.9	16.4
+1	+1	+1	+1	+1	0.33	20.73	96.4	15.4
0	0	0	0	0	0.45	25.06	95.0	20.3
0	0	0	0	0	0.44	24.49	95.5	19.8
0	0	0	0	0	0.48	25.34	94.7	20.6
0	0	0	0	0	0.45	25.03	94.8	20.3
0	0	0	0	0	0.43	25.88	91.5	20.9
0	0	0	0	0	0.45	25.25	94.3	20.6

Table 5. VARIABLES AND SETTINGS FOR THE ALABAMA OIL SHALE
COLUMN FLOTATION RANDOM FACTORIAL DESIGN EXPERIMENT

<u>Variable</u>	<u>Units</u>	<u>Coded Values</u>		
		<u>-1</u>	<u>0</u>	<u>+1</u>
Air Sparger Pore Size	μm	15	50	85
Solids, %	%	3	5	7
Air Flow Rate	SLPM	3	5	7
Frother (MIBC)	ppm	40	60	80
Sodium Silicate	lbs/ton	0	5	10

up volume). Analysis of the test results is not complete. However, limited data indicate that, in general, high kerogen recoveries were achieved, but the concentrates were of lower grade than achieved in the 1-meter column tests.

Column flotation testing is currently being held in abeyance until the NETZSCH mill is operational. In the interim, provisions are being made to perform flotation tests in continuous mode. The continuous mode is preferred because it permits the test to be performed in an equilibrium condition and allows for realistic evaluation of all column operating parameters.

Subtask 4.2.2. Air Sparged Cyclone

A 2-inch diameter air-sparged cyclone was received in July. Preliminary tests indicated that within the range of conditions tested (inlet pressure 7 to 10 psig, air flow 100 to 200 SLPM), the water balance in the products remained constant. The observed water balance was 80% to the underflow and 20% to the overflow. Subsequent to the preliminary tests, leaks in the cyclone developed and were corrected by the manufacturer. The cyclone has since been re-installed.

No tests are currently in progress. Air-sparged cyclone tests require large quantities of sample and will, therefore, be delayed until the NETZSCH mill is fully operational.

Subtask 4.2.3. Licado Process

The LICADO process is a surface property based technique to separate mineral matter from kerogen. It relies on the relative wettabilities of kerogen and the ash components of oil shale with liquid carbon dioxide (CO_2) and water, respectively. When liquid CO_2 is dispersed into an oil shale/water slurry, it tends to form agglomerates with the oil-rich particles and float them into the liquid CO_2 phase, while the oil-lean components remain in the aqueous phase as refuse.

The objectives of this subtask is to determine the appropriate range of operating conditions for the different LICADO process parameters.

An existing Batch Research Unit (BRU) was modified and utilized to obtain basic process performance data. The unit (shown in Figure 23) consists of two high-pressure cells of 2-inch I.D. connected by a 2-inch ball valve. The system is provided with two variable speed mixers (operating up to 1700 rpm) for agitation of both the aqueous and liquid CO₂ phases.

The batch experiments were performed in the BRU. A 900 ml oil shale-water slurry was fed to the lower section of the BRU in each test. Liquid CO₂ was injected from the bottom of the column to produce the clean oil shale-refuse separation. At the end of the test the upper and lower sections of the BRU were separated by closing the 2-inch ball valve. The bottom aqueous slurry constitutes the refuse fraction. The upper contents of the vessel contains the upgraded product.

Two samples of Eastern oil shale were supplied by MRI for the initial parametric studies. The particle size of one sample was -200 mesh; that of the other sample (ground in a rod mill) was about 10 μ m. Ash analysis showed that the nominal ash content of the -200 mesh sample was 80.0%, that of the fine ground material was 77.5% ash.

Batch experiments were carried out with both samples at various process conditions. The impeller speed in both phases was varied from 1000 to 1600 rpm and the flowrate of liquid CO₂ was varied from 100 to 350 ml/min. In some of the experiments, the contact time of liquid CO₂ was varied from 5 to 15 minutes. The slurry concentration was maintained constant at about 5% in all the tests.

Initial test results indicate that it was difficult to upgrade the -200 mesh sample. The ash content in the product was about 78% regardless of changes in process parameters. The ash content of the refuse fraction was approximately 81%, suggesting that very little separation of mineral matter from the kerogen occurred. Next quarter, tests will be conducted with selective dispersants for the mineral matter in order to achieve improved results with the larger particle size samples.

Tests with the finely ground oil shale sample showed that a partial upgrading of the sample was possible. Table 6 lists the experimental

Figure 23. BATCH RESEARCH UNIT

conditions and results of a series of tests performed at various liquid CO₂ flowrates and agitation speeds.

Table 6. THE EFFECT OF OPERATING CONDITIONS TESTED ON PRODUCT DISTRIBUTION FROM LICADO PROCESS TESTS

<u>No.</u>	<u>Impeller Speed, rpm</u>	<u>Flowrate of Liquid CO₂, ml/min</u>	<u>Yield</u>	<u>Product Ash</u>	<u>Refuse Ash</u>
			----- % -----		
1	1000	100	15.5	69.5	78.6
2	1000	200	17.6	69.8	80.7
3	1000	300	24.4	71.4	80.5
4	1000	350	25.5	71.7	80.7
5	1200	200	20.6	71.0	80.1
6	1400	200	23.8	72.5	80.3

Rod mill ground sample,
Slurry concentration: 5%
Contact time of liquid CO₂: 5 min.

It can be observed from Table 6 that the yield increases with the flowrate of liquid CO₂. Higher flowrates would facilitate better contact between the droplets of liquid CO₂ and the oil shale particles. However, it can also be observed that higher yields are accompanied by a small increase in the product ash content. This phenomena might be attributed to entrapment of fine ash material in the liquid CO₂-oil shale agglomerate at the higher flowrates. The effect of dispersion of the liquid CO₂ droplets in the slurry was investigated by increasing the impeller speed up to 1600 rpm. The yield increased at the higher agitation speeds at the expense of a slight increase in product ash content. Several experiments will be repeated in the presence of selective dispersants with new samples of finely ground oil shale.

Since only a limited quantity of the oil shale samples was available, it was not possible to undertake a comprehensive investigation of all the process parameters to determine the optimum conditions for upgrading. A detailed test program will be carried out after receipt of new samples of oil shale from MRI.

UP is also investigating the mechanism of the LICADO process through surface and interfacial property measurements. The results will be utilized to formulate a theoretical model for the LICADO process. A high-pressure apparatus equipped with the necessary optical and photographic accessories (Figure 24) was utilized for contact angle measurements. An overhead mixing cell was used to equilibrate the immiscible liquid CO₂ and water phases and to feed either of these two liquids to the measurement cell by gravity. The measurement cell, equipped with 2-inch windows on opposite sides, was mounted on a rotary table capable of a 180° rotation. The connections from this cell were high-pressure flexible metal tubes.

For the contact angle measurement, a sessile drop was deposited on a 1-inch x 1/4-inch thick polished pellet of an Eastern oil shale held by a special specimen holder. This specimen holder was mounted from the side of a 2-inch flanged opening on the tip of a shaft assembly. The shaft assembly was designed in such a way that both rotational and translational movement could be externally controlled. The horizontal rotation of the specimen holder enabled the contact angle to be measured from any direction of the sessile drop. The vertical movement permitted the adjustment of distance between the oil shale sample and the tip of the liquid feed tube during the formation of the sessile drop. The contact angle of water was measured with the angular protractor inside the eyepiece of the microscope at various liquid CO₂ pressures ranging from zero to saturation pressure at room temperature (about 850 psia).

In addition, the contact angle of water was measured at room temperature and pressure in a conventional goniometer by the sessile-drop technique. The same polished pellet of oil shale was also utilized for these measurements.

Figure 25 illustrates the variation of the equilibrium contact angle of water on polished samples of oil shale at various CO₂ pressures up to the saturation pressure of CO₂ at 22°C. At room temperature, the average contact angle is about 44°, but increases to 115° at the saturation pressure liquid CO₂ at 22°C (870 psi). This indicates that the oil shale surface is being rendered hydrophobic in the presence of CO₂. Therefore, it is possible to affect a significant upgrading of the oil shale by the LICADO process.

Figure 24. CONTACT ANGLE MEASUREMENT APPARATUS

Figure 25. EFFECT OF CO₂ PRESSURE ON THE OIL SHALE CONTACT ANGLE

Subtask 4.3. Waste Treatment and Disposal Studies

Subtask 4.3.1. Process Water Treatment Studies

This subtask will be initiated during the second program year.

Subtask 4.3.2. Tailings Disposal Studies

Tailings produced in the beneficiation of Alabama shale were collected. Tests were performed to determine the pozzolanic properties of the materials. The tests performed measured setting time and strength over a prolonged curing time. Final strength tests are in progress and will be reported in the October monthly report.

ASTM slump tests and the effect of tailings as a cement additive are scheduled for the coming quarter.

Task 5. Operation of PFH on Beneficiated Shale

The objective of this task is to modify the PFH process to facilitate its use for fine-sized, beneficiated Eastern oil shales. This task is divided into three subtasks: Non-Reactive Testing, Reactive Testing, and Data Analyses and Correlations.

Discussion

Work continued during the quarter on Subtask 5.1. (Non-Reactive Testing). The objective of this subtask is to determine operating conditions necessary to achieve the desired residence time of fine shale particles in a fluidized bed (or fluidized in the interstices of a packed bed of inert material). The results of Subtask 5.1 will be used to select the configuration, gas velocities and particle sizes to be used in the reactor for Subtask 5.2 (Reactive Testing).

The pulsing of fluidizing gas through beds of very fine materials has been suggested as a means of improving the quality and degree of fluidization at reasonable superficial gas velocities. In order to evaluate this technique with beneficiated oil shale, the equipment required to conduct pulsed-fluidization tests in the 6-inch diameter Plexiglas column was installed as shown in Figure 26. Modifications to the column included a new 19-point gas distributor (Figure 27) and associated fluidizing-gas supply lines.

F881001

Figure 26. EQUIPMENT INSTALLED FOR PULSED FLUIDIZATION TESTS

F881002

Figure 27. DIAGRAM OF 19-POINT GAS DISTRIBUTOR
FOR PULSED FLUIDIZATION TESTS

Shakedown tests of the equipment for pulsed-fluidization tests in the 6-inch column were carried out with beneficiated Alabama Chattanooga shale. Smooth fluidization and good solids mixing were obtained at gas velocities where gas channeling and only local fluidization were previously found with a continuous fluidizing gas flow. The results of both standard screen analysis and a Coulter Counter particle size distribution for this material are given in Table 7. The larger apparent particle sizes of the standard screen analysis are a result of the shale's tendency to form soft agglomerates at ambient conditions.

Pulsed-fluidization tests were then conducted at 24, 40, 60, and 150 pulses/minute over a superficial gas-velocity range of 0.04 to 0.20 ft/s. The best fluidization occurred at a superficial gas velocity of 0.2 ft/s and 40 pulses/minute (0.5 sec ON/1.0 sec OFF), when the pulses seemed to lift the shale up off the grid, and the bubbles caused good solids mixing. A gas velocity of approximately 0.6 ft/s is necessary to fluidize an equal fraction of the bed with continuous gas flow.

At 24 pulses/minute (0.5 sec ON/2.0 sec OFF), the bed level would rise as much as 4 inches and then fall back again before the next gas pulse occurred, resulting in intermittent fluidization and little solids mixing. Although fluidization was smoother at 60 pulses/minute (0.5 sec ON/0.5 sec OFF), a smaller portion of the bed was actively fluidized. Gas bubbles tended to rise up one side of the column, causing a downward flow of solids on the opposite side over the upper two-thirds of the bed.

At 150 pulses/minute (0.2 sec ON/0.2 sec OFF), some solids segregation occurred between 0.1 and 0.2 ft/s through the bed, but to a lesser extent than with continuous fluidization. The magnitude of the gas pulses was noticeably less than with the other pulse rates, resulting in reduced activity near the distributor at the same gas velocities. A gas velocity of approximately 0.36 ft/s was required to achieve the same degree of bed mixing that occurred at 0.2 ft/s and 40 pulses/minute.

Plans are presently underway to fluidize beneficiated shale at elevated temperatures, approximately 500°F, to determine whether beneficiated shale can be fluidized with continuous gas flow without channeling in a high-temperature fluidized bed. Particle carryover rates will also be determined. Only minor modifications will be required to fluidize beneficiated shale in the existing

Table 7. COMPARISON OF COULTER COUNTER AND STANDARD SCREEN
ANALYSIS OF BENEFICIATED ALABAMA SHALE

Coulter Counter

<u>Cumulative Weight Percent Less Than</u>	<u>Diameter, μm</u>
0.0	3.2
9.4	4.0
21.4	5.0
35.8	6.4
51.8	8.0
67.5	10.1
80.4	12.7
89.4	16.0
95.3	20.2
99.4	32.0
100.0	40.3

Standard Screen

<u>Cumulative Weight Percent Less Than</u>	<u>Diameter, μm</u>
4.4	44
29.3	74
33.4	125
39.5	177
45.8	250
56.6	420
78.4	841
99.9	1680

high-temperature fluidization unit. Testing will begin when a new sample of beneficiated Alabama New Albany shale is received from MRI.

Task 6. Environmental Data and Mitigation Analyses

The overall objectives of Task 6 are to obtain environmental data relating to PFH and shale beneficiation, and also to analyze the potential environmental impact of the integrated PFH process. This task is divided into four subtasks: Characterization of Processed Shales, Water Availability and Treatment Studies, Heavy Metals Removal, and PFH System Analyses.

Discussion

Subtask 6.1. Characterization of Processed Shales

This subtask will be initiated next quarter when suitable samples of spent shales are available from the tests conducted in Subtask 1.1.

Subtask 6.2. Water Availability and Treatment Studies

The objectives of this subtask are to assess the availability of water for PFH facilities for processing eastern oil shales, and to determine suitable techniques for treating wastewater generated during shale processing. Tennessee Technology University (TTU) is conducting the work on this subtask.

During the quarter, TTU essentially completed work on determining the locations and quantities of water flows in areas containing shale outcrops in the 6 states being considered in this study. Specific counties have been selected for siting a plant in Alabama, Indiana, Kentucky, Michigan, Ohio and Tennessee. At each location, the quantity of processing water needed to support a 50,000 bbl/day plant was determined adequate. An example for each of the six states is shown below:

Kentucky Site Selection. The location of major oil shale outcrops are shown in Figure 28. This outcrop area covers approximately 1,000 square miles¹ and extends across several counties. The site selected for this example is in Rowan County and is depicted in Figure 29. It is a site where the Sunbury Oil Shale is exposed and is located on the north side of Interstate 64 and about 3.2 miles from the Licking River Bridge at the Barth-Rowan county line.²

Required Process Water. The gallons of net import water and the minimum flow rate of a free-flowing stream required for the Sunbury Shale are shown below:

Figure 28. LOCATION OF OIL SHALE OUTCROP AREAS IN KENTUCKY

Figure 29. LOCATION OF SHALE OUTCROP AND WATER SOURCE FOR PFH PLANT SITE IN KENTUCKY

Plant Size, bbl/day	Required Import Water, mgd	Flow Rate of Stream, cfs
10,000	3.45	5.34
25,000	8.63	13.36
50,000	17.26	26.72

Availability of Processing Water. The major stream for a potential source of processing water is the Licking River. A few miles upstream, the river has been dammed to form the Cave Run Reservoir. The drainage area for the Cave Run Lake is 826 square miles. The flow in the river as measured at Farmers, Kentucky, is regulated at the minimum design flow of 50 cfs (7 day-10 year low-flow). The flow rate is sufficient to support a processing plant most likely without storage. This U.S. Corps of Engineers reservoir could serve as a source of water to augment the Licking River withdrawal site. The Corps' policy is not to consider that their reservoirs have excess capacity, but there is always the opportunity for petition for reallocation of the existing storage capacity.

Ohio

Site Selection. A view of the outcrop area of the Devonian-Mississippian shales in Ohio is shown in Figure 30. The Cleveland Shale selected for this study is in the upper Devonian immediately under the Mississippian formation. There are several locations where the Cleveland Shale crops out in road cuts and can be sampled. A selected listing of the counties follows:

Adams	Pickaway
Delaware	Pike
Franklin	Ross

The specific site selected as an example is in Pike County and is identified as follows:

"Proceed west on Ohio 32 about 2.4 miles past its intersection with Ohio 124 to road leading north to Elm Grove. Follow only road leading north out of Elm Grove up hill to road cuts in which Ohio shale is exposed."²

A map showing the approximate location in Pike County, Ohio, is shown in Figure 31.

Required Process Water. The gallons of net import water and the minimum flow rate of a free-flowing stream required for the Ohio Shale (Cleveland Member) are shown below.

Figure 31. LOCATION OF SHALE OUTCROP AND
WATER SOURCE FOR PFH PLANT SITE IN OHIO

Plant Size, bbl/day	Required Import Water, mgd	Flow Rate of Stream, cfs
10,000	2.46	3.81
25,000	6.15	9.52
50,000	12.30	19.04

Availability of Processing Water. The selection of a specific site in relationship to the availability of processing water is governed by the laws and regulations of the state in which the site is to be located. The capacity of a free-flowing stream to support a processing plant is predicted on the current and planned water uses. The adequacy of the stream for supporting broad categories of uses, both upstream and downstream, from the intake and discharge openings is a critical determination during the plant siting process. Among the many possible users are municipal water supplies, disposal of liquid wastes from industry, steam electric generation, aquatic life, etc. In Ohio, the legal basis for water pollution control is tied to water quality standards that incorporate 7 day-10 year low-flow characteristics of the receiving stream.⁵

The site selected in Pike County, Ohio, is near Elm Grove and is located in the immediate vicinity of the Long Fork and Sunfish creeks, small tributaries of the Scioto River. Although low-flow data is not reported for these two creeks, there is a possibility that they could serve as water withdrawal stations during certain periods of the year. The Pike County site, however, is within 25 miles of the Scioto River. The nearest gauging station is at Higby, Ohio, and records show that the 7 day-10 year low-flow is an average of 416 cfs. The Scioto at this location serves a drainage area above the gauging station of 5,131 square miles. Since the import water for the 50,000 bbl/day plant would require slightly less than 5% of the average 7 day-10 year low-flow, it is unlikely that a problem of water usage caused by the plant would be detrimental to the river. It depends, however, on the quantities required by other users. The U.S. Water Resources Council describes the greatest water issue for the Scioto River is at Columbus, Ohio, because of the large populations and municipal water treatment plants in the reach above and below Columbus.⁶

Tennessee Site Selection. Chattanooga shale in Tennessee has been extensively investigated and reported in the literature.^{7,8} The specific sites selected for the assessment of the availability of water are located in DeKalb and Jackson Counties.

Figure 32 shows the two sites in DeKalb County. Site A is from a road cut on the north side of U.S. 70 about 5.4 miles west of the center of Smithville, Tennessee. Site B is in a road cut at the east end of the Sligo Bridge over the Center Hill Reservoir on U.S. 70 about 5.6 miles east of Smithville. Figure 33 shows the two sites in Jackson County. The site on the west side of

Figure 33. LOCATION OF SHALE OUTCROP AND WATER SOURCE FOR PFH PLANT SITE IN TENNESSEE (Jackson County)

Gainesboro is in a road cut on Tennessee Route 85 and 0.2 miles north of the junction with Tennessee Route 54.⁷ The site northeast of Gainesboro is in a road cut on Tennessee Route 85 about 2.0 miles from the intersection of Route 85 with Tennessee Route 53.

Required Process Water. The gallons of net import water and minimum flow rate of a free-flowing stream required for the Chattanooga Shale (Cassaway Member) are shown below.

<u>Plant Size, bbl/day</u>	<u>Required Import Water, mgd</u>	<u>Flow Rate of Stream, cfs</u>
10,000	3.36	5.30
25,000	8.40	13.00
50,000	16.80	26.00

Availability of Processing Water. The sites selected in Tennessee have the availability of processing water from impounded reservoirs. The DeKalb County sites are essentially on the Center Hill Reservoir. This Reservoir is formed by the U.S. Corps of Engineers Center Hill Dam that is on the Caney Fork River. It lies in the Cumberland River Basin. The Reservoir drainage area is 2,174 square miles. The Jackson County sites are near the Reservoir formed by the Cordell Hull Dam on the Cumberland River. The drainage area for the segment of the Cumberland River Basin upstream from the Dam is 8,095 square miles. Both of these reservoirs have ample water that would be available to serve the needs of a 50,000 bbl/day processing plant — and for even larger plants. The Tennessee regulation of maintaining 3 day-20 year low-flows is not a matter of concern at the Tennessee sites. A more important issue will be the maintenance of water quality in the reaches of the lake effected by the water intake and outflow for the plant.⁹ Also, as mentioned above, the U.S. Corps of Engineers' policy does not recognize excess capacity in the reservoir; therefore, it would be necessary to negotiate the volume of withdrawal water required.

Michigan

Site Selection. The Antrim Shale in the upper Devonian of the Michigan Basin occurs principally in seven counties located in the lower peninsula.¹⁰ They are:

Alpena	Emmet
Antrim	Leelanau
Charlevoix	Presque Isle
Cheboygan	

The other counties where the shale occurs are in the lower southeastern and lower southwestern sections of the state. It is reported that suitable surface mining of the Antrim Shale covers an area of approximately 160 square miles.¹¹ In Figure 34 the areas in solid black are where the Antrim Shale occurs in relation

Figure 34. AREA UNDERLAIN BY DEVONIAN BLACK SHALE IN MICHIGAN (Ref. 11)

to the state boundaries.² The site selected is for a 50,000 bbl/day plant to be located in Charlevoix County.¹² It is identified in the South Arm Township within Tier 32 North and Range 7 west as contained in the Ellsworth, Michigan quadrangle. The specific location is in the central west one-half of Section 18 and is shown in Figure 35.

Required Process Water. The volume of net import water and the minimum flow rate of a free-flowing stream required for the Antrim Shale are shown below.

Plant Size, bbl/day	Required Import Water, mgd	Flow Rate of Stream, cfs
10,000	2.26	3.50
25,000	5.65	8.75
50,000	11.30	17.49

Availability of Processing Water. As a result of glaciation, the northern lower peninsula of Michigan is pockmarked by numerous lakes and streams. The annual freshwater withdrawals in 1975 were 42,813 mgd, but it is expected to decrease to 25,623 mgd by the year 2000. Withdrawals for manufacturing will have decreased by 20%. Although withdrawals will be reduced, it is estimated that consumption in the manufacturing sector will nearly quadruple between 1975 and the year 2000. Because the withdrawals are projected to decrease significantly due to reuse, water resource supplies are estimated to be adequate to meet future demands by the year 2000.¹³ Since there is an abundance of lakes in the region where the oil shale occurs, it was decided to identify a lake impoundment as the source for a 50,000 bbl/day plant. The site selected is where there is a chain of lakes south of town of Ellsworth, Michigan. The water intake for the plant would be located on the St. Clair Lake in Antrim County. There are several options for plant location since the Antrim Shale is widely identified.

Indiana

Site Selection. The New Albany Shale crops out or underlies a cover of unconsolidated deposits from Newton County in Northwest Indiana to Floyd County in the southeast along the Ohio River. The areal extent of the shale is shown in Figure 36. The Clegg Creek member is the uppermost member of the New Albany Shale and contains the highest concentrations of organic material.¹⁴ It has been estimated that the total area of New Albany Shale suitable for surface mining is 600 square miles.¹¹ The site selected for a 50,000 bbl/day plant location is in Clark County, Indiana. The Clegg Creek member outcrops in a road cut on Indiana Highway 160 about two miles southeast of Henryville.² The site is plotted on the hydrologic unit map for Indiana and is shown in Figure 37. This site was selected since it is near the Ohio River where adequate surface water is available.

Figure 35. LOCATION OF SHALE OUTCROP AND WATER SOURCE FOR PFH PLANT SITE IN MICHIGAN

Figure 36. AREAL EXTENT OF OIL SHALE RESOURCES IN INDIANA

Required Process Water. The quantity of net import water and minimum flow rate of a free-flowing stream required to provide the quantities of import water are shown below.

<u>Plant Size,</u> <u>bbl/day</u>	<u>Required Import</u> <u>Water, mgd</u>	<u>Flow Rate</u> <u>of Stream,</u> <u>cfs</u>
10,000	2.30	3.56
25,000	5.75	8.90
50,000	11.50	17.80

Availability of Processing Water. For water resources planning, the area designated as the Ohio Region encompasses much of Indiana. The region's primary river is the Ohio which begins at the confluence of the Allegheny and the Monongahela rivers. The area has about 170 major man-made reservoirs and many more small impoundments. In a survey review of the free-flowing minor streams where shale outcrops had been identified, it was noted that the 7 day-10 year low flow was inadequate to sustain a 10,000 bbl/day processing plant. The major streams, such as the Wabash and the Ohio, have 7 day-10 year low flows sufficient to supply the import water for a 50,000 bbl/day plant. The total water withdrawn from surface streams was about 34.9 bgd in 1975 and is estimated to be about 16.9 bgd in the year 2000. This reduction is principally in the use of water in manufacturing processes. Many plants are recycling process water. Consumption will increase due to the increase in domestic use and steam-electric systems.⁶ The Ohio River was selected as the water source for a 50,000 bbl/day plant in Clark County, Indiana. The 7 day-10 year low flow in the reach between Cincinnati and Louisville averages about 10,800 cfs. In order to sustain the plant, only 17.8 cfs of net import water is needed.

Alabama

Site Selection. The Chattanooga Shale outcrops at several locations in northern Alabama. The areal extent is shown in Figure 38. It is estimated that the total area suitable for surface mining of the Chattanooga Shale in Alabama covers an area of 300 square miles.¹¹ Among the northern tier Alabama counties are the following:

Jackson	Limestone
Lauderdale	Madison

The site selected for this study is in Madison County and is located at Quicks Mill on Flint River about 12 miles north-northeast of Huntsville, Alabama. The site location is shown in Figure 39.

Required Process Water. The quantities of net import water and minimum flow rate of a free-flowing stream required for the Chattanooga Shale from northern Alabama are shown below.

Figure 38. AREAL EXTENT OF THE CHATTANOOGA SHALE IN TENNESSEE AND ADJACENT AREAS. (Adapted from Conant and Swanson [1961]; Plate from Hickman and Lynch [1967])

Figure 39. LOCATION OF SHALE OUTCROP AND WATER SOURCE
FOR PFH PLANT IN ALABAMA

<u>Plant Size, bbl/day</u>	<u>Required Import Water, mgd</u>	<u>Flow Rate of Stream, cfs</u>
10,000	2.72	4.21
25,000	6.80	10.53
50,000	13.60	21.05

Availability of Processing Water. The north Alabama site is in the Tennessee Region as defined by the U.S. Water Resources Council. The Tennessee River is the major surface water resource in the region. It has a slack-water channel for its entire length and, consequently, provides a significant source for water withdrawals. Total water withdrawals are expected to decrease by 19% from 1975 to the year 2000. Unfortunately, water consumption will increase by 251% by the year 2000. The major increase in consumption will be by thermal electric plants. Manufacturing consumption is not expected to increase significantly between the years 1975 and 2000.¹⁵ The site selected for a 50,000 bbl/day plant to process the Chattanooga Shale in northern Alabama is located on the Flint River which empties into the Tennessee River. The 7 day-10 year low flow at the site selected for the withdrawal to support a 50,000 bbl/day plant is 67 cfs which is more than adequate to maintain a reasonable flow during withdrawals.

Subtask 6.2.2. Water Treatability

In this subtask, TTU continued work on developing biological and physical methods for treating water from the PFH process. Batch biological experiments were performed to determine the rates and degrees of removal of two single substrates, propionitrile and acetone, individually, and in a mixture of the two. Bacterial seed used in the experiments had been previously acclimated to aerated solutions containing both acetone and propionitrile as the only carbon sources. Also included in the growth media were excess essential inorganic nutrients and minerals to insure that bacterial growth would not be nutrient limited. Experiments were initiated by filling batch reactors with the "synthetic waste solution" of nutrients and the desired amount of substrate. At "time zero," the 2-liter reactors were inoculated with 20 ml of acclimated seed. Samples were taken at "time zero" and several times during the duration of the experiment. Chemical oxygen demand (COD) analyses (closed reflux, colorimetric method) were conducted on the filtered samples. Preliminary experiments had indicated that solutions of either acetone or propionitrile could be biologically degraded to acceptable COD levels in about 50 hours.

Batch experiments conducted previously with either acetone or propionitrile as substrate were repeated to verify reproducibility of the results. The results of both sets of experiments are shown in Figures 40 and 41. Table 8 lists the COD achieved after about 50 hours. The data show that most of the CODs were reduced to about 30 mg/l or less. This level of residual COD can be attributed to accumulation of metabolic by-products.

Because bacterial growth generally follows first-order kinetics, a semi-log plot of COD with time should be linear (or at least a portion of the plot should be). Semi-log plots of the data are shown in Figures 42 and 43. Specific removal rate constants, or the slopes of the semi-log plots, are listed in Table 8. In each case, data linearity was verified by high correlation coefficients.

One experiment was performed using both acetone and propionitrile as substrates in concentrations of 300 mg/l each. The results of this experiment (Figure 44) show that COD was reduced to 38 mg/l, and the specific removal rate constant was 0.0583 hour^{-1} . Samples from this experiment were also analyzed using GC/MS. Preliminary results indicate that substrate removal occurred simultaneously, rather than sequentially, and that both substrates were reduced to less than 1 mg/l.

The procedure used for COD tests (closed reflux, colorimetric method) was modified to standardize treatment conditions and reduce the variability of results. The results obtained for pyrrole, propionitrile, and acetone using the modified procedure were quite reproducible. A linear regression analysis of the data yielded correlation coefficients of greater than 0.99 for the three compounds tested.

Carbon adsorption tests were performed with pyrrole to determine the approximate concentration of pyrrole and dosage of carbon required. Poor results obtained in initial tests were traced to a questionable solution of pyrrole and sampling techniques.

Three tests were run using an analytically determined concentration of the stock solution. The concentrations of pyrrole in the reactors were determined immediately before the addition of activated carbon and at the end of the reaction period. The results obtained from the three tests and values calculated for the Freundlich isotherm are presented in Table 9. Although the

Figure 40. BIOLOGICAL REMOVAL OF ACETONE (Excess Essential Nutrients and Minerals)

Figure 41. BIOLOGICAL REMOVAL OF PROPIONITRILE
(Excess Essential Nutrients and Minerals)

Figure 42. BIOLOGICAL REMOVAL OF ACETONE
(Excess Essential Nutrients and Minerals)
Semi-Log Plot

Figure 43. BIOLOGICAL REMOVAL OF PROPIONITRILE
(Excess Essential Nutrients and Minerals)
Semi-Log Plot

Table 8. RESULTS OF AEROBIC DIGESTION TESTS CONDUCTED
WITH A SINGLE SUBSTRATE

Substrate	Approximate Initial Substrate Concentration, mg/l	COD Achieved, mg/l	Specific Removal Rate, Hour ⁻¹
Propionitrile	600 (#1)	25	0.0314
Propionitrile	600 (#2)	57	0.0229
Propionitrile	300 (#1)	35	0.0254
Propionitrile	300 (#2)	29	0.026
Propionitrile	100 (#1)	55	0.0171
Propionitrile	100 (#2)	26	0.0255
Acetone	600 (#1)	27	0.0324
Acetone	600 (#2)	80	0.017
Acetone	300 (#1)	20	0.0477
Acetone	300 (#2)	9	0.0203
Acetone	100 (#1)	34	0.0236
Acetone	100 (#2)	26	0.0256

Figure 44. BIOLOGICAL REMOVAL OF ACETONE AND PROPIONITRILE
(Excess Essential Nutrients and Minerals)

Table 9. RESULTS OF ACTIVATED CARBON ADSORPTION TESTS WITH PYRROLE

Test No.	1			2			3		
<u>M,</u> <u>mg</u>	<u>C_f,</u> <u>mg</u>	<u>X,</u> <u>mg</u>	<u>X/M,</u> <u>mg/g</u>	<u>C_f,</u> <u>mg</u>	<u>X,</u> <u>mg</u>	<u>X/M,</u> <u>mg/g</u>	<u>C_f,</u> <u>mg</u>	<u>X,</u> <u>mg</u>	<u>X/M,</u> <u>mg/g</u>
250	58	12	46.19	63	9	36.64	62	8	40.13
	448	22	83.88	228	16	66.00	222	19	78.14
	696	23	90.89	659	60	273.76	698	25	93.10
	945	25	100.02	902	43	173.16	924	31	125.29
	1418	32	130.85	1177	32	127.36	1141	39	155.03

$X = C_o - C_f$ is the amount of compound adsorbed from a given volume of solution.

M = the weight of activated carbon.

C_o = the amount of compound in the untreated solution.

C_f = the amount of compound remaining in the treated water.

current techniques appear to have reduced randomness of the data (compared to previous results), the results of individual tests show significant variation. The combined data from Tests 1, 2 and 3 are presented in Figure 45 with the linear regression line.

Subtask 6.3. Heavy Metals Removal

The objective of this subtask is to develop a unified description of the kinetics and mechanisms of the catalyzed and uncatalyzed dissolution of a number of heavy metals and other important minerals from eastern oil shale samples. The work on this task is being conducted by the University of Michigan (UM).

During the quarter, laboratory experiments were conducted with samples of raw and hydroretorted shale to develop an understanding of the uncatalyzed dissolution kinetics. The dissolution of aluminum, arsenic, cadmium, chromium, iron and silicon in acid were considered. The dissolutions were carried out in three different acids: hydrobromic (HBr), hydrochloric (HCl) and nitric (HNO_3), all at 1 mol/l concentration. The experimental equipment and procedures were described in the previous quarterly report.

Iron was chosen as a surrogate for further investigation because of its ease of analysis. Data collection was completed for the dissolution of iron and cadmium from both raw and retorted shale in 0.1 and 1.0 mol/l HBr, HCl, and HNO_3 . The rate of iron dissolution from raw and hydroretorted shale was determined by measuring the iron concentration as a function of time with an atomic adsorption spectrophotometer (AAS). The measured cadmium concentrations were below the acceptable range of measurement to be used for rate law calculations.

The results of iron dissolution experiments have been fitted to third-order polynomial equations by least-squares polynomial regression, to obtain iron concentration as a function of time. An initial rate of change of concentration with time was calculated from this correlation and a rate law for each case was developed.

Table 10 presents the rate laws in the form of rate of dissolution of iron from shale in each acid. Table 11 compares the rates of dissolution from raw shale to the rates of dissolution from retorted shale at acid concentrations of 0.1 and 1 mol/l. This comparison shows that iron dissolves the

Figure 45. PRELIMINARY FREUDLICH CARBON-ADSORPTION ISOTHERM DATA FOR PYRROLE

Table 10. RATE LAWS FOR DISSOLUTION OF IRON FROM
RAW AND HYDRORETORTED OIL SHALE

$$+r_{\text{Fe}}^{\text{HBr, raw}} = 0.0003817 C_{\text{HBr}}^{0.590}$$

$$+r_{\text{Fe}}^{\text{HBr, retorted}} = 0.00006680 C_{\text{HBr}}^{0.390}$$

$$+r_{\text{Fe}}^{\text{HCl, raw}} = 0.0007558 C_{\text{HCl}}^{0.879}$$

$$+r_{\text{Fe}}^{\text{HCl, retorted}} = 0.00004553 C_{\text{HCl}}^{0.766}$$

$$+r_{\text{Fe}}^{\text{HNO}_3, \text{raw}} = 0.0004412 C_{\text{HNO}_3}^{1.014}$$

$$+r_{\text{Fe}}^{\text{HNO}_3, \text{retorted}} = 0.0001035 C_{\text{HNO}_3}^{0.613}$$

$r = \text{g-mol/l*min}$

$C = \text{g-mol/l}$

Table 11. COMPARISON OF THE RATE OF IRON DISSOLUTION
FOR RAW AND RETORTED SHALE SAMPLES WITH ACID
CONCENTRATIONS OF 0.1 AND 1 MOL/L

<u>Acid</u>	<u>Concentration, mol/l</u>	
	<u>0.1</u>	<u>1</u>
Raw retorted Rate Ratio		
HBr	3.6	5.7
HCl	12.8	16.6
HNO ₃	1.7	4.3

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fastest from raw shale with HCl at 1M acid concentration. Table 12 compares the different rates at 1 mol/l acid concentration.

Data collected for cadmium dissolution from both raw and retorted shale into both 0.1 and 1 mol/l acids indicated that the AAS was yielding inaccurate results. The cadmium tests and results will be repeated and verified next quarter.

The information gained from these uncatalyzed dissolution tests will help in the study of catalyzed dissolution by varying the solvent and catalyst that are used. In analyzing the dissolution trends, some factors discussed by Povarennykh¹⁷ regarding the solubility of minerals in water and acids will be examined. These factors relate the equilibrium solubility of minerals to their structure. While the order of trends of equilibrium processes (for example, solubility) do not necessarily dictate the order of rate processes (for example, kinetics), the guidelines of Povarennykh will be used as a first step in relating the structure of mineral to the rate of dissolution.

In general, the equilibrium solubility of a mineral decreases with (1) increasing bond valency, (2) increasing atomic valency, (3) increasing coordination number, (4) decreasing tendency to form crystal hydrates, (5) decreasing interatomic distances, and (6) increasing size of atomic or ionic constituents. In addition to these factors, the relationships and trends of mineral dissolution kinetics focusing on the positions of the above atoms or ions in the periodic table will be examined to determine what trends exist within groups or periods of metals. Preliminary work at the UM laboratory with the oxides of manganese indicates that the more reduced the oxide, the more rapid the rate of dissolution. A number of acids, as well as possible catalytic agents, will be examined for each heavy metal to delineate the relationships discussed above.

Future work will include measurement of the iron dissolution rate from raw and retorted shale at initial acid concentrations of 0.01M and 0.3M; atomic absorption spectrum Al, Si, and Cr concentration measurements for samples already collected; and fundamental studies on the dissolution of CdS.

Table 12. COMPARISON OF RATES AT 1 MOL/L ACID CONCENTRATION*

<u>Acid, Shale Condition</u>	<u>Acid Concentration Rate at 1 mol/l</u>	<u>Normalized Rate</u>
HBr, raw	0.0003817	8.383
HBr, retorted	0.00004672	1.467
HCl, raw	0.0007558	16.600
HCl, retorted	0.00004553	1.000
HNO ₃ , raw	0.0004412	9.690
HNO ₃ , retorted	0.0001035	2.273

rates normalized to $r_{\text{Fe}}^{\text{HCl, retorted}} = 1.000$

Subtask 6.4. PFH System Analyses

The objective of this subtask is to define the effluent streams, quantities, and compositions for a fluidized-bed hydroretorting plant utilizing various Eastern raw and beneficiated oil shales.

Modifications to the computer program that simulates a PFH process plant have been essentially completed. The major modifications made for the PFH process simulation are as follows:

1. Two models proposed to simulate the retort of the PFH process have been incorporated in the program. Detailed descriptions of the models were presented in previous reports. Model A is in essence a limiting case of Model B in which the flow of streams 4 and 5 are set to zero.
2. The nominal temperatures in each fluidized-bed zone have been specified for PFH retort process. Based on these input zone temperatures, material and energy balances are calculated.
3. A subroutine that calculates the minimum fluidization velocity (U_{mf}) of oil shale particles, based on the pressure, temperatures and gas composition in each zone has been written and incorporated into the program.
4. The dimensions (diameter and height) required for each zone can be calculated, based on the requirements for fluidization velocities and residence times of oil shale in each zone.

The modified program can now be utilized to compute mass and energy balances, gas velocities and dimensions in the PFH reactor. Experimental data from Task 1 (PFH) will be incorporated into the program when available.

In the subroutine that calculates the minimum fluidization velocity (U_{mf}), the gas viscosity is computed based on temperature, pressure and composition. A total of 24 gas components can be included in the calculations. The effects of gas temperature, pressure and particle size on U_{mf} for a given recycle gas composition (H_2 - 90%; CO - 4%; CH_4 - 4.8%; etc.) are shown in Figure 46. The figure shows that U_{mf} is not sensitive to temperature, but is somewhat sensitive to pressure, as expected. In general, U_{mf} decreases about 30% as the pressure increases by a factor of 2. The size of the particle significantly effects U_{mf} , as shown in the figure. However, since the shale feed has a size distribution of particle sizes and the calculated particle size could be determined by different ways, the U_{mf} of the different particles will be significantly different. To insure that the beds are well fluidized,

Figure 46. CALCULATED MINIMUM FLUIDIZATION VELOCITY (U_{mf}) OF OIL SHALE PARTICLES IN RECYCLE GAS MIXTURE

the actual gas velocity is maintained at 1.5 to 2.5 times the U_{mf} , depending upon the particle size distribution and the calculated average particle size.

Because Model B has independent recycle gas streams for the retort and preheat zones, respectively, the temperature ranges in these beds are quite flexible. However, in Model A, the temperature and flow rate of the recycle gas (Stream 2) must satisfy the mass and energy balances in both the retort zone and the preheat zone. Therefore, the temperature of the recycle gas is quite sensitive to the temperatures selected in each zone. A parametric study was conducted for Model A. The major goals of the calculation are as follows:

- Determine the flow rates and temperatures of the recycle gas (Streams 1 and 2) based on the mass and energy balances in each zone.
- Determine dimensions (diameters and heights) of each zone based on the requirements for fluidization velocities and the residence times of shale particles.

Based on calculated results for different parameters, the feasible temperature ranges for Model B have been found (Figure 47). The results show that the calculated recycle gas temperature (T_2) is very sensitive to retort zone temperature $T(c)$. The right-side area of the curve 1 corresponds to the temperatures in the preheating zone and the cooling zone higher than the maximum selection — 700°F. The left-side area of the curve 3 corresponds to the temperatures in the preheating zone and the cooling zone lower than the minimum selection — 600°F. Therefore, only the area between curves 1 and 3, and the lines as $T(c) = 900^\circ\text{F}$ corresponding to the minimum selected temperature in the retort zone is the feasible temperature range. Moreover, because the recycle gas temperature $T(2)$ is limited to below 1400° to 1500°F, the feasible temperature range of each zone can be concluded as follows:

Preheating zone:	600° to 700°F
Retorting zone:	900° to 1000°F
Cooling zone:	600° to 700°

Therefore, a basic temperature selection for Model A is recommended as follows:

Figure 47. CALCULATED RESULTS FOR DIFFERENT ZONE TEMPERATURES

Temperatures in preheating zone:	650°F
Temperatures in retorting zone:	950°F
Temperatures in cooling zone:	650°F

Thus, the range of temperature variation in each zone could be $\pm 50^{\circ}\text{F}$.

Since the effect of inlet gas temperature $T(1)$ on $T(2)$ is small and the variable range of $T(1)$ is limited in practice, a variation of $T(1)$ does not significantly impact on the operating regime.

Further modification and finalization of the computer program by adding the parametric effects on the retort process and the down stream simulation will be completed when the results from other tasks in the program are available. Additional parametric studies for both Models A and B will be conducted upon request. An overall review of the modified program will be conducted in the next quarter.

Task 7. Sample Procurement, Preparation, and Characterization

The objective of this task is to procure, prepare, and characterize raw and beneficiated Eastern oil shale samples for all of the experimental tasks in this program. Six Eastern oil shales will be procured and prepared for testing. This task is being conducted by MRI.

Subtask 7.1. Sample Procurement

In Subtask 7.1 (Sample Procurement), samples of five Eastern oil shales have been collected, crushed to 1 inch, and stored under nitrogen in plastic-lined drums. The planned first year allotment of 300 lbs each of these shales has been forwarded to IGT.

Arrangements have been made with the Tennessee Geologic Survey to procure a sixth sample from the Chattanooga formation. This sample will be returned to MRI and processed in the coming quarter.

The analyses shown in Table 13 are reported for the five Eastern shale samples collected to date.

Subtask 7.2. Beneficiated Shales

Scheduled activities in this task have not been completed due to equipment delays in Subtask 4.1.3.

Table 13. ANALYSIS OF EASTERN OIL SHALE SAMPLES

[illegible]

Task 8. Project Management and Reporting

The objective of this task is to coordinate all aspects of the program among DOE, IGT, and the various subcontractors to insure that a cohesive program is maintained.

Discussion

In July, a report describing the work conducted during April through June 1988 was prepared and submitted to DOE. During September, IGT toured the facilities at the University of Pittsburgh where the batch/continuous unit for testing the LICADO process (Subtask 4.2.3) has recently been commissioned. A project progress review was also conducted with IIT personnel at IGT.

FUTURE PLANS

Work on all the scheduled tasks will continue as planned.

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TTU:	Professor W. P. Bonner
UM:	Professor H. S. Fogler
UP:	Professor S.-H. Chiang

REFERENCES

1. Leung, S.S., Leist, D.W., and Davis, R.W., "Leaching Study of Oil Shale in Kentucky with Section on Hydraulic Reconnaissance of the Oil Shale Outcrop in Kentucky," U.S. Geological Survey, Water Resources Investigations Report 84-4073, 1984.
2. "A Survey of the Major Devonian Oil Shale Resources in the Eastern United States," Institute of Gas Technology, 1979, (unpublished). Communicated from M.C. Mensinger.
3. Sullivan, J.N., "Low-Flow Characteristics of Kentucky Streams," U.S. Geological Survey, Open-File Report 80-1225, 1980.
4. Hoover, K.V., "Devonian-Mississippi Shale Sequence in Ohio," Information Circular No. 27, Ohio Department of Natural Resources, 1960, page 3.
5. Anonymous, "Low-Flow Characteristics of Ohio Streams," U.S. Geological Survey, Open-File Report 81-1195, 1981, page 191.
6. Anonymous, "The Nation's Water Resources 1975-2000," U.S. Water Resources Council, Volume 4, Ohio Region, December 1978.
7. Conant, L.C. and Swanson, V.E., "Chattanooga Shale and Related Rocks of Central Tennessee and Nearby Areas," U.S. Geological Survey, Professional Paper 357, 1961.
8. Goodwin, W.A., Kerr, C.P., Leimer, H.W., and McGowan, C.W., "Converting Chattanooga Oil Shale to Synthetic Liquid Fuel," Tennessee Energy Authority, 1981 (unpublished research paper).
9. Lowery, J.F., Counts, P.H., Edmiston, H.L., and Edwards, F.D., "Water Resources Data - Water Year 1986," U.S. Geological Survey, Water Data Report TN-86-1, 1986.
10. Martin, H. and Straight, M., "An Index of Michigan Geology," Publication 50, Michigan Geological Survey, Department of Conservation, 1956.
11. Matthews, R.D., "The Devonian-Mississippian Oil Shale Resource of the Eastern United States," Sixteenth Oil Shale Symposium Proceedings, Golden, Colorado, April 1983.
12. Holtschlag, D.J. and Croskey, H.M., "Statistical Models for Estimating Flow Characteristics of Michigan Streams," Water Resources Investigations Report 84-4207, U.S. Geological Survey and Michigan Department of Natural Resources, 1984.
13. Anonymous, "The Nation's Water Resources 1975-2000," Volume 4, Great Lakes Region, U.S. Water Resources Council, December 1978.
14. Hasenmueller, N.R. and Leininger, R.K., "Oil Shale Prospects for the New Albany Shale in Indiana," 1987.

15. Anonymous, "The Nation's Water Resources 1975-2000," Volume 4, Tennessee Region, U.S. Water Resources Council, December 1978.
16. Bingham, R.H., "Low Flow Characteristics of Alabama Streams," Geological Survey Water Supply Paper 2083, 1982.
17. Povarennykh, A.S., Trans. All-Union Mineral, Mineral Society, 87, pp 215-223, 1958.

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