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**PRESSURIZED FLUIDIZED-BED HYDRORETORTING
OF EASTERN OIL SHALES**

Progress Report for the Period October-December 1988

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T. Y. Xiong
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February 1989

Work Performed Under Contract No.: DE-AC21-87MC11089

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia 26505

By
Institute of Gas Technology
Chicago, Illinois 60616

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Institute of Gas Technology
IIT Center, 3424 S. State Street
Chicago, Illinois 60616

MASTER

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EXECUTIVE SUMMARY

This report presents the work performed during the fifth program quarter from October 1 through December 31, 1988, under U.S. 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. Seven 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), a total of 21 tests, including 14 successful tests, were conducted in the batch PFH reactor, and 1 successful test in the continuous PFH reactor. All batch tests were made with Indiana New Albany shale. Batch tests were conducted to study the effects of preheater conditions, shale particle size, and hydroretorting temperature, pressure, and residence time on oil yield and product carbon distribution. Preliminary results indicate that preheater temperatures and residence times in the ranges of 70 to 600°F, and 0 to 30 minutes, respectively, have no effect on product oil yield or carbon distribution. For hydroretorting conditions of 1050°F and 400 psig, an increase in particle size from -60+100 to -40+60 mesh had no effect on total carbon conversion, but increased carbon conversion to gas and decreased carbon conversion to oil. No particle size effect was seen for particles smaller than -60+100 mesh. Samples of shale with particle size consists of -60+100 and -100+140 mesh were hydroretorted at 1050°F and 1000 psig. The test results showed the same oil yield and product carbon distributions.

Indiana shale hydroretorting tests at 1000 psig with average temperatures between 922° and 1347°F showed that oil yield decreases slightly with increasing temperature. Increasing temperature does result in higher carbon conversion to gas. Increasing the hydroretorting pressure from 400 to 1000 psig for -60+100 mesh shale at 1050°F increases both the oil yield and the carbon conversion to gas. Decreasing the shale residence time from 30 to 10 minutes at 1050°F and 1000 psig did not affect the oil yield or carbon conversion to gas.

One successful test was conducted this quarter in the continuous PFH reactor. Test C-1 was made at 1000°F and 600 psig with -60+100 mesh Indiana shale. The carbon conversion for Test C-1 shows a reconciled oil yield of 27.5 gallons per ton (63 percent of the feed carbon) and a carbon conversion

to gas of 10 percent. Test C-1 had 3 percent more carbon to oil and 7 percent less carbon to gas than predicted based on batch test results. Both Subtasks 2.3 (Bench-Scale Tests) and 2.4 (Data Analyses and Correlations) were initiated this quarter.

In Subtask 3.2 (Electrostatic Desulfurization), the Illinois Institute of Technology (IIT) conducted tests with the cyclone tribocharger and shale that had been conditioned with the addition of a light oil. The results showed that pyrite and kerogen were both enriched at the negative electrode. Because these results were unacceptable, IIT installed a spiral-shaped copper tube tribocharger to replace the cyclone. Also, a new venturi-type feed system was installed to eliminate the erratic flow caused by the original screw feeder. One test was conducted in the new system with Indiana New Albany shale (5 μm). The results showed that the layer of product shale became progressively thinner along the 100-cm length of the conveyor. Chemical analyses of aliquot samples of product shale showed that the kerogen content was 19.9 wt % at the entrance to the conveyor on the negative electrode and decreased to about 13.5 wt % at the exit (feed kerogen content is 12.4 wt %). The sulfur content of the kerogen-enriched samples was relatively steady at about 2 wt % (feed sulfur is 3.4 wt %). Based on the results of this test, IIT designed and constructed a new, shorter (40-cm) conveyor with means for continuous product withdrawal. Testing of the new system will begin next quarter.

In Subtask 3.3.1 (Microbial Desulfurization and Denitrification), Ohio State University (OSU) continued experiments to determine the effects of enriched microbial growth on sulfur removal from Indiana New Albany shale. They found that pretreatment of the shale with 5M HNO_3 reduced the sulfur content by about 57%. Subsequent biological incubation at specific conditions led to further sulfur reductions of as much as 9.45%. These active sulfur metabolizing cultures will be used for further testing next month.

In Subtask 3.3.2 (Microbial Process Development), settling tests were conducted with shale-water slurries containing 12 wt % solids that had been aerated and agitated or incubated with a sulfur-metabolizing culture (IGTS7) for 49 days. The results of these tests showed that increasing the solids content reduced the rate of movement of the clarification zone in the uninoculated slurry. In the settling test conducted with IGTS7-inoculated slurry, no clarification zone was observed. Tests were subsequently conducted with

4 wt % shale-water slurries to determine the reason that no clarification zone formed in the IGTS7 slurry. The results of these tests suggest that the ionic composition of the medium and combined effects of agitation and aeration may have affected the settling characteristics.

Also, the feeding procedure for the bioreactor inoculated with IGTS7 was changed from batch mode to fed-batch mode. The growth characteristics of the culture indicated that the organisms may be nutrient limited. Therefore, each week, about 10% of the culture will be removed and replaced with fresh slurry. Microbial growth will continue to be monitored.

In Subtask 3.5 (Restricted Pipe Discharge System [RPDS]), modification of the RPDS unit to a new "vertical transfer" configuration was completed and 6 tests were conducted with -20+40 mesh shale at pressures of 150 and 300 psig. Nominal solids flow rates of 1500; 3000, and 6000 lb/h were tested at each pressure. The results of these tests showed that increasing system pressure increased the gas flow from the RPDS pipe. Also, increasing the solids flow rate significantly increased the gas flow in the RPDS pipe, a phenomenon not observed in the "vertical downward" configuration. All of the tests planned to be conducted in this task have been completed.

The University of Alabama Mineral Resources Institute (MRI) is responsible for the work being conducted in Task 4 (Beneficiation Research). The subcontract between the University of Alabama and the University of Nevada (UN, Reno) was approved by the DOE. Samples of shale have been subsequently shipped to UN for testing on this subtask to be initiated.

In Subtask 4.1.3 (Stirred Ball Mill Grinding), no tests were conducted in this subtask during the quarter because of problems experienced with feeding shale to the NETZSCH stirred ball mill. Other operating problems with the ball mill have been corrected.

Under Subtask 4.2.1 (Column Flotation Tests), MRI conducted a series of tests in the 1-meter column modified for continuous-mode operation. The results show that at constant feed size and frother concentration, flotation performance is improved when the feed is introduced onto the froth bed rather than into the pulp.

In Subtask 4.2.2 (Air Sparged Cyclone), 4 series of tests were conducted in the air-sparged hydrocyclone with Alabama shale at inlet pressures of 2 and 5 psig and air flow rates of 150 to 600 slpm. The best results were achieved at the higher inlet pressure and lower air flow rates.

In Subtask 4.2.3 (LICADO Process), tests were conducted this quarter in the batch research unit with slurries of finely ground (about 7 μ m) Indiana shale. The operating conditions were impeller speeds, liquid CO₂ flow rates, and contact times in the ranges of 800 to 1600 rpm, 200 to 350 ml/min, and 2.5 to 15 minutes, respectively. The results showed that the ash content of the product ranged from 71 to 77%, while that of the refuse was about 80%, suggesting inefficient separation. Also, lower impeller speeds yielded improved results. The effect of dispersants will be studied next quarter to improve the separation.

In Subtask 4.3.2 (Tailings Disposal Studies), detailed chemical analyses were conducted on samples of wastewater simulating a processing plant tailing stream. The results show that the tailing stream from Alabama shale processing contains higher quantities of impurities than that from Indiana shale processing.

In Task 5 (Operation of PFH on Beneficiated Shale), a second sample of beneficiated Alabama shale was tested in the 6-inch diameter fluidization column at about 530°F with nitrogen. The results show that this material can be fluidized at this temperature.

In Subtask 6.2 (Water Availability and Treatment Studies), Tennessee Technological University (TTU) completed work on determining the availability of water for PFH processing plants from the 6 states with significant Eastern shale resources, and continued work on studying the removal of selected compounds from wastewater by biological and physical methods. Batch studies were conducted with pyrrole, and with mixtures of acetone/propionitrile, acetone/pyrrole, and propionitrile/pyrrole. The results show that the compounds were metabolized simultaneously rather than sequentially. The results of activated carbon adsorption tests conducted with the selected compounds indicate that removal is low.

In Subtask 6.3 (Heavy Metals Removal), the University of Michigan continued laboratory studies on dissolution of barium and chromium from raw and

hydroretorted shale samples using HCl and HBr. The results show that increasing the acid concentration increased the dissolution of both Ba and Cr from the shale. The extent of Ba dissolution is generally higher from raw shale than from retorted shale. UM also conducted cadmium sulfide dissolution experiments in which laser light irradiated the CdS in the presence of HCl. The results of these tests showed that rate enhancements of up to 350% were achieved at low light intensities.

In Subtask 6.4 (PFH System Analyses), modifications to the computer program that simulates a PFH process plant have been essentially completed.

In Task 7 (Sample Procurement, Preparation and Characterization), a site has been selected for bulk sampling of Tennessee (Chattanooga) shale. The sample is scheduled to be taken early next quarter. This will complete the procurement of the 6 shale samples for the program.

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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. Department of Energy (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 seven other institutions; the University of Alabama/Mineral Resources Institute (MRI), Illinois Institute of Technology (IIT), the University of Michigan (UM), the University of Nevada (UN), Ohio State University (OSU), Tennessee Technological University (TTU) and the University of Pittsburgh (UP).

This report presents the work performed during the fifth program quarter from October 1 through December 31, 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.

Subtask 1.1. Batch Tests

The objective of this task is to construct and operate a laboratory-scale batch unit to determine the effects of a number of independent variables that may affect the product yields of the PFH process.

Discussion

A total of 47 tests have been conducted to date in the batch PFH reactor including 21 tests this quarter using Indiana New Albany shale. Six of the tests conducted this quarter were terminated due to mechanical failures; 1 was unsuccessful because the bed thermocouples failed and a reliable temperature profile could not be determined. Table 1-1 gives analyses of the Indiana shale used for the batch tests and the continuous test.

Table 1-1. CHEMICAL ANALYSES OF INDIANA NEW ALBANY
SHALE USED FOR BATCH AND CONTINUOUS PFH TESTS

Feed Sample	<u>Batch Tests</u>	<u>Continuous Test</u>
Test No.	33 to 47	C-1
Moisture, wt %	2.07	1.82
Ultimate Analysis, wt % (dry basis)		
Carbon	14.72	14.89
Hydrogen	1.66	1.68
Ash	78.16	78.21

Two modifications were made in the batch PFH unit operating procedure to improve the stability of the temperature profiles. A preheat furnace was installed to heat the inlet gas to the reactor. This furnace permits finer control of the bed temperatures and helps to keep the temperature at the bottom of the bed close to the average bed temperature. The second modification was to keep the recycle gas flowing for 10 minutes after the furnaces

were turned off and opened at the end of the test. This change prevents any temperature spikes from occurring at the end of a test and allows for more accurate control of the shale residence time-temperature history in the reactor.

Summaries of the operating conditions and results of the 16 successful batch PFH tests (Tests 24 and 26 conducted last quarter, and 14 conducted this quarter) are presented in Table 1-2. Operating conditions include the preheat and reactor temperatures and residence times, reactor pressure, and the minimum fluidization (U_{mf}) and actual superficial gas velocities. Test results include the reconciled product carbon distributions and oil yields, the oil specific gravities, and the product gas compositions.

Carbon balances were reconciled by assuming that the carbon found in the residue shale was correct, and that the ratio of measured carbon in product oil to measured carbon in gas was correct. Unreconciled carbon balances ranged from 89% to 106% for 12 of the 16 tests. The other 4 tests had unreconciled carbon balances ranging from 83% to 129%.

The batch tests were conducted to determine the effects of reactor temperature, pressure, and residence time, preheater temperature and preheat time, and shale particle size on carbon distribution and oil yield. Preliminary results of the effects of changing these independent variables have been determined over the ranges of conditions studied to date.

The effects of preheater conditions and reactor residence time on carbon distribution were determined by hydroretorting -60+100 mesh Indiana shale at 1050°F and 1000 psig. Results are shown in Figure 1-1. Tests 38 and 41 were conducted with the same 30-minute reactor residence times and preheat temperatures of 550°F, but with preheat residence times of 30 and 15 minutes. In Test 46, the reactor temperature and residence time were the same, but no preheat was used. The results of these tests indicate that there is no effect of preheat temperature or residence time on oil yield or carbon distribution. Oil yields for these tests were between 28.1 and 30.6 gallons per ton (GPT) (68% to 71% of the feed carbon), while gas yields ranged from 19% to 21% of the feed carbon.

Test 47 was conducted under the same conditions as Test 46 (no preheat, 1050°F and 1000 psig in the reactor), but with a residence time reduced from

Table 1-2. SUMMARY OF TEST CONDITIONS AND RESULTS OF BATCH
PFH TESTS WITH INDIANA NEW ALBANY SHALE

Test No.	24	26	33	34	35	36	37	38	39	41	42	43	44	45	46	47
Average Feed Hopper Temperature, °F	614	564	573	624	564	582	415	506	610	567	588	529	611	553	70	70
Feed Hopper Residence Time, min	30	30	35	32	34	33	32	32	33	15	13	13	32	33	0	0
Average Reactor Temperature, °F	994	1028	1089	1054	965	1347	1133	1065	1081	1062	1074	1058	1060	922	1050	1076
Reactor Residence Time, min	30	30	41	30	31	30	30	30	30	30	30	30	30	30	30	10
Pressure, psig	987	1012	605	402	1008	999	1013	1010	1015	996	1003	1012	403	998	1001	986
Shale Particle Size, mesh	----- -60+100 -----										-- -100+140 --		-40+60		----- -60+100 -----	
Superficial Gas Velocity, ft/s	0.073	0.062	0.081	0.165	0.065	0.078	0.068	0.071	0.064	0.089	0.057	0.086	0.187	0.062	0.068	--
Minimum Fluidization Velocity, ft/s	0.051	0.051	0.051	0.051	0.051	0.051	0.051	0.051	0.051	0.051	0.025	0.025	0.15	0.051	0.051	0.051
Product Distribution, % of feed carbon																
Residual Shale	15.7	17.5	22.5	29.7	14.1	7.4	10.0	10.6	13.8	10.0	12.1	13.0	31.5	14.2	10.6	11.1
Product Gas	17.3	10.3	20.6	11.9	14.3	24.2	21.5	19.9	12.5	18.6	20.5	22.3	23.8	14.9	21.5	17.5
Oil	67.0	72.2	56.9	58.4	71.6	68.4	68.5	69.5	73.7	71.4	67.4	64.7	44.7	70.9	67.9	71.4
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Oil Specific Gravity, °API	9.3	7.2	1.6	6.4	11.0	10.4	12.9	10.9	12.3	12.3	9.0	6.4	6.7	12.0	10.1	10.3
Oil Yield, gpt	27.5	29.3	22.5	24.8	30.2	28.5	29.0	29.0	30.8	30.6	28.9	25.6	18.1	29.8	28.1	29.6
Product Gas*, mole %																
H ₂	95.78	97.88	94.83	94.55	98.52	96.43	97.70	98.05	98.80	97.47	97.33	97.31	95.45	98.06	97.00	97.72
CO	0.23	0.07	0.21	0.33	0.13	0.00	0.02	0.07	0.00	0.09	0.11	0.14	0.31	0.13	0.11	0.09
CO ₂	0.01	0.01	0.02	0.02	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.01	0.02	0.00
CH ₄	2.21	1.09	2.79	2.98	0.67	2.74	1.36	1.05	0.67	1.43	1.41	1.45	2.46	0.94	1.62	1.26
C ₂ H ₆	1.09	0.67	1.53	1.33	0.33	0.80	0.68	0.52	0.35	0.69	0.73	0.81	1.05	0.50	0.88	0.64
C ₂ H ₄	0.06	0.00	0.02	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
C ₃ H ₈	0.46	0.20	0.46	0.51	0.16	0.01	0.19	0.22	0.12	0.24	0.30	0.21	0.48	0.26	0.30	0.23
C ₃ H ₆	0.02	0.00	0.02	0.03	0.00	0.00	0.01	0.00	0.00	0.01	0.01	0.01	0.02	0.00	0.00	0.00
C ₄ H ₁₀	0.07	0.04	0.06	0.09	0.07	0.00	0.02	0.05	0.03	0.04	0.07	0.04	0.12	0.06	0.05	0.04
C ₄ H ₈	0.00	0.00	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
C ₅ H ₁₂	0.03	0.00	0.01	0.03	0.08	0.00	0.00	0.01	0.00	0.01	0.01	0.01	0.02	0.01	0.00	0.00
C ₆ ⁺	0.04	0.03	0.04	0.08	0.04	0.02	0.02	0.03	0.02	0.02	0.03	0.02	0.06	0.03	0.02	0.02
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

* H₂S-free basis.

Figure 1-1. EFFECT OF SHALE RESIDENCE TIME IN THE REACTOR ON PRODUCT CARBON DISTRIBUTION

30 to 10 minutes. Test 47 had a slightly higher oil yield than Test 46, indicating 10 minutes at 1050°F and 1000 psig is sufficient time for complete conversion of kerogen to oil for -60+100 mesh shale. The gas yield was also unaffected by the reduction in reactor residence time.

Seven tests were conducted to study the effect of reactor temperature on the product carbon distribution and oil yield. All 7 tests were conducted at 1000 psig with -60+100 mesh Indiana shale, and a preheater temperature and residence time of 550°F and 30 minutes. The average reactor temperatures tested ranged from 922° to 1347°F, and residence times were at least 30 minutes for all tests. Carbon distributions and oil yields (in gallons per ton per weight percent feed carbon) are presented in Figures 1-2 and 1-3.

The results show that oil yield is either unaffected or decreases slightly with increasing temperature over the range studied. Test 45, with an average reactor temperature of 922°F, had an oil yield of 29.8 gallons per ton (GPT) while Test 36, with the highest average reactor temperature of 1347°F, had a slightly lower oil yield of 28.5 GPT. Carbon conversion to gas was found to increase with increasing reactor temperature. Increasing the reactor temperature from 922° to 1347°F increased the carbon conversion to gas from 15% to 24%. For -60+100 mesh Indiana shale at 1000 psig, the highest oil yield and lowest carbon conversion to gas are at a reactor temperature below 950°F.

The effects of pressure on carbon conversion and oil yield were studied by conducting tests with -60+100 mesh Indiana shale at 400 (Test 34), 600 (Test 33), and 1000 psig (Test 38). Preheater conditions (550°F and 30 minutes residence time) and reactor conditions (1050°F and 30 minutes residence time) were the same for all 3 tests. Although the reconciled carbon conversions for Test 33 (600 psig) are less reliable than the other carbon conversions due to a low carbon balance, the overall effects of reactor pressure on hydroretorting are clear. For -60+100 mesh Indiana shale at 1050°F, the carbon conversion to both oil and gas was found to increase with increasing pressure (Figure 1-4). The reconciled oil yield increased from 24.8 GPT (58% of the feed carbon) at 400 psig to 29.0 GPT (69% of the feed carbon) at 1000 psig (Figure 1-5). Carbon conversion to gas increased from 12% to 20% with an increase of pressure from 400 to 1000 psig.

Figure 1-2. EFFECT OF REACTOR TEMPERATURE ON PRODUCT CARBON DISTRIBUTION

Figure 1-3. EFFECT OF REACTOR TEMPERATURE ON NORMALIZED OIL YIELD

Figure 1-4. EFFECT OF REACTOR PRESSURE ON PRODUCT CARBON DISTRIBUTION

Figure 1-5. EFFECT OF REACTOR PRESSURE ON NORMALIZED OIL YIELD

The size of Indiana shale particles hydrotreated in the batch PFH reactor has been found to affect the oil yield and product carbon distribution. Tests 44 and 34 were conducted at 400 psig with -40+60 and -60+100 mesh shale, respectively, and a reactor temperature of 1050°F and residence time of 30 minutes. Tests 41 and 42 were conducted at 1000 psig with -60+100 and -100+140 mesh shale and the same reactor temperature of 1050°F and residence time of 30 minutes. Two pressures had to be used to study particle size effects, because the flow rate needed to fluidize the large particles (-40+60 mesh) at 1000 psig, could not be achieved in the batch unit.

At a reactor pressure of 400 psig, increasing the particle size from -60+100 to -40+60 mesh did not affect the overall carbon conversion, but did result in a significant decrease in the oil yield and a large increase in the gas yield (Figure 1-6). The -60+100 mesh shale had an oil yield of 24.8 GPT (68% of the feed carbon), a carbon conversion to gas of 12% and a total carbon conversion of 70%. Hydrotreating of the -40+60 mesh shale produced a lower oil yield of 18.1 GPT (45% of the feed carbon), a higher carbon conversion to gas of 24%, and a similar total carbon conversion of 69%.

Tests with -60+100 and -100+140 mesh shale at 1000 psig, showed similar oil yields and carbon conversions to gas. The -60+100 and -100+140 mesh samples had oil yields of 30.6 and 28.9 GPT (71% and 67% of the feed carbon), carbon conversions to gas of 19% and 21%, and total carbon conversions of 90% and 88%.

One or two additional tests will be conducted in the batch PFH reactor with Indiana New Albany shale to examine the effects of shorter residence times and lower reactor temperatures, on oil yields and product carbon distributions.

Subtask 1.2. Continuous Tests

The objective of this task is to obtain steady-state data for laboratory-scale PFH processing in a continuous test unit for the Indiana New Albany shale to determine the effects of temperature, pressure, fluidization gas velocity, and solids residence time on the product yields and quality.

Discussion

One successful test was conducted this quarter in the continuous PFH reactor. Test C-1 was made with -60+100 mesh Indiana New Albany shale (see

Figure 1-6. EFFECT OF AVERAGE PARTICLE SIZE AND PRESSURE ON PRODUCT CARBON DISTRIBUTION

Table 1-1). Shale was preheated to approximately 600°F and then introduced to the reactor. Reactor conditions were 1000°F at 600 psig with an average shale residence time of 150 minutes. The results from batch tests show carbon conversions in a long-residence time test should not differ significantly from a test with the intended 30-minute-residence time.

A summary of the operating conditions and results of Test C-1 is presented in Table 1-3. Comparisons of the carbon conversions and oil yield from Test C-1 with those from the batch test are presented in Figures 1-7 and 1-8. Carbon conversions from Test C-1 show a reconciled oil yield of 27.5 GPT (63% of the feed carbon) and a gas yield of 10%, for a total carbon conversion of 73%. The continuous test carbon conversion to oil was approximately 3% higher than predicted by the batch tests, and the carbon conversion to gas was 7% lower than predicted by the batch tests. Part of the lower gas yield in Test C-1 was due to a reactor temperature of 1000°F compared to 1050°F for the batch tests.

The slightly higher oil yield and lower gas yield in the continuous test may be a result of less gas recycle during the continuous test. Future continuous PFH tests will compare the oil yield and carbon conversion obtained under similar operating conditions in the batch and continuous PFH reactors.

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.

Subtask 2.3. Bench-Scale Tests

The objectives of this subtask are to determine the effects of using a range of particle sizes (below 1/8 inch), and process scale-up from laboratory- to bench-scale using a modified reactor system, and to provide data for environmental mitigation analyses. This subtask is further divided into two subtasks: Equipment Modification and Bench-Scale Tests.

Table 1-3. SUMMARY OF TEST CONDITIONS AND RESULTS OF PFH
CONTINUOUS TEST WITH INDIANA NEW ALBANY SHALE

Test No.	C-1
Operating Conditions	
Average Feed Hopper Temperature, °F	639
Feed Hopper Residence Time, min.	--
Average Reactor Temperature, °F	1000
Reactor Residence Time, min.	151
Pressure, psig	618
Shale Particle Size, mesh	-60+100
Superficial Gas Velocity, ft/s	0.077
Minimum Fluidization Velocity, ft/s	0.05
Operating Results	
Product Distribution, % of feed carbon	
Residue Shale	26.6
Product Gas	10.1
Oil	63.3
Total	100.0
Oil Yield, GPT	27.5
Oil Sp. Gravity, °API	14.2
Oil Sp. Gravity, gr/ml	0.971
Product Gas,* mol %	
H ₂	89.44
CO	0.81
CO ₂	0.24
CH ₄	5.50
C ₂ H ₆	2.29
C ₂ H ₄	0.05
C ₃ H ₈	0.98
C ₃ H ₆	0.06
C ₄ H ₁₀	0.33
C ₄ H ₈	0.05
C ₅ H ₁₂	0.13
C ₆ +12	0.12
Total	100.00

* H₂S-free basis.

Figure 1-7. COMPARISON OF CARBON DISTRIBUTIONS FROM BATCH AND CONTINUOUS PFH TESTS WITH INDIANA NEW ALBANY SHALE

Figure 1-8. COMPARISON OF NORMALIZED OIL YIELD FROM BATCH AND CONTINUOUS PFH TESTS WITH INDIANA NEW ALBANY SHALE

Discussion

This subtask was initiated this quarter with a review of the basic flow diagram and a list of the equipment required for modification of the high-temperature, high-pressure fluidization unit. An alternate design that would significantly reduce the feed hydrogen requirements and potentially improve product gas analysis is currently being evaluated. Hydrogen-rich product gas would be recycled by a small compressor after the product oil and water have been recovered. Vendors have been contacted to determine costs and availability of the necessary equipment.

Subtask 2.4. Data Analyses and Correlations

The objectives of this subtask are to analyze the data obtained in Tasks 1 and 2, and to develop correlations describing the performance of various shales in the PFH process. Data from the batch and continuous lab- and bench-scale tests generated in the above subtasks will be used to develop empirical correlations that will relate the effects of operating temperature and pressure on oil, gas, and water yields and conversions of carbon, hydrogen, sulfur, and nitrogen.

Discussion

This subtask was initiated this quarter by inputting the data obtained to date from tests in the batch and continuous units into a computer spreadsheet.

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 conducted tests with the cyclone tribocharger system and found that the pyrites tended to migrate along with the kerogen. The particle layer deposited at the negative electrode was found to be enriched in both kerogen and pyrite. The pyrite level increased from 3.56 to 4.06% and the kerogen from 12.2 to 16.3% in the layer deposited at the negative electrode.

In order to enhance the separation of kerogen and mineral matter, a small amount of a light hydrocarbon oil was added to finely ground (5 μ m) shale and dried overnight in a vacuum oven. The conditioned shale was tested in the system and the separation was improved compared to the case without conditioning. Pyrite sulfur content increased from 4.5 to 9.5% in the layer deposited at the negative electrode, while the kerogen content increased from 12.4 to 19.9% in the same layer.

Because the positive charge of the kerogen may be neutralized by the negative charge of either pyrites or minerals present predominantly in the shale matrix, IIT replaced the cyclone tribocharger with a spiral-shaped copper tube (5 feet long and 1-inch O.D.). In previous tests, particles were exiting from the cyclone at a low velocity, therefore there was a possibility that the negatively charged particles could be attracted to the positively charged particles. The geometry of the new spiral tribocharger was selected to obtain maximum particle-to-wall contact at reasonable velocities.

IIT measured the surface charge of chemically pure iron pyrites, shales with different kerogen contents, spent shale, Illinois No. 2 coal, and beneficiated Alabama shale (BAS) mixed with agents like Tullanox and micron-sized alumina to improve flow. Table 3-1 summarizes the charge values determined for these materials.

Table 3-1. SURFACE CHARGE OF VARIOUS MATERIALS

<u>Sample</u>	<u>Surface Charge, Coulomb/kg</u>
Pyrites	$-7.00 * 10^{-4}$
Spent Shale	$-1.85 * 10^{-3}$
Shale ¹	$-6.30 * 10^{-5}$
Illinois #2 Coal	$+1.34 * 10^{-5}$
BAS ²	$+2.00 * 10^{-3}$
Tullanox + BAS	$-4.00 * 10^{-5}$
Alumina + BAS	$-1.50 * 10^{-4}$

1 Indiana-New Albany Shale

2 Beneficiated Alabama Shale

These charge values were obtained at a velocity of about 5 m/s and with an average particle size of 5 μ m. The data indicate that the spent shale and pyrite acquire similar charges. However, the spent shale has 2.6 times more negative charge than pyrite under the same conditions. Figure 3-1 shows the particle charge as a function of kerogen content. The surface charge goes from positive to negative as the kerogen content in the shale increases.

The addition of Tullanox and alumina to the shale improved the flow characteristics. However, the surface charge of the shale mixture changed drastically. These agents will not be tested further.

A new feeding system was designed and built for feeding the fine particles in the new spiral tribocharging system. The variable speed screw feeder used previously was not adequate for feeding the fine shale particles. The new venturi-type feed system (Figure 3-2) is simple and easy to operate. Both particle loading and air flow can be controlled by adjusting the primary and secondary air flows.

One test was conducted in the new system with Indiana New Albany shale ground to an average particle size of 5 μ m under nitrogen. Particles were charged in the new spiral tribocharging system. The polarity of the top electrode plate was kept negative while the bottom electrode was positive.

Figure 3-1. EFFECT OF KEROGEN CONTENT ON SHALE SURFACE CHARGE

Figure 3-2. SCHEMATIC DIAGRAM OF THE NEW VENTURI FEEDER

Layers of shale formed at both negative and positive electrodes. As expected, the layer is thicker at the entrance to the conveyor and becomes progressively thinner toward the exit of the conveyor. Also, some particles migrated through the perforations in the bottom electrode. To study the migration behavior of pyrites and kerogen as a function of position in the separator, samples of these particle layers were collected in 20-cm segments from the positive and negative electrodes and analyzed for kerogen and pyritic sulfur contents.

Figure 3-3 shows the variation of kerogen content in the shale at the positive and negative electrodes along the length of the conveyor. Maximum separation is achieved at the conveyor entrance. The difference in the kerogen content of the positive and negative layers decreases along the length of the conveyor.

Figure 3-4 shows the variation of pyritic sulfur content in the shale at the positive and negative electrodes along the length of the conveyor. At the negative electrode, where kerogen is enriched, the pyritic sulfur content is almost constant at about 2%. The feed has a pyritic sulfur content of 3.43%. However, at the positive electrode, the pyritic sulfur content decreases from 4.3% at the entrance of the conveyor to 0.83% at the exit. The pyrite sulfur content of the shale collected in the conical section beneath the perforated positive electrode was found to be 7%. This stream accounted for 55% of the pyrite present in the shale.

The results show that a conveyor length of 30 to 40 cm is adequate under the conditions being tested. Also, the particle layer deposited at each electrode must be removed from the side where feed is entering. A suction mechanism could be used to continuously withdraw the particles from both electrodes. A constant pyrite composition in the kerogen-rich layer indicates that there is significant interaction between the positively and negatively charged particles, even though the new spiral tribocharger has reduced this interaction. The particle transport velocity is very important and additional tests must be made to determine the optimum velocity.

In view of the experimental results achieved to date, IIT designed and built a new separator (Figure 3-5). The major changes in the new unit are (a) the length is 40 cm compared to 1 meter, (b) there is no conical section, (c) the electrodes are not perforated, and (d) it can be operated in continuous

Figure 3-3. VARIATION IN KEROGEN CONTENT OF SHALE SAMPLES ALONG THE LENGTH OF THE CONVEYOR

Figure 3-4. VARIATION IN PYRITE CONCENTRATION OF SHALE SAMPLES ALONG THE LENGTH OF THE CONVEYOR

Figure 3-5. SCHEMATIC DIAGRAM OF THE NEW SEPARATOR

mode by withdrawing the particles using vacuum ejectors. The particle withdrawal rate can be controlled by adjusting the air flow similar to the mechanism shown in Figure 3-2. IIT will begin testing the new unit next quarter.

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 continued experiments to determine the effects of enriched microbial growth on the sulfur content of Indiana New Albany shale. The effect of pretreating the shale with 5M HNO_3 on sulfur reduction was also investigated; the results are presented in Table 3-2. The results show that after pretreatment with HNO_3 , about 57% of the sulfur is removed from the feed shale. Samples of the pretreated shale were then incubated at different conditions with microbial cultures. After 7 days of incubation, the concentration of sulfur in the -100+200 and -200 mesh pretreated shale samples showed 4 test conditions that resulted in an apparent reduction (>6%) in the sulfur. Three of these flasks were at pH 7 and 25°C, with the highest sulfur reduction (9.45%) occurring in the -100+200 mesh shale. Therefore, during the next quarter, an aliquot of the culture media saved and refrigerated from this flask will be applied to pretreated -100+200 and -200 mesh shale samples in S-free media at pH 7 and 25°C.

Table 3-2. EFFECT OF PRETREATMENT WITH 5M HNO_3 ON THE SULFUR CONTENT OF INDIANA NEW ALBANY SHALE

<u>Sample Consist</u>	<u>Sulfur Content, wt %</u>		<u>Sulfur Decrease, %</u>
	<u>Raw</u>	<u>After Pretreatment</u>	
-100+200 mesh	3.67	1.60	56.4
-200 mesh	3.73	1.59	57.4

Work is continuing to develop 1) a screening method to determine the ability of isolated microorganisms to degrade dibenzothiophene and pyridine,

2) techniques to utilize electron microscopy to gain useful particle and elemental information, and 3) cultures to apply to shale and test compounds.

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.

For the efficient operation of a reactor used for biologically removing sulfur and nitrogen from shale, the shale particles should be suspended in the slurry. Once the slurry leaves the bioreactor, however, the shale particles should settle rapidly to facilitate the separation of microbial cells, water, and shale. Settling characteristics can be influenced by several parameters, including modification of the particle surface by adhesion of the microbial cells, bioproducts, media components, ionic strength of the media, and the concentration and particle size distribution of the shale.

A batch settling test without agitation was performed on a 12 wt % shale slurry prepared with deionized water. The test results were analyzed by the method by Kynch (in Introduction to Chemical Engineering, Eds. Badger and Banchero, pp. 650-657). The change in height of the interface between the shale and clear liquid was monitored with time. Last quarter, the settling characteristics of slurries containing 4 and 8 wt % shale were reported. Figure 3-6 shows the effect of slurry solids concentration on the interface height for shale slurries with 4, 8, and 12 wt % solids. As expected, the results show that increasing the solids concentration in the slurry slows the movement of the clarification zone.

A batch settling test was also done on the 4 wt % shale slurry from the aerated and agitated reactor. The slurry was prepared in phosphate buffer and inoculated with the IGTS7 culture. After 49 days of incubation, there was no clarification zone observed in the slurry with the microbial culture, whereas in the slurry without the culture, a clarification zone was observed (Figure 3-7). The settling characteristics may have changed due to the presence of the microbes, the change in the ionic properties of the medium, and/or the agitation and aeration.

To determine the reasons for the change in the settling characteristics, additional batch settling tests were conducted with 4 wt % shale slurries

Figure 3-6. EFFECT OF CONCENTRATION ON THE SETTLING CHARACTERISTICS OF SHALE-WATER SLURRIES

Figure 3-7. EFFECT OF BACTERIAL CULTURE (IGTS7) ON THE SETTLING CHARACTERISTICS OF SHALE-WATER SLURRIES

prepared in phosphate buffer without organisms and with or without agitation and aeration in a bioreactor. The results of these tests showed that settling did take place in a freshly prepared 4 wt % shale slurry in phosphate buffer without agitation and aeration (no clarification zone was observed, but coalescence did take place which is attributed to settling). No clarification zone was observed in the 4 wt % shale in phosphate buffer that had been agitated and aerated for one week. These results suggest that the ionic composition of the medium and the combined effects of agitation and aeration may be affecting the settling characteristics of the shale. The absence of a clarification zone in the 4 wt % shale sample from the bioreactor indicates minimal to no settling of the shale in the bioreactor. This is desirable for efficient microbial removal of nitrogen and sulfur from shale, but is undesirable for the downstream separation operations.

Chemical analyses of shale samples taken before addition to the bioreactor and after 27 days of incubation with IGTS7 are shown in Table 3-3. The results show essentially no sulfur reduction and less than 10% nitrogen removal. Hence, there was no significant removal of either component.

Table 3-3. CHEMICAL ANALYSES OF SHALE SAMPLES AND COMPONENT REDUCTIONS

<u>Compound</u>	<u>Oil Shale Sample</u>		<u>Component[*] Reduction</u>
	<u>Day 0</u>	<u>Day 27</u>	
	----- % -----		
Nitrogen	1.55	1.36	7.5
Sulfur	8.36	7.89	0.5

* By ash balance.

Microbial Growth in Shale Bioreactor

Microbial growth in the bioreactor was monitored by plate counts to ensure the culture was growing. Glucose was added as an auxiliary carbon source. Initially, there was an increase in growth, however, plate counts at the end of the quarter indicated that the organisms were just maintaining themselves. The shale bioreactor inoculated with IGTS7 has been in batch mode

for 3 months. It may be that the nutrients needed for cell growth have been exhausted, resulting in no growth. To ensure the availability of nutrients, the bioreactor will be operated in fed-batch mode. Each week, 10% of the shale slurry will be removed and a fresh 10% slurry will be added. Microbial growth will be monitored.

In a solid particle bioreactor, the rate of agitation must be balanced to ensure that the microbes and the solid particles remain suspended, that adequate oxygen and nutrient transfer is achieved, and that no excessive shear forces are generated to avoid abrasive destruction of the microbial cells or further reduction of the shale particle size. Studies in the fed-batch bioreactor will be initiated next quarter to determine the desirable agitation rate. Uniformity of the shale particle concentration at different levels in the bioreactor, and cell viability and growth by plate counts will be determined at different rates of agitation. The settling characteristics of the bioreactor effluent will also be determined.

In addition, microbial growth studies in shale flasks will be done to determine the stimulation or inhibition of various shale concentrations on cell growth, and nitrogen and sulfur removal.

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.

Summary

During the quarter, modification of the RPDS unit to a new "vertical transfer" configuration was completed. The schematic drawing of the test unit is shown in Figure 3-8. Six tests were conducted using the -20+40 mesh shale material at system pressures of 150 and 300 psig. Three different nominal solids flow rates (1500, 3000, and 6000 lb/hr) were tested at each pressure.

During the tests, it was observed that the unit became noisier as the solids flow rate was increased. Pressure drop readings in the lower section of the vertical transfer pipe were found to decrease as the solids flow rate

Figure 3-8. SCHEMATIC DIAGRAM OF VERTICAL TRANSFER TEST UNIT

was increased, indicating that the solids were no longer in a moving packed-bed or stick-slip type of flow.

A plot of the amount of gas flow from the disengaging vessel versus system pressure, is shown in Figure 3-9. The results show that at all solids flow rates, increasing system pressure increased the gas flow from the RPDS pipe. This result was expected because similar results were observed when testing with the "vertical downward" configuration. However, with the "vertical transfer" configuration, it was found that increasing the solids flow rate also significantly increased the gas flow in the RPDS pipe. This was not observed with the "vertical downward" configuration.

Pressure-drop-per-unit-length ($\Delta P/L$) profiles are also shown in Figures 3-10 and 3-11 for the tests conducted. In general, for the same transfer pipe diameter, the $\Delta P/L$ essentially increased continuously over the length of the pressure reduction line. However, as the solids flow rate was increased, the pressure drop profile also began to shift. The $\Delta P/L$ readings were found to decrease in the lower part of the vertical transfer line as the solids flow rate was increased. The $\Delta P/L$ typically dropped to a reading of 0.5 psi/ft, which is slightly higher than the value (0.4 psi/ft) required for minimum fluidization. Solids flow in that portion of the vertical transfer pipe was, therefore, considered to be in a slugging type of flow. It was observed that the length of the slugging portion of the line increased with increasing solids flow rate. The figures also show that increasing the system pressure improved the operation of the RPDS by reducing slugging in the vertical transfer line.

All the RPDS tests have now been completed. The final report for this subtask is being prepared.

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.

Figure 3-9. EFFECT OF PRESSURE ON THE GAS FLOW FROM THE DISENGAGING VESSEL (VERTICAL TRANSFER UNIT)

Figure 3-10. PRESSURE-DROP PROFILE FOR DIFFERENT SOLIDS FLOW RATES IN THE VERTICAL TRANSFER UNIT (150 psig)

Figure 3-11. PRESSURE-DROP PROFILE FOR DIFFERENT SOLIDS FLOW RATES IN THE VERTICAL TRANSFER UNIT (300 psig)

Discussion

This task is being carried out by the Mineral Resources Institute (MRI) of the University of Alabama. One subtask of this program is being conducted by the University of Pittsburgh (UP) as a subcontractor to MRI. A second subtask has been subcontracted to the University of Nevada, Reno (UN). The activities undertaken during the quarter are described below.

Subtask 4.1 Grinding Studies

Subtask 4.1.1. Ultrasonic Grinding

There was no activity on this subtask this quarter.

Subtask 4.1.2. Pressure Cycling Commination

A subcontract between the University of Alabama and UN was approved by the DOE. UN was informed of that approval prior to the end of the quarter. Samples of Alabama (Chattanooga) and Indiana (New Albany) shales have been supplied to the principal investigator at UN.

Subtask 4.1.3. Stirred Ball Mill Grinding

The NETZSCH stirred ball mill received and installed the previous quarter was made operational. Initial testing indicated that the feed pump supplied with the mill was incapable of handling the coarse feed required to pursue the original research plan. A peristaltic pump was ordered, but had not been received at the end of the current quarter. Other operating difficulties observed in the course of using the NETZSCH mill to prepare feed for beneficiation tests have been corrected.

Due to the inadequacy of the feed pump and other operating problems, no research tests were conducted this quarter.

A new principal investigator, Dr. R. K. Mehta, has been hired and will assume responsibility for this subtask effective on or about February 1, 1989.

Subtask 4.1.4. Grinding Circuit Optimization

There was no activity on this subtask this quarter.

Subtask 4.2. Kerogen/Mineral Matter Separation

Subtask 4.2.1. Column Flotation

The 1.0-meter column flotation cell was modified for continuous operation. In this arrangement, feed is pumped into the cell at a constant, predetermined rate. Likewise, dilution water, spray water, and air are also supplied at constant rates. After start-up, the cell is allowed to run for approximately one-half hour (to reach an equilibrium condition) before samples are taken. Samples of concentrate and tailing are collected simultaneously for a 10-minute period. After collection of the test samples, a change in operating conditions (e.g., air flow rate, tailing discharge height, etc.) are made and the cell is again allowed to reach equilibrium before samples are taken. Concentrate and tailing samples collected during equilibration periods were retained for future use, but were not analyzed or included in the test data.

The first series of tests in the continuous mode were performed on a sample of Alabama shale ground to 90% finer than 18.6 mm. The results of that series, previously reported, are presented graphically in Figure 4-1 (Curve A).

Subsequent series of column flotation tests on the Alabama shale were performed on a sample ground to 90% finer than 9.5 mm and 50% finer than 3.7 mm. The results of these tests are tabulated in Table 4-1, and are plotted in the form of grade-recovery curves (B, C and D) in Figure 4-1. The difference between Curves A and B is attributed to the finer grind. The improvement in results shown in Curve C, compared with Curve B, shows that at constant feed size and frother concentration, flotation performance is improved when the feed is introduced onto the froth bed rather than into the pulp. The recovery is increased despite lower apparent retention times in the cell. Curve D shows that marginal increases in recovery can be obtained with an increase in frother concentration.

Subtask 4.2.2. Air-Sparged Hydrocyclone

Four series of tests were conducted in an air-sparged hydrocyclone (ASH) with Alabama shale during the quarter. The first two series of tests were conducted at a solids content of 4% and inlet pressures of 5 psi (Series 1) and 2 psi (Series 2). Air flows in both series were varied from 150 slpm to

Figure 4-1. EFFECT OF OIL RECOVERY ON SHALE GRADE FOR DIFFERENT COLUMN FLOTATION TEST CONDITIONS

Table 4-1. COLUMN FLOTATION TEST CONDITIONS AND RESULTS

Pulp Height, cm	Air Flow, slpm	Frother, ppm	Concentrate			Tailing				Figure 4-1
			Weight, %	Oil Grade, GPT	Oil Dist., %	C Dist., %	Weight, %	Oil Grade, GPT	Oil Dist., %	C Dist., %
55.9	5.2	30	25.3	40.1	91.7	80.2	74.7	1.2	8.3	19.8
55.9	6.0	30	37.1	35.2	96.0	86.0	62.9	0.7	4.0	14.0
68.6	5.2	30	26.0	38.5	87.9	77.4	74.0	1.9	12.1	22.6
68.6	6.0	30	47.6	22.7	96.3	88.0	52.3	0.8	3.7	12.0
55.9	4.3	42	27.1	38.0	94.3	82.7	72.9	0.9	5.7	17.3
55.9	5.2	42	40.0	27.6	98.1	88.2	60.0	0.3	1.9	11.8
55.9	6.0	42	55.1	20.7	99.8	92.4	44.9	0.1	0.2	7.6
68.6	4.3	42	26.0	37.2	84.2	74.3	74.0	2.5	15.8	25.7
										-

600 slpm. The results of these tests showed that the best results were obtained at the higher inlet pressures and lower air flow rates.

Two other series of tests were performed at a feed solids content of 1.4 wt %. In these series, air flow rates were held constant at 170 slpm and 255 slpm, while inlet pressures were varied from 2 to 8 psig. These adjustments yielded more favorable weight distributions in the underflow and overflow product. Again the preferred conditions were observed at the highest inlet pressures.

Visual examination of the overflow and underflow products from the ASH indicated that very little concentration is being achieved. Tests planned for next quarter will be directed toward improving the flotation kinetics and reagent balance in the ASH.

The possibility of utilizing oil shale tailings as a cement additive (a pozzuolon) was investigated. The data from this investigation (reported previously) show that tailings are unsuitable for use as a cement additive.

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.

Subtask 4.2.3.1. Initial Parametric Study

The objective of this subtask is to establish proper operating conditions for the different process parameters to be considered in various experimental studies.

Subtask 4.2.3.1. Initial Parametric Study

As reported last quarter, the existing Batch Research Unit (BRU) was modified and utilized to obtain basic process performance data. Two 5-gallon drums of slurry containing finely ground Indiana shale were received from MRI in December. The slurry (about 40 wt % solids) was diluted and separated into individual samples of 90 ml each to be utilized in the batch experiments.

Particle size analysis revealed that at least 50 wt % of this material was finer than 7 μm . The Fischer Assay reported by MRI for this sample is 11.4 GPT.

Batch experiments were carried out with the Indiana shale sample at various process conditions. The impeller speed in both phases was varied from 800 to 1600 rpm, and the flow rate of liquid CO_2 was varied from 200 to 350 ml/min. The contact time of liquid CO_2 ranged from 2.5 to 15 min. The slurry concentration was maintained constant at about 5 wt % in most of the tests. In a separate series of experiments, the slurry concentration was varied from 2.5 to 15 wt %.

The test results showed that the ash content in the product varied from 71 to 77%, while the ash content of the refuse was approximately 80%, suggesting an inefficient separation of mineral matter from the kerogen. Table 4-2 presents the experimental conditions and results of these tests. The yields obtained with the Indiana shale were higher than those presented last quarter for the Alabama shale furnished by MRI. It was also observed that the upgraded product from the Indiana shale appeared to contain oily substances that coated the glass in the high-pressure cell.

The results show that the yield increases marginally with an increase in the liquid CO_2 flow rate (Experiments 1 to 4). Higher flow rates would promote better contact between the oil shale particles and the liquid CO_2 , but this is concomitant with an increase in the ash content of the product. This observation is similar to those made for the Alabama oil shale samples last quarter. The effect of contact time of liquid CO_2 is shown in the results from Experiments 1, and 5 to 7. A contact time of 2.5 minutes resulted in a yield of 32.6%, while the longer contact times resulted in lower yields. It is suspected that particle sedimentation at the longer contact times could be responsible for this phenomena. The effect of hydrodynamics and dispersion of liquid CO_2 droplets was studied by varying the impeller speed from 800 to 1600 rpm (Experiments 1, and 8 through 10). It is interesting to note that an agitation speed of 800 rpm yielded improved results with regard to ash reduction and yield. This result will be checked for reproducibility.

Table 4-3 shows the effect of varying the slurry concentration from 2.5 to 15 wt %. In this series of runs, the flow rate was maintained constant at 200 ml/min and the contact time of liquid CO_2 was fixed at 5 minutes.

Table 4-2. OPERATING CONDITIONS AND RESULTS OF LICADO TESTS
CONDUCTED IN THE BRU (Slurry Concentration: 5%)

Test No.	Impeller Speed, rpm	Flow Rate of Liquid CO ₂ , ml/min	Contact Time, min	Yield, %	Product Ash, %	Refuse Ash, %
1	1200	200	5	23.9	74.4	80.4
2	1200	250	5	24.0	74.9	80.6
3	1200	300	5	24.9	74.9	79.9
4	1200	350	5	26.5	75.0	80.3
5	1200	200	2.5	32.6	75.0	80.2
6	1200	200	10	22.9	74.8	79.8
7	1200	200	15	15.8	71.6	79.6
8	800	200	5	27.8	71.6	81.1
9	1400	200	5	24.5	74.9	80.1
10	1600	200	5	25.3	74.3	79.8

Table 4-3. EFFECT OF SLURRY CONCENTRATION ON RESULTS OF LICADO TESTS
CONDUCTED IN THE BRU (Contact Time of Liquid CO₂: 5 minutes)

Test No.	Impeller Speed, rpm	Flow Rate of Liquid CO ₂ , ml/min	Slurry Concentration, %	Yield, %	Product Ash, %	Refuse Ash, %
1	1200	200	2.5	22.7	74.3	80.1
2	1200	200	5	23.9	74.4	80.4
3	1200	200	10	28.2	76.4	80.1
4	1200	200	15	30.6	77.1	80.4

The effect of slurry concentration is demonstrated clearly from the results shown in the table. There is a perceptible increase in yield at the higher slurry concentrations, but it is accompanied by an increase in the ash content of the upgraded oil shale. It is proposed to conduct all tests in the future at a slurry concentration of 5 wt %.

Future plans include a comprehensive study of the effect of dispersants on the process. Several tests without dispersants will also be conducted at short contact times and lower agitation speeds. A detailed test program with the Indiana shale will be carried out. The results thus obtained will be analyzed statistically to elucidate any trends.

The mechanism of the LICADO process was also investigated by carrying out surface and interfacial property measurements. The results will be utilized to formulate a theoretical model for the LICADO process. Repeat experiments were performed in the high-pressure contact angle chamber on pelletized samples of an Eastern shale. The results were reproducible within 10% of those discussed in the last quarterly report. Contact angle measurements will be performed on the Indiana shale samples next quarter.

Subtask 4.3. Waste Treatment and Disposal Studies

Subtask 4.3.1. Process Water Treatment Studies

Samples of Indiana and Alabama shales were individually rod-mill ground in deionized water (40 wt % solids). After grinding, the water from each sample was diluted to 7500 ml (a 9:1 dilution). The composition of the diluted water approximates that expected in a processing plant tailing stream. Analyses of this simulated wastewater yielded the following results:

Shale	<u>Alabama</u> ----- mg/l	<u>Indiana</u> -----
BOD	5.7	4.8
COD	69.4	49.0
Sulfates	316.5	208.0
Phenols	0.30	0.55
Oil and Grease	7.8	6.4
Nitrates (as NO ₃)	0.12	0.06
Cyanides	0.23	<0.10
TSS	1.0	2.0
TDS	932.0	476.0
Chlorides	2.5	2.0
Iron	17.77	9.75

These data show that the Alabama shale releases a higher concentration of impurities in all categories except phenols and suspended solids (TSS).

Subtask 4.3.2. Tailings Disposal Studies

Settling tests were conducted both with and without flocculants on samples of Indiana and Alabama shale flotation tailings. From these data the thickener area required ($\text{ft}^2/\text{ton}/24 \text{ hr}$) was calculated. The results of the calculations are as follows:

	Thickener Area, $\text{ft}^2/\text{ton}/24 \text{ hours}$	
	<u>Natural</u>	<u>With Flocculant</u>
<u>Shale</u>		
Alabama	28.72	2.11
Indiana	41.30	2.37

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 shales. This task is divided into three subtasks: Non-Reactive Testing, Reactive Testing, and Data Analysis 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).

Subtask 5.1. Non-Reactive Testing

A second sample of beneficiated Alabama Chattanooga shale was received from MRI this quarter. A Coulter Counter particle-size distribution for this

material is given in Table 5-1. The weighted average particle size of approximately 7 μm is the same as that of the sample received previously. However, 17% was smaller than 3.2 μm , which was the lower limit of the size range detected in the first sample.

A fluidization test was conducted with a portion of this shale at approximately 530°F in a 6-inch column with nitrogen. The purpose of this test was to determine if the beneficiated shale would form soft agglomerates at elevated temperatures as it did at ambient temperature. The design of this unit made it necessary to use purged rather than static pressure taps for the pressure-drop readings. The resulting fluidization curve shown in Figure 5-1 is significantly different from the curve obtained in the Plexiglas column with the original shale sample (Figure 5-2). A second fluidization test will, therefore, be made in the same equipment at ambient temperature to allow for direct comparison of the results at high temperature.

The fines carryover rate was also measured at 500°F at gas velocities from 0.3 to 0.8 ft/s in the bed. The results of this test are shown in Figure 5-3, along with the results obtained in the Plexiglas column. Fines carryover will also be measured at ambient temperature in the same equipment for direct comparison.

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.

Subtask 6.1. Characterization of Processed Shales

Samples of raw and spent shales from the tests conducted in Subtask 1.1 were obtained. Tests to determine the physical and chemical characteristics of these shale samples will be initiated next quarter.

TABLE 5-1. SIZE ANALYSIS OF BENEFICIATED ALABAMA SHALE

Cumulative, wt %	Diameter, μm
0.6	32.0
1.5	25.4
5.0	20.2
11.0	16.0
19.5	12.7
30.5	10.1
42.5	8.0
53.6	6.4
64.0	5.0
73.7	4.0
82.3	3.17
92.0	2.0
96.9	1.26
98.1	1.0
99.7	0.50

$$D_p \text{ (average)} = 7.0 \mu\text{m}$$

F890101

Figure 5-1. EFFECT OF FLUIDIZATION VELOCITY ON BED PRESSURE DROP ($\Delta P/L$)
 AT ELEVATED TEMPERATURE

F880602

Figure 5-2. EFFECT OF FLUIDIZATION VELOCITY ON BED PRESSURE DROP ($\Delta P/L$)
 AT AMBIENT CONDITIONS

F890102

Figure 5-3. EFFECT OF GAS VELOCITY AND TEMPERATURE ON THE ENTRAINMENT RATE OF BENEFICIATED SHALE

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 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 (Subtask 6.2.1). Specific counties were 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. Also, a paper describing the results of this subtask was prepared and presented at the 1988 Eastern Oil Shale Symposium.

Subtask 6.2.2. Water Treatability

In this subtask, TTU continued work on batch biological experiments for treating water from the PFH process. Having previously completed single substrate experiments on acetone and propionitrile, batch studies with pyrrole were initiated. Experiments were performed using pyrrole as the sole carbon source in approximate concentrations of 600, 300, and 100 mg/l. As with previous biological experiments, excess inorganic nutrients and minerals were added to the solution. Experiments for each of the three pyrrole concentrations were conducted in duplicate to determine reproducibility of the results. Chemical oxygen demand (COD) was used as a nonspecific parameter to monitor substrate removal. Shown in Table 6-1 are initial and final COD values and the length of biological treatment for the batch pyrrole experiments.

Table 6-1. EFFECT OF INITIAL CONCENTRATION ON
BIOLOGICAL REMOVAL OF PYRROLE

<u>Pyrrole Concentration,</u> <u>mg/l</u>	<u>Initial COD,</u> <u>mg O₂/l</u>	<u>Final COD,</u> <u>mg O₂/l</u>	<u>Treatment Time,</u> <u>hours</u>
600	1155	35	80
600	1216	50	78
300	621	51	91
300	580	79	71
100	210	53	54
100	246	20	54

The data are shown in Figures 6-1 through 6-3. Semi-log plots, (Figures 6-4 through 6-6) illustrate the exponential growth exhibited by the batch reactors.

The final report was received for GC/MS analyses of a double substrate biological experiment which included initial concentrations of acetone and propionitrile of approximately 300 mg/l each. As shown in Figure 6-7, the two substrates were removed simultaneously. Biological treatment of the solution for 48 hours resulted in a propionitrile concentration of 0.26 mg/l and an undetectable level of acetone. This experiment was repeated, and results were very similar with a minimal COD following 47 hours of batch biological treatment.

Preliminary biological studies involving the two other substrate combinations, acetone/pyrrole and propionitrile/pyrrole, were performed. The results indicated that removal of substrates in combination did not require longer than removal of the more slowly removed single substrate. Further work regarding the substrate combinations will be done next quarter to verify these findings.

Batch carbon adsorption tests were conducted on single substrates of pyrrole, propionitrile and acetone. Tests with pyrrole were conducted to confirm earlier data and obtain additional data points needed for the Freundlich isotherm. These data are presented in Figure 6-8.

Carbon adsorption tests with propionitrile and acetone were conducted to establish the range of concentrations needed for the Freundlich isotherm. The data for propionitrile are presented in Figure 6-9. Results for acetone show that negligible quantities were adsorbed. Similar results were obtained by Dobb, et al. when compounds similar to acetone were subjected to carbon adsorption.¹

Experiments were conducted to determine the concentration range applicable to double substrate removal by carbon adsorption. The double substrate combinations were: Pyrrole/acetone, pyrrole/propionitrile, and propionitrile/acetone. COD was used as the laboratory control parameter in these preliminary experiments. Since COD does not identify the individual compounds, these data (Figures 6-10 through 6-12) are useful only in the evaluation of technique and concentration range. These results will be used

Figure 6-1. BIOLOGICAL REMOVAL OF PYRROLE
(100 mg/l Pyrrole Initially)

Figure 6-2. BIOLOGICAL REMOVAL OF PYRROLE
(300 mg/l Pyrrole Initially)

Figure 6-3. BIOLOGICAL REMOVAL OF PYRROLE
(600 mg/l Pyrrole Initially)

Figure 6-4. BIOLOGICAL REMOVAL OF PYRROLE (Semi-Log Plot)
(100 mg/l Pyrrole Initially)

Figure 6-5. BIOLOGICAL REMOVAL OF PYRROLE (Semi-Log Plot)
(300 mg/l Pyrrole Initially)

Figure 6-6. BIOLOGICAL REMOVAL OF PYRROLE (Semi-Log Plot)
(600 mg/l Pyrrole Initially)

Figure 6-7. BIOLOGICAL REMOVAL OF TWO SUBSTRATES
(Acetone and Propionitrile)

Figure 6-8. PRELIMINARY FREUNDLICH CARBON-ADSORPTION ISOTHERM DATA FOR PYRROLE (Test #1, 2, 3, and 4)

Figure 6-9. PRELIMINARY FREUNDLICH CARBON-ADSORPTION ISOTHERM DATA FOR PROPIONITRILE (Test # 1 and 2)

Figure 6-10. PRELIMINARY DOUBLE SUBSTRATE FREUNDLICH
CARBON-ADSORPTION ISOTHERM DATA
FOR PYRROLE AND ACETONE

Figure 6-11. PRELIMINARY DOUBLE SUBSTRATE FREUNDLICH CARBON-ADSORPTION ISOTHERM DATA FOR PYRROLE AND PROPIONITRILE

Figure 6-12. PRELIMINARY DOUBLE SUBSTRATE FREUNDLICH
CARBON-ADSORPTION ISOTHERM DATA FOR
PROPIONITRILE AND ACETONE

to plan double substrate experiments in which the concentration of each substrate is determined by GC or GC/MS.

Permission was received in December to include thiocyanate as the fourth substrate. Sodium thiocyanate has been purchased for use in treatability studies, and biological acclimation to the compound will begin in January. It is anticipated that thiocyanate will be treatable biologically under aerobic conditions. Removal by activated carbon remains the subject of speculation.

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).

The first stage of laboratory work concentrated on uncatalyzed dissolution studies of the raw and retorted shale samples using hydrochloric (HCl) and hydrobromic (HBr) acids. The heavy metals chosen for the experiments were barium and chromium due to the toxic limit levels found in the shale. The HCl dissolution tests were carried out at 1.0M, 0.1M, and 0.01M. Data collection for Ba dissolution has been completed from raw and retorted shale with 1.0M, 0.1M, and 0.01M HCl. Data collection was also completed for barium dissolution from raw and retorted shale in 1.0M and 0.1M HBr. Partial data collection has been completed for Cr dissolution from raw and retorted shale in 1.0M, 0.1M and 0.1M HCl.

The second stage of the laboratory work concentrated on developing a better understanding of the kinetics of catalyzed and uncatalyzed dissolutions of heavy metals. Cadmium (as amorphous cadmium sulfide) was chosen as a model compound for the fundamental study of the kinetics of heavy metal dissolution. The dissolution kinetics of CdS have been studied in HCl and HBr solutions.

Experimental Procedure

The raw and retorted shale dissolution experiments concentrated on varying the HCl and HBr concentrations. The samples collected were then analyzed for their elemental concentrations as a function of time.

To determine the effects of the concentration of HCl, the following experiments were performed. Two grams of shale were added to 20 ml of either 1.0M, 0.1M, or 0.01M HCl in a 50-ml stoppered Erlenmeyer flask with a magnetic stirrer. The samples were allowed to mix for 4 hours. It was determined that barium dissolution levels off after 4 hours of dissolution. Each sample was filtered through a 0.45 μ m Gelman filter to separate the two phases. Elemental concentrations in the solution phase were analyzed with the use of a GBC-903 Atomic Absorption Spectrophotometer.

To determine long-term kinetics, the following experiments were performed. Two grams of shale were added to 200 ml of 1.0M HCl in a stoppered 250-ml Erlenmeyer flask with a magnetic stirrer. The first 20-ml sample was withdrawn as soon as the shale and acid were mixed. Timed samples were withdrawn at 5, 15, 30, 60, 120, and 240 minutes. Samples were also withdrawn at 24, 48 and 72 hours. Each sample was filtered through a 0.45 μ m Gelman filter to separate the two phases. Elemental concentrations of the solution phase were analyzed by atomic absorption.

Time-dependence studies with HBr followed the HCl experiments with a few modifications. Twenty grams of shale was mixed with 200 ml of 1.0M and 0.1M HBr, respectively. Both raw and retorted shale were tested individually. Timed samples were withdrawn at 5, 15, 30, 60, 120, and 240 minutes. Samples were also withdrawn after 24 hours. After each sample was withdrawn, 20 ml of HBr were added back to the reaction mixture to keep the volume of acid constant at 200 ml through the experiment. The HBr samples were treated identically to the HCl samples.

The CdS dissolution experiments were performed using a rotating disk apparatus in the following manner. A 5-cm disk of amorphous CdS was mounted concentrically on the bottom end of a vertical shaft connected to a Pine Instruments Rotator. All but the bottom face of the disk was carefully covered with epoxy to prevent contact with the solvent. The disk was placed in the appropriate solvent while rotating, and samples of the solution were removed as time progressed. These samples were analyzed by atomic absorption to determine the cadmium concentration from which the rate was then determined.

Results and Discussion

Analysis of the time-dependence study of raw and retorted shale with 1.0M HCl yielded results close to the detection limit of the GBC-903 Atomic Absorption Spectrophotometer. Therefore, this experiment should be repeated with a higher shale-to-solvent ratio to insure reliable results.

Table 6-2 shows the dissolution of Ba from raw and retorted shale in 1M, 0.1M, and 0.01M HCl and 1.0M and 0.1M HBr. It can be seen that at low HCl concentration, raw and retorted shale have similar Ba dissolution characteristics. At higher HCl concentrations, more Ba dissolves in raw than retorted shale. As expected, the percent Ba from raw and retorted shale and Cr (3+) from retorted shale decreases with decreasing acid concentration. It should be noted that the levels of Cr (3+) in the solution are also close to the detection limit of the GBC-903 Atomic Absorption Spectrophotometer. The data also indicate similar Ba dissolution characteristics for 1.0M and 0.1M HBr in raw and retorted shale, respectively.

The data in the table indicates that for raw shale, 0.1M HBr has the greater Ba dissolution; and for retorted shale, 1.0M HCl has the greater Ba dissolution.

Table 6-2. EFFECT OF ACID CONCENTRATION AND TYPE ON THE DISSOLUTION OF BARIUM AND CHROMIUM FROM RAW AND RETORTED SHALES

Element	Shale	Concentration, mol/l			
		Acid	1.0	0.1	0.01
			-----	% of feed	-----
Barium	Raw	HCl	33.4	15.4	4.5
	Retorted	HCl	19.0	13.5	6.0
	Raw	HBr	34.5	36.2	NA
	Retorted	HBr	10.2	9.8	NA
Chromium	Retorted	HCl	2.9	1.4	0.7

Measurements made after 4 hours of dissolution.
NA = Not analyzed.

Calibration Experiments

The first set of experiments performed with CdS measured the dissolution rate as a function of rotation speed in 1.0M HCl. By plotting the dissolution rate against the square root of the rotation speed (Figure 6-13), it was determined that the process is diffusion limited for rotation speeds less than about 300 rpm. All subsequent runs were performed well in excess of this speed to assure that the reaction rate was the limiting process.

The dissolution rate was measured for a variety of different HCl concentrations. The rate law was assumed to be the form $R = k C^n$; where R is the dissolution constant, k is the specific reaction rate, C is the HCl concentration, and n is the order of the reaction. Linear regression of the data yields the rate law:

$$R = 1.08 \times 10^{-7} C^{1.41} \text{ (gmol/min/cm}^2\text{)}$$

The dissolution rate of CdS while subjected to laser irradiation in 1.0M HCl was measured. Laser powers of 15 and 55 mW/cm² were used at both 514 and 465 nm wavelengths. These results are shown in Figure 6-14. Rate enhancements of up to 350% were obtained with relatively low intensities, indicating that the mechanism is predominantly photochemical and not thermal. The wavelength has been found to dramatically effect the degree of rate enhancement where irradiation at 456 nm enhanced the rate 50% more than at 514 nm.

Table 6-3 represents a series of runs that were carried out at room temperature and various concentrations of HBr as the solvent. The rates observed suggest that the mechanism does not follow simple power kinetics. The data shows a large increase in the rate above HBr concentrations of approximately 1.5M. More data is required to verify these results and discount the possibility of experimental error.

Table 6-3. EFFECT OF HBr CONCENTRATION ON RATE OF CADMIUM DISSOLUTION FROM AMORPHOUS CdS

<u>Concentration of HBr, M</u>	<u>Rate, mol/min-cm²</u>
0.10	6.87×10^{-8}
0.42	1.03×10^{-7}
0.70	8.95×10^{-8}
1.17	1.19×10^{-7}
1.96	4.70×10^{-7}

Figure 6-13. EFFECT OF AGITATION SPEED ON CdS DISSOLUTION RATE IN HCl

Figure 6-14. EFFECT OF LASER LIGHT INTENSITY AND WAVELENGTH ON CdS DISSOLUTION RATE IN HCl

Future work will include Cr dissolution experiments from raw and retorted shale with 1.0M, 0.1M and 0.01M HCl, and 1.0M and 0.1M HBr. Also, barium dissolution from raw and retorted shale time with varying HNO_3 concentrations will be initiated and fundamental studies of CdS in HBr will continue.

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 were completed during the quarter. Additional modifications will incorporate correlations developed in Task 1 on the effects of PFH operating conditions on product yields and distribution.

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 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), five prospective sites for the procurement of a sample of Tennessee (Chattanooga) shale were reviewed. Samples from each site were analyzed and one, which yields 9.1 GPT Fischer Assay, was selected for bulk sampling. The sample site is located in a road cut on Interstate I-40. Permission from the Tennessee Department of Transportation to take a sample was requested and subsequently granted. Sampling has been scheduled for the fourth week of January.

Samples of the Indiana and Alabama shales were provided to the University of Pittsburgh and the University of Nevada.

Samples of each of the five Eastern shales currently in possession are being prepared for chemical analysis and will be sent to a commercial laboratory for "whole rock" analyses. The analyses will be an oxide and trace element analyses of the shales on a kerogen-free basis.

Subtask 7.2. Beneficiated Shales

There was no activity on this subtask this quarter.

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

IGT sought and received approval from DOE to let a subcontract to Dr. Mano Misra of the University of Nevada (Reno) to continue the work in Subtask 4.1.2 (Pressure Cycling Commintution). Dr. Misra relocated from the University of Alabama, Mineral Resources Institute to the University of Nevada. During the quarter, IGT personnel met and reviewed project progress with IIT, UM, and the University of Alabama's MRI. IGT personnel also attended and presented technical papers at the 1988 Eastern Oil Shale Symposium held at Lexington, Kentucky. Papers were also presented by the project subcontractors from IIT and TTU.

FUTURE PLANS

Work on all the scheduled tasks will continue as planned.

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UM: Professor H. S. Fogler

UP: Professor S.-H. Chiang

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