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PRESSURIZED FLUIDIZED-BED HYDRORETORTING OF EASTERN OIL SHALES

Final Report for the Period June 1992-January 1993

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EXECUTIVE SUMMARY

The Institute of Gas Technology (IGT) is developing the Pressurized Fluidized-Bed Hydroretorting (PFH) process for producing oil from the Devonian shales in the Eastern United States. The original 3-year program was initiated in September 1987 under U.S. Department of Energy (DOE) Contract No. DE-AC21-87MC11089 for the project "Pressurized Fluidized-Bed Hydroretorting of Eastern Oil Shales." The Final Report (in four volumes) describing the results of that work has been published by IGT. A one-year program extension was subsequently authorized by DOE from June 1, 1991 through May 31, 1992. The objective of the one-year program extension was to expand the data base for the PFH process to include beneficiated shales. The results of the one-year program extension have been published by IGT as an annual report for the period June 1991 through May 1992.

This report presents the work performed by IGT from June 1, 1992 through January 31, 1993, under a second program extension for the U.S. DOE under Contract No. DE-AC21-87MC11089 for the project "Pressurized Fluidized-Bed Hydroretorting (PFH) of Eastern Oil Shales." The DOE contract was modified for a second one-year extension; however, budget cutbacks required that the overall program be shortened. Therefore, the scope of work was reduced for some subtasks and other subtasks were eliminated. The task achievements discussed below represent the active tasks of the program. IGT was the prime contractor for the program to develop the PFH II system technology. The University of Alabama Mineral Resources Institute (MRI) and College of Engineering (UA), the University of Kentucky Center for Applied Energy Research (UK-CAER), and Tennessee Technological University (TTU) worked with IGT as subcontractors; their responsibilities and achievements in the program are discussed below in the appropriate tasks.

The objective of Subtask 3.7 (Innovative Reactor Concept Testing) was to demonstrate the technical feasibility of generating hydrogen by cracking by-product methane gas and combusting the carbon produced by the cracking reactions. IGT conducted methane cracking tests with mixtures of hydroretorted and combusted Alabama shale and inert material at temperatures, pressures, and gas residence times in the ranges of 1660° to 2000°F, 50 to 1000 psig, and 4 to 13 seconds, respectively. Methane conversion increased with increasing temperatures and decreased with increasing pressures. A product gas containing 80 percent hydrogen and 20 percent methane can be obtained at cracking conditions of 1850°F and 50 psig, 1900°F and 200 psig, and 2000°F and 600 psig. Minerals present in the combusted shale play an active catalytic role in the methane cracking reaction. Catalytic cracking activity appears to increase from silica sand, to alumina, to combusted shale.

The objective of Subtask 3.9 (Catalytic Hydroretorting) was to improve the quality of PFH-produced shale oil by utilizing both regenerable and throw-away catalysts in-situ. IGT conducted the tests with beneficiated Alabama shale in an existing laboratory-scale reactor at 925°F and 1000 psig with a 20-minute residence time. Tests conducted with the regenerable catalysts improved the quality of the product oil by reducing the sulfur and nitrogen contents up to 98 and 74 percent, respectively, and reduced the specific gravity of the product oil 10 percent to 0.909 g/mL while still achieving over

200 percent of Fischer Assay oil yield. Results of the tests conducted with the throw-away catalysts showed that these catalysts essentially had little or no effect on the quality of the product oil and increased the carbon conversion to gas.

The objective of Subtask 3.10 (Autocatalysis in Hydroretorting) was to investigate the effects of potentially catalytic minerals or alkali metal oxides naturally present in shale on hydroretorting characteristics and product yields. The University of Alabama College of Engineering (UA) conducted the work on this subtask. During the program, UA modified a bench-scale unit for hydroretorting and conducted four tests with salts of metal compounds (copper, iron, nickel, and potassium) to determine their potential catalytic activity for Eastern oil shale processing. Tests were conducted at 400 psig and 900°F. Results indicate that addition of the salts to the shales promoted gasification rather than retorting reactions. Approximately two-thirds of the overall carbon conversions were to gaseous products with one-third to liquid products.

The objective of Subtask 3.11 (Shale Oil Upgrading and Evaluation) was to investigate conventional and novel methods for upgrading the oil produced by shale hydroretorting. IGT conducted the work on this subtask. The catalysts tested included two commercially available oil hydrotreating catalysts and one catalyst prepared at IGT. The nickel-containing conventional catalyst reduced the specific gravity of the whole oil from 0.996 to 0.895 g/mL and decreased the sulfur and nitrogen contents up to 89 and 72 percent, respectively, for operation at 2000 psig and 770°F with hydrogen. Tests were also conducted with the -650°F fraction of shale oil using the conventional catalyst with and without a tungsten promoter. Results of the test with the tungsten promoter at 2000 psig and 740°F with hydrogen feed yielded sulfur and nitrogen reductions of 97 and 98 percent, respectively. Results of tests conducted without the tungsten promoter gave sulfur and nitrogen reductions of 93 and 85 percent, respectively, at similar operating conditions.

For most of the novel upgrading tests, the pressure was reduced from 2000 to 1000 psig and the temperature was 750°F. The novel upgrading tests utilized methane as feed rather than the conventional hydrogen feed. Tests were also conducted at milder operating conditions than are normally used for upgrading. Results of the oil upgrading tests using methane feed showed sulfur and nitrogen removals up to 46 and 31 percent when a tungsten promoter was used.

The University of Alabama Mineral Resources Institute (MRI) was responsible for the work conducted in Task 4 (Beneficiation Research). The overall objective of Task 4 was to develop a physical beneficiation system that would improve the quality of feedstock to the PFH process. Five tasks were active during the program: Subtask 4.1.3. Stirred Ball Mill Grinding, Subtask 4.1.5. Alternative Technology Evaluation, Subtask 4.1.6. Ultrafine Size Separations, Subtask 4.2.1.1. Column Flotation Modeling, and Subtask 4.7. Economic Analyses.

In Subtask 4.1.3 (Stirred Ball Mill Grinding), MRI conducted stirred ball milling tests in batch mode to assess the grindability behavior of three

shale fractions: raw shale, concentrate and tailings. The tests were conducted in a polyurethane-lined attrition grinder using -12+20 mesh silica sand as grinding media. Two types of tests were conducted, one using -20 micrometer (μm) material of each fraction, and another by making a synthetic particle size distribution from particles of given size from each shale fraction. Three size fractions were used: -37+30 μm , -30+20 μm , and -20 μm . Both types of tests revealed that concentrate (kerogen-rich fraction) was relatively easier to grind than tailings (mineral-matter-rich fraction). The power draw was independent of the shale fraction. The test results showed that sand could be effectively used as a grinding media in regrinding mills.

Comminution of oil shales constitutes both the largest capital cost and the largest operating cost in the beneficiation process. Another objective of the program was to evaluate new comminution technologies or technologies from other industries to determine whether they should be included in the research.

MRI evaluated two technologies from the cement industry: roller mills and roller presses. Both technologies were observed in operating cement plants. In each case the technologies were efficient but appeared to be a specialty application that could not be adapted to a mineral processing application. No further consideration of these technologies is recommended.

Previous experience at MRI in the beneficiation of Alabama oil shales indicated that the key to reducing the cost of beneficiation lay in reducing the amount of material ground in the stirred ball mill. To accomplish this end, however, requires that correctly sized material be removed from the grinding circuit by cycloning or by some other fine size separation.

The objective of Subtask 4.1.6 (Ultrafine Size Separations) was to determine the conditions for efficient size separation at ultrafine sizes. A factorially designed experiment was conducted using Mozley cyclones with three different sized apex spigots and three sizes of vortex finders. The data showed that the recovery of fines (i.e. -24 μm material) in the cyclone overflow was greatest using the largest diameter apex and vortex finder (9.4 and 14 mm, respectively). Further tests revealed that 86 percent of the -24 μm material could be removed from the primary ball mill product by a two-stage cyclone circuit.

Column flotation tests on the -24 μm product showed that a clean rougher tailing could be produced and that the rougher concentrate could be substantially upgraded in a cleaner flotation column. The cleaner flotation tailing, however, proved to be a true middling that would require further grinding to achieve liberation.

The flotation tests indicated that an energy efficient grinding-flotation circuit could be achieved with an estimated energy consumption of 42 kWh/ton. Further work would be required, however, to optimize the circuit.

Subtask 4.2.1.1 (Column Flotation Modeling) was divided into two parts. In the first part, an axially dispersed plug flow model was successfully used to describe deep froth column flotation. Residence time distribution (RTD) parameters were estimated by fitting the experimental data to the RTD model.

The estimated mean residence time was found to be equal to the experimental value. The dispersion number was close to zero (0.14) indicating plug flow behavior. The induction time measurement on concentrate and tailings yielded considerably different values, i.e., 10 and 23 milliseconds, respectively. The simulation results showed that optimum recovery is possible within a specific particle size range (35 to 55 μm). The results showed poor recoveries for particles smaller than 5 μm .

In the second part, an x-ray back-scatter technique was used to measure the oil yield of shales, assuming kerogen was a four-component system. The scattering intensity equation modeled for oil shale in terms of carbon, hydrogen, nitrogen, and sulfur produced a strong correlation of scattering intensity with oil yield for Indiana and Tennessee shales. The influence of sulfur and the scattering intensity was found to be significant. To make this technique suitable for any shale sample regardless of its chemical state, moisture and temperature effects must be incorporated in the model.

Subtask 4.4 (Integrated Grinding and Flotation) was conducted by the University of Kentucky Center for Applied Energy Research (UK-CAER). Physical beneficiation of Eastern oil shale using the froth flotation technique has the potential to provide an economical route for obtaining high-grade kerogen for hydrotreating via the PFH process. Beneficiation will have the net effect of reducing both the size of the high-pressure retorting vessels and the cost of hydrotreating. The main objectives of this subtask were to conduct pilot-scale column flotation studies with Alabama oil shale to obtain a high grade (>30 gallons per ton) oil shale at more than 90 percent recovery of kerogen and to conduct dewatering studies of the concentrate using a novel preconditioning technique developed at the UK-CAER. Another objective of the program was to conduct beneficiation studies using the SYMUSEP Separator. Due to budget cuts by the DOE, the pilot-scale and dewatering studies were reduced.

The sample of Alabama oil shale used by UK-CAER had 16.39 percent carbon and contained 11.3 gallons per ton (GPT) of oil as determined by Fischer Assay. Release analysis, which determines flotation limits on grade and recovery, conducted on a 90 percent passing 10 μm shale showed that 90 percent recovery of kerogen could be obtained at 24 percent carbon grade.

Pilot-scale Ken-Flote column flotation studies provided only 50 percent recovery of organic carbon containing about 35 percent carbon. This result was in contrast to recovery of more than 80 percent at 40 percent carbon grade obtained with 2-inch ID Ken-Flote column. The SYMUSEP Separator, which utilizes grinding and cleaning in a single stage, was not effective in improving grade or recovery or carbon. However, combining the SYMUSEP Separator with the Ken-Flote column produced a concentrate with more than 90 percent recovery of carbon at a grade of about 27 percent carbon.

Limited dewatering studies conducted on the oil shale concentrate showed that using a vacuum or pressure (40 psig) filtration system, a 45 percent moisture filter cake could be obtained after two minutes of filtration.

UK-CAER recommends that detailed liberation studies be conducted with different shale samples and also that the impact of various grinding systems

on the liberation of kerogen be evaluated. Additional studies should also be conducted on the pilot-scale beneficiation and dewatering of oil shale concentrate.

Subtask 4.7 (Economic Analysis) was conducted to determine the impact of MRI research on the cost of beneficiating Eastern oil shales. A previous study of processing costs had been performed by the Roberts and Schaefer Company in 1988. The economic analysis was performed in two steps. First, the Roberts and Schaefer estimate was updated to 1992 economic conditions. This was done by using inflation factors generated from industry cost indices available in the trade literature. In the second step, specific technological and equipment substitutions were incorporated into the updated capital and operating cost estimates.

The analysis indicates that a shale beneficiation processing plant capable of producing feedstock for a PFH plant producing 20,000 barrels of oil per day could now be built for a cost of \$215 million. This represents a reduction of \$40 million from the Roberts and Schaefer estimate. Similarly, the operating costs were reduced by \$2.00 per ton of concentrate.

In terms of the delivered cost of oil (by the PFH process) the costs were reduced from \$21.95/bbl to \$19.92/bbl.

The objective of Subtask 6.2.2 (Wastewater Treatability) was to determine suitable techniques for treating wastewater generated during shale processing. This subtask was conducted by Tennessee Technological University (TTU, Cookeville). TTU conducted acclimation and treatability studies with samples of synthetic PFH product water and water generated during a bench-scale PFH test with beneficiated Alabama shale. The synthetic product water was comprised of mixtures of aniline, methyl ethyl ketone (MEK), phenol, and 4-methyl pyridine. Component analysis of the water generated during the bench-scale PFH test showed that these compounds were present. During the previous three-year program, TTU successfully acclimated and conducted treatability studies with four other compounds (acetone, propionitrile, pyrrole, and thiocyanate) present in PFH product water.

TTU was successful in acclimating microorganisms to solutions containing aniline, phenol, MEK and mixtures thereof. During treatability studies with these compounds, the concentration of MEK was reduced to less than 1 mg/L within 40 to 50 hours. The concentrations of aniline and phenol were each reduced to less than 1 mg/L within about 90 hours. However, even after repeated efforts using different inoculants, microorganisms would not acclimate to 4-methyl pyridine. Also, no growth was observed in tests to determine if microorganisms would use 4-methyl pyridine as a sole nitrogen source. The presence of 4-methyl pyridine did not appear to inhibit the microbial degradation of the other compounds during the treatability studies.

Prior to acclimation and treatability studies with the product water from the PFH test, the sample was air stripped to remove hydrogen sulfide and ammonia. TTU inoculated samples of diluted PFH product water (up to 50 volume percent) with microbial seed. Initially, biological growth was observed in

solutions containing up to 50 volume percent PFH product water. However, the growth was not viable and microbial acclimation was not achieved.

The objective of Subtask 6.2.3 (Waste Management Facility Conceptual Design) was to design a conceptual wastewater and process water treatment facility for a commercial-scale PFH plant. During the program, TTU estimated the total quantity of water required for a commercial-scale PFH plant to be 10.7 million gallons per day. The three major areas of water consumption were boiler feed, quench, and cooling water. TTU compiled water quality criteria for initial import water and for reuse and recycling. Due to the reduction in program scope, TTU did not conduct a conceptual design.

In Task 9 (Information Required for the National Environmental Policy Act [NEPA]), IGT and the subcontractors working on the program collected and compiled information on the expected environmental and social impacts of the project. The DOE reviewed the NEPA document and determined that an Appendix B Categorical Exclusion (C-B) (B.3.6, "Indoor bench-scale research projects or conventional laboratory operation within existing laboratory facilities") was the appropriate level of documentation for the project.

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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 multi-year program, initiated in September 1987 by the U.S. Department of Energy (Contract No. DE-AC21-87MC11089), was 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 upgrading, 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 was divided into the following active* tasks:

- Task 3. Testing of Process Improvement Concepts
- Task 4. Beneficiation Research
- Task 6. Environmental Data and Mitigation Analyses
- Task 9. Information Required for the National Environmental Policy Act

In order to accomplish all of the program objectives, the Institute of Gas Technology (IGT), the prime contractor, worked with four other institutions: The University of Alabama/Mineral Resources Institute (MRI), the University of Alabama College of Engineering (UA), University of Kentucky Center for Applied Energy Research (UK-CAER), and Tennessee Technological University (TTU).

This report presents the work performed by IGT from June 1, 1992 through January 31, 1993, under a second program extension for the U.S. DOE under Contract No. DE-AC21-87MC11089 for the project "Pressurized Fluidized-Bed Hydroretorting (PFH) of Eastern Oil Shales." The original 3-year program was initiated in September 1987 under U.S. Department of Energy (DOE) Contract No. DE-AC21-87MC11089 for the project "Pressurized Fluidized-Bed Hydroretorting of Eastern Oil Shales." The Final Report (in four volumes) describing the results of that work has been published by IGT. A one-year program extension was subsequently authorized by DOE from June 1, 1991 through May 31, 1992. The objective of the one-year program extension was to expand the data base for the PFH process to include beneficiated shales. The results of the one-year program extension have been published by IGT as an annual report for the period June 1991 through May 1992. The DOE contract was modified for a second one-year extension; however, budget cutbacks required that the overall program be shortened. Therefore, the scope of work was reduced for some subtasks and other subtasks were eliminated.

* Some of the tasks in the original program were not continued in the current program extension. The task achievements discussed below represent the active tasks of the program.

ACHIEVEMENTS

Task 3. Testing of Process Improvement Concepts

The objective of this task was to obtain data on novel process concepts that have the potential to improve the economics for PFH processing of beneficiated Eastern shales. This task is divided into four subtasks corresponding to the novel concepts being tested: 3.7. Innovative PFH Reactor Concept Testing (Methane Cracking and Cracking-Combustion Tests), 3.9. Catalytic Hydroretorting, 3.10. Autocatalysis in Hydroretorting, and 3.11. Shale Oil Upgrading and Evaluation. Subtask 3.10 was conducted by the University of Alabama College of Engineering (UA) and the other tasks were conducted by IGT.

Subtask 3.7. Innovative Reactor Concept Testing

The objective of this subtask was to demonstrate the technical feasibility of generating hydrogen by cracking by-product methane gas and combusting the carbon produced by the cracking reactions. Work was divided into two subtasks: 3.7.1. PFH Methane Cracking and 3.7.2. PFBC of Carbon From Cracking. Because of the reduction in funding, the subtask on fluidized-bed combustion of carbon from cracking was not conducted.

Subtask 3.7.1. PFB Methane Cracking

The objective of this subtask was to determine operating conditions needed to crack the hydrocarbon gases from the PFH process to generate hydrogen and carbon by conducting laboratory-scale tests. An existing laboratory-scale reactor was to be modified to include continuous gas flow through a batch fluidized bed. On-line gas detectors were to be used to collect data during the cracking and combustion tests.

Discussion

Work in this subtask included modifying an existing batch cracking-combustion unit for semi-batch operation and conducting a series of cracking tests over a wide range of operating conditions. Reactor modifications were completed, and nine tests were conducted. The early conclusion of this project prevented the completion of all scheduled tests.

Experimental

An existing batch cracking-combustion unit was used for tests in this subtask. The batch reactor was removed from the pressure shell and replaced with a reactor which allowed the feed gas to enter the fluidized bed from the bottom and to exit through tubing in the top flange. Instead of using a gas distribution plate or grid that could be plugged with deposited carbon, a 9-inch section of the reactor below the heated zone was filled with 1/8-inch diameter alumina balls, which served as a gas distributor. The -60+100 mesh combusted shale (with sand or alumina) was placed directly on top of the alumina balls in the heated part of the reactor. The reactor was constructed of a 1-1/4-inch Schedule 40 type 309 stainless steel pipe similar to that used in the earlier cracking unit.

An expansion section was constructed of 4-inch diameter type 316 stainless steel packed with glass wool and in-line absolute filters were included in the new gas exit line to prevent carryover of fine deposited carbon into the on-line instruments and the dry test meter. Use of the pressure shell allowed a balanced pressure to be maintained across the reactor tube. This eliminated pressure stresses on the reactor tube even at high absolute pressures. The balanced pressure between the gas in the reactor and the shell-side nitrogen was maintained by a differential gauge-controller, which activated nitrogen feed and discharge solenoid valves, which bled nitrogen into or out of the shell. Controlling the shell-side nitrogen pressure allowed a balanced pressure to be maintained without changing the process feed gas rate.

The modified cracking-combustion unit is capable of operation at maximum conditions of 2100°F and 1000 psig. A schematic diagram of the modified unit is shown in Figure 3-1. The unit includes the reactor tube, an outside pressure shell, a differential pressure controller which activates solenoid valves, an expansion section, in-line filters, internal reactor thermocouples, shell-side tungsten-rhenium thermocouples for furnace temperature control, a three-zoned 2400°F furnace, and furnace temperature controllers. The reactor thermowell contains four thermocouples for measurement of reactor temperatures. The reactor tube - 1.38-inch ID and 28.75 inches in length - is constructed of type 309 stainless steel to operate up to 2100°F. All other system components are constructed of type 316 stainless steel. Separate mass flowmeter/controllers control the feed rates of the various gases, and a dry test meter is used to measure the total exit gas rate. Multiple gas samples can be taken in 10-cm³ gas bombs mounted in a sampling manifold. On-line infrared CO, CO₂, and CH₄ analyzers are located downstream of the back pressure regulator.

The reactor tube was passivated with hydrogen sulfide before any tests were conducted. A stream of 1 percent H₂S and 99 percent H₂ was passed through the reactor at 1500°F to neutralize any catalytic activity of the stainless steel surface.

Cracking tests are initiated by charging a known weight of alumina balls (1/8 inch) to the bottom of the reactor. A weighed amount of combusted shale and either sand or alumina is carefully placed on top of the alumina balls. The reactor is sealed and pressure tested with nitrogen. The reactor and shell are pressurized to targeted test conditions with nitrogen. Nitrogen flows are established to fluidize the reactor solids and balance the shell-side pressure. The furnaces are energized and the reactor is heated to 50° to 150°F above the targeted test temperature. The elevated temperature is required because the endothermic cracking reaction lowers the reactor temperature.

A test is initiated after reaching stable operating conditions with nitrogen. Methane is introduced to the reactor and nitrogen flow is reduced while maintaining the fluidized bed. Introduction of methane causes a significant decrease in reactor temperature because cracking is endothermic. Gas sampling is begun as soon as the feed gas is 100 percent methane, the temperature is fairly steady, and the infrared (IR) methane detector has a steady methane concentration. Tests are usually brief (less than 30 minutes) because

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Figure 3-1. SCHEMATIC DIAGRAM OF THE MODIFIED CRACKING AND COMBUSTION APPARATUS

deposited carbon builds up quickly in the reactor. A test is terminated by switching the feed gas back from methane to nitrogen. The furnaces are turned off, and the reactor is allowed to cool with the bed still fluidized to prevent packing and sintering. After cooling, the feed nitrogen is shut off and the reactor is depressurized.

When the unit has cooled and depressurized, the solids are vacuumed from the reactor. The solids containing deposited carbon are analyzed for total carbon. Product gas samples collected during the test are analyzed for hydrogen, carbon oxides, and hydrocarbon gases.

Results

A total of nine cracking tests were conducted in this program. Temperature was varied from 1660° to 2000°F. Pressure was varied from 50 to 1000 psig. The bed material for the first two tests was 75 weight percent silica sand and 25 weight percent combusted shale. The next 6 tests were conducted with a bed material of 75 weight percent alumina and 25 weight percent combusted shale. A bed containing 100 percent alumina was used in the last test. The use of sand and alumina was designed to minimize any problems associated with sintering. The combusted shale feedstock was beneficiated Alabama shale. After combustion, the shale contained 0.4 percent carbon, 0.8 percent sulfur, and no hydrogen or nitrogen.

A summary of the operating conditions and results of the methane cracking tests is presented in Table 3-1. Operating conditions include temperature, pressure, superficial gas velocity, and gas residence time. Gas velocity was above the minimum fluidization velocity of the bed material but well below the minimum fluidization velocity of the alumina balls. Residence times ranged from 4 to 13 seconds.

Test results include gas compositions from the two to four samples taken during each test. All product gas samples taken in this subtask contained only hydrogen and methane with low concentrations of carbon monoxide. No higher hydrocarbons were detected. Carbon monoxide concentrations were between 0 and 2 percent. No analyses were performed for H_2S , but some may have been formed by the reaction of combusted shale residual sulfur with hydrogen produced by the cracking reaction.

The conversion of methane to hydrogen and carbon by thermal cracking increases with increasing temperature but decreases with increasing pressure. Higher conversions are favored by lower pressure because two moles of product gas (H_2) are produced for each mole of feed methane. Equilibrium controls the maximum conversion of methane to hydrogen and carbon at specific conditions. To achieve a desired level of methane conversion, either the pressure must be low enough at a specific temperature or the temperature must be high enough at a specific pressure with sufficient residence time provided.

The equilibrium curve isobars at 50, 100, 200 and 1000 psig for methane cracking are shown in Figure 3-2. These equilibrium data are based on Gibbs free energy data for the reaction feed and products. Also included on the figure are data from six tests with 25 percent combusted shale and 75 percent

Table 3-1. OPERATING CONDITIONS AND RESULTS FOR
SEMI-CONTINUOUS METHANE CRACKING TESTS

Test No.	<u>33-CR-25</u>	<u>33-CR-26</u>	<u>33-CR-27</u>	<u>33-CR-28</u>	<u>33-CR-29</u>
Pressure, psig	206	198	600	603	200
Bed Material,* wt %					
Combusted Shale	25	25	25	25	25
Silica Sand	75	75	0	0	0
Alumina	0	0	75	75	75
Superficial Gas Velocity, ft/s	0.126	0.169	0.058	0.063	0.158
Gas Residence Time, s	6	4	13	12	5
Gas Sample 1					
Temperature, °F	1875	1960	1730	1880	1900
Product Gas Methane, mol %	42	32	53	27	17
Gas Sample 2					
Temperature, °F	1820	2000	1790	1890	1905
Product Gas Methane, mol %	54	23	44	28	18
Gas Sample 3					
Temperature, °F	1760	--	1800	1920	1920
Product Gas Methane, mol %	55	--	38	26	15
Gas Sample 4					
Temperature, °F	1770	--	--	1925	--
Product Gas Methane, mol %	51	--	--	25	--

* Particle size -60+100 mesh.

Table 3-1 (Cont.). OPERATING CONDITIONS AND RESULTS FOR
SEMI-CONTINUOUS METHANE CRACKING TESTS

Test No.	<u>33-CR-30</u>	<u>33-CR-31</u>	<u>33-CR-32</u>	<u>33-CR-33</u>
Pressure, psig	997	50	202	600
Bed Material*, wt %				
Combusted Shale	25	25	25	0
Silica Sand	0	0	0	0
Alumina	75	75	75	100
Superficial Gas Velocity, ft/s	0.096	0.149	0.151	0.112
Gas Residence Time, s	8	5	5	6
Gas Sample 1				
Temperature, °F	1660	1825	1760	1840
Product Gas Methane, mol %	67	19	38	40
Gas Sample 2				
Temperature, °F	1660	1840	1760	1880
Product Gas Methane, mol %	69	18	38	37
Gas Sample 3				
Temperature, °F	1670	1845	1780	1930
Product Gas Methane, mol %	69	18	37	34
Gas Sample 4				
Temperature, °F	1670	1860	--	--
Product Gas Methane, mol %	69	20	--	--

* Particle size -60+100 mesh.

Figure 3-2. EFFECT OF TEMPERATURE AND PRESSURE ON THE RESULTS OF METHANE CRACKING TESTS AND THERMODYNAMIC EQUILIBRIUM

alumina. The temperature plotted for each data point was the highest value indicated of the four internal reactor thermocouples. These tests were conducted over a pressure range from 50 to 1000 psig. Multiple data points are included from each test.

Methane conversion increased with increasing temperature and decreased with increasing pressure. The slopes of curves through the experimental data are steeper than the slopes of the equilibrium curves. While conversions were less than the equilibrium value at all test conditions, the conversion approaches the equilibrium value as temperature and pressure are increased. A product gas containing 80 percent hydrogen and 20 percent methane can be obtained at cracking conditions of 1850°F and 50 psig, 1900°F and 200 psig, and 2000°F and 600 psig (data for the latter are not shown in the figure).

Tests were conducted with combusted shale mixed with both sand and alumina. Two tests were conducted at 200 psig using 75 percent sand and 25 percent combusted shale, and two later tests were conducted at the same pressure using 75 percent alumina with 25 percent combusted shale. Sand was only used in the first two tests in this subtask. At the high temperatures of the cracking reactor, the silica fused to form glass. All subsequent tests were conducted using alumina to avoid sintering or fusing of the bed material. The alumina and combusted shale did not fuse, melt, sinter, or agglomerate at temperatures as high as 2000°F. Methane conversions obtained in the four tests at 200 psig are shown in Figure 3-3.

Methane conversion at 200 psig increased with increasing temperature. Higher conversions were achieved with alumina in the bed than with sand present. This suggests alumina may have some catalytic activity toward the thermal cracking of methane. A product gas composition close to the equilibrium mixture was achieved at a temperature of 1900°F and a short residence time of only 5 seconds. At 1770°F, the experimental methane content was 38 percent compared to an equilibrium value of 14 percent. At 1920°F, the experimental product gas methane content of 16 percent was much lower and closer to the equilibrium value of 9 percent.

Three thermal cracking tests were conducted at 600 psig. Test results are presented in Figure 3-4. The bed material was 25 percent combusted shale and 75 percent alumina for two tests and 100 percent alumina for the third test. Data shows methane conversion increases with increasing temperature. The data approach the equilibrium curve at higher temperatures. At 1920°F, the experimental product gas and equilibrium mixture contained 25 and 20 percent methane, respectively.

A bed containing 25 percent combusted shale produced greater methane cracking than a bed containing only alumina. Minerals present in the combusted shale ash may play an active catalytic role in the methane cracking reaction. Catalytic activity appears to increase from silica sand, to alumina, to combusted shale.

Figure 3-3. EFFECT OF TEMPERATURE AND MEDIA ON METHANE CRACKING RESULTS ACHIEVED AT 200 PSIG

Figure 3-4. EFFECT OF TEMPERATURE AND MEDIA ON METHANE CRACKING RESULTS ACHIEVED AT 600 PSIG

Subtask 3.9. Catalytic Hydroretorting

The objective of this subtask was to improve the quality of PFH-produced shale oil in-situ by using catalysts. Tests were to be conducted in a small laboratory-scale hydroretorting unit using hydrotreating catalysts. The catalysts were of two types - regenerable and throw-away.

Discussion

The evaluation of catalytic hydroretorting was conducted using a single shale at a baseline PFH operating condition in a batch laboratory-scale PFH reactor. The shale was riffled from a batch of pelletized beneficiated Alabama Chattanooga shale. The nominal operating conditions for the baseline PFH test (925°F, 1000 psig hydrogen pressure, and a 20-minute residence time) were found in an earlier program to be optimum for producing high oil yields and high carbon selectivity to oil from Alabama shale.

A total of twenty-seven successful tests were conducted. The first five tests were replicate PFH tests conducted at baseline conditions with no catalyst. They were designed to provide a bench mark for evaluating the effectiveness of the various catalysts. In a second series of tests, the shale was impregnated with six different throw-away catalysts prior to hydroretorting. A third and fourth series of tests were conducted with regenerable catalysts either placed in the exit line or mixed with the shale.

Experimental

The batch PFH reactor system is capable of operation at a temperature and pressure up to 1200°F and 1000 psig, respectively. The 2-inch internal diameter (ID) reactor pipe and all other major system components are constructed of type 316 stainless steel. The batch PFH system components include the reactor and feed hopper with individual furnaces, liquid collection vessel, liquid collection filters, recycle gas compressor, split-tube furnace for gas preheating, mass flow controllers, and data acquisition. The split-tube furnaces for the reactor and the feed hopper are enclosed in the same furnace housing but are controlled individually. Product oil vapor is swept downward through the bed from the reactor and passes into an exit line. The gas and liquid vapors are cooled in a condenser, the oil is collected, and the gases are recycled to the recycle compressor. When exit line catalysts were evaluated, the catalyst was placed in the exit line section inside the reactor furnace. The temperature of the gases and vapors in the exit line decreased from about 850° to 550°F through the 18 inches of catalyst in the 0.5-inch diameter exit line. A schematic diagram of the unit is shown in Figure 3-5.

In each PFH test, 125 grams of feed material (shale or shale with catalyst) was charged to the feed hopper and 225 grams of sand was placed in the reactor. Next, the system was pressurized to 1000 psig with hydrogen, the reactor was heated to the desired temperature, and the gas was circulated at fluidization velocities using the recycle compressor. A small flow of make-up hydrogen was used. After a fluidized bed of sand was established in the reactor and temperatures and gas flow rates were established at the targeted test conditions, the slide valve was opened, and the shale was dropped into

Figure 3-5. SCHEMATIC DIAGRAM OF THE BATCH LABORATORY-SCALE PFH UNIT (Showing Location of Exit-Line Catalyst)

the reactor. Operating conditions of temperature, pressure, and gas flow were then maintained throughout the PFH test. At the conclusion of each test, the power to the furnaces was shut off and the reactor was allowed to cool. Residue solids, product liquids, and gases were carefully collected and analyzed.

Catalyst Preparation

Catalysts tested in this subtask included throw-away, impregnated catalysts (identified as IGT-TA-), two regenerable commercial hydrotreating catalysts, tungsten-promoted commercial hydrotreating catalysts, and a regenerable catalyst (identified as IGT-MS-).

The IGT-TA- throw-away catalysts were impregnated into the shale using a solution or colloidal suspension containing catalytic metal compounds. The catalysts were dissolved in sufficient de-ionized water to wet the batch of oil shale being prepared. Approximately 110 grams of water were required to wet 180 grams of -20+50 mesh beneficiated Alabama shale.

Three catalysts; ammonium heptamolybdate, cobalt acetate, and nickel acetylacetonate, were dissolved in the de-ionized water. Molybdenum carbonyl and molybdenum sulfide are insoluble in water. Powders of these compounds were suspended in the water. The water-catalyst solution or suspension was slowly poured on the oil shale. The shale was stirred continuously to provide an even coating of active metal on the shale surface. The catalyzed shales were dried at 150°F to remove moisture but not remove volatile hydrocarbons.

Two commercial, regenerable hydrotreating catalysts were obtained from Criterion Catalysts Inc. These catalysts contained either Ni/Mo/P on an alumina support (PS-85-765) or Co/Mo/P on an alumina support (SPS-0674-92). These catalysts were used as received. To evaluate catalyst effectiveness, the catalysts were either mixed with the shale or placed in the exit line. Catalyst size was not altered when placed in the exit line, but when mixed with the shale, the catalysts were crushed to -60+100 mesh to promote good mixing.

The catalysts were pre-sulfided in an oxygen-free environment. A sample of catalyst was heated slowly to 575°F under flowing nitrogen. The flowing nitrogen was then switched to hydrogen containing 1 percent hydrogen sulfide (H_2S), and the heating was continued to 845°F. The catalyst was held at 845°F for one hour and then cooled to 575°F. The H_2/H_2S purge was then replaced with nitrogen, and the catalyst was cooled to room temperature. When the catalyst reached ambient conditions, air was then slowly bled into the reaction chamber. These catalysts were used as soon as possible after sulfidation.

The tungsten promoter was added to the commercial catalysts by pouring a solution of tungstic acid ($WO_3 \cdot H_2O$) in concentrated ammonium hydroxide over the catalyst. The catalyst was stirred during this procedure to ensure uniform coverage. After tungsten addition, the catalysts were dried at 220°F and then calcined at 750°F for two hours.

The IGT-MS- series of catalysts was prepared by decomposing ammonium tetrathio-molybdate (ATM) in the presence of other solid powders. The details of the decomposition, including the temperature, pressure, flow rate, and identity of a stabilizing and enhancing compound, are proprietary to IGT. The first step in preparing these catalysts is to mix all the solids in a ball mill. Solids include ATM, a support material that is usually a mixed oxide including zirconium oxide, a stabilizing and enhancing compound, and any promoter oxides such as cobalt oxide. The powders are well mixed and then placed in a reactor for the ATM decomposition. After the ATM decomposition, the catalyst powder is formed into wafers at 12,000 to 18,000 psi. The wafers are broken apart and sieved to -8+20 mesh.

Discussion

All of the catalytic PFH tests were conducted with beneficiated Alabama shale. The feed shale composition, Fischer Assay (FA) oil yield, and the FA oil composition are presented in Table 3-2. Alabama shale has a high sulfur content. Beneficiation removes a significant amount of pyritic sulfur from the shale, but the shale concentrate still contains high sulfur (organic) and nitrogen contents (low in terms of C/S and C/N ratios). The Fischer Assay produces much of the light oil from a shale as reflected by the low oil specific gravity of 0.933 g/mL. The oil contains 3.2 weight percent sulfur and 0.5 weight percent nitrogen. While the oil contains only 3.9 percent of the feed sulfur and 6.5 percent of the feed nitrogen, the oil still would require hydrotreating prior to use as a refinery feedstock.

The catalysts used for hydrotreating the oil in-situ were either throw-away or regenerable. The throw-away catalysts were impregnated in the shale. The regenerable catalysts were either mixed with the shale or placed in the exit gas line. A description of the various catalysts used in this subtask is presented in Table 3-3. Throw-away catalysts included ammonium heptamolybdate (AHM), molybdenum carbonyl, molybdenum sulfide, cobalt acetate, nickel acetylacetonate, and AHM combined with cobalt acetate. The catalysts mixed with the shale included commercial Ni/Mo/P on alumina (PS-85-765) and commercial Co/Mo/P on alumina (SPS-0674-92) as received, pre-sulfided, and as-received with tungsten added. The exit line catalysts included the two commercial catalysts as-received and pre-sulfided and an IGT catalyst containing MoS_2 on ZrO_2 .

A summary of the operating conditions and overall carbon conversions for the catalyzed batch PFH tests is presented in Tables 3-4 through 3-8. The first five tests were conducted with no catalyst to provide baseline data. Six throw-away impregnated catalysts were then tested. Exit-line catalysts were used in six tests; two of these tests also included a catalyst mixed with the shale. Six tests were conducted with pre-sulfided catalysts mixed with the feed shale. The final four tests were conducted with non-pre-sulfided catalysts mixed with the feed shale.

Tests 36-B-2, -3, and -4 were averaged to obtain baseline test data. Data from 36-B-1 were not included because the carbon balance was only 84 percent, and data from 36-B-5 were considered unreliable because the recycle pump had a small leak producing an average pressure of only 959 psig. Product

Table 3-2. BENEFICIATED ALABAMA SHALE COMPOSITION
AND FISCHER ASSAY OIL YIELD

Moisture, wt %	1.62
Ultimate, wt % (dry)	
Ash	53.61
Carbon	31.91
Hydrogen	2.73
Sulfur	8.43
Nitrogen	0.68
Fischer Assay, GPT	22.5
Fischer Assay Oil Composition, wt %	
Carbon	83.42
Hydrogen	10.19
Sulfur	3.72
Nitrogen	0.51
Sp.gr., g/mL	0.933

Table 3-3. CATALYSTS EVALUATED IN CATALYTIC PRESSURIZED
FLUIDIZED-BED HYDRORETORTING TESTS

PS-85-765	Commercial*	Ni/Mo/P on Al ₂ O ₃
SPS-0674-92	Commercial*	Co/Mo/P on Al ₂ O ₃
TA-M201	IGT	Mo - ammonium heptamolybdate (AHM)
TA-M202	IGT	Mo - Mo(CO) ₆
TA-M203	IGT	Mo - MoS ₂
TA-C204	IGT	Co - cobalt acetate
TA-N205	IGT	Ni - Ni acac (acetyl acetate)
TA-MC206	IGT	Mo/Co - AHM and cobalt acetate
MS-Z1008	IGT	MoS ₂ on ZrO ₂

* Criterion Catalysts, Inc.

Table 3-4. BATCH PFH TEST CONDITIONS AND CARBON
CONVERSIONS WITH BENEFICIATED ALABAMA SHALE
(No Catalyst)

Test No.	<u>36-B-1</u>	<u>36-B-2</u>	<u>36-B-3</u>	<u>36-B-4</u>	<u>36-B-5</u>
Average Reactor Temperature, °F	920	950	942	951	941
Reactor Residence Time, min	18	21	20	19	20
Pressure, psig	995	989	999	980	959
Shale Particle Size, mesh	----- -20+50 -----				
Superficial Gas Velocity, ft/s	0.076	0.076	0.078	0.076	0.080
Minimum Fluidization Velocity, ft/s	----- 0.047 -----				
Product Distribution, % of Feed Carbon					
Residue Shale	19.5	21.6	20.0	22.0	21.7
Product Gas	16.9	13.3	14.1	13.0	12.0
Oil	<u>63.6</u>	<u>65.1</u>	<u>65.9</u>	<u>65.0</u>	<u>66.3</u>
Total	100.0	100.0	100.0	100.0	100.0

**Table 3-5. BATCH CATALYZED PFH TEST CONDITIONS AND
CARBON CONVERSIONS WITH BENEFICIATED ALABAMA SHALE
(Throw-Away Catalyst)**

Test No.	<u>36-B-6</u>	<u>36-B-7</u>	<u>36-B-8</u>	<u>36-B-9</u>	<u>36-B-10</u>	<u>36-B-11</u>
Average Reactor Temperature, °F	928	950	948	954	932	932
Reactor Residence Time, min	20	19	22	21	21	21
Pressure, psig	961	978	989	979	1024	981
Shale Particle Size, mesh	----- -20+50 -----					
Superficial Gas Velocity, ft/s	0.075	0.076	0.078	0.075	0.075	0.074
Minimum Fluidization Velocity, ft/s	----- 0.047 -----					
Impregnated Catalyst Catalyst/Shale, g/g	TA-M201 0.001	TA-M202 0.001	TA-M203 0.001	TA-C204 0.001	TA-N205 0.001	TA-MC206 0.01
Product Distribution, % of Feed Carbon						
Residue Shale	23.1	22.6	21.9	19.4	22.4	21.3
Product Gas	10.8	13.3	13.3	10.1	11.2	12.9
Oil	<u>66.1</u>	<u>64.1</u>	<u>64.8</u>	<u>70.5</u>	<u>66.4</u>	<u>65.8</u>
Total	100.0	100.0	100.0	100.0	100.0	100.0

Figure 4-36. PARTICLE SIZE DISTRIBUTION OF THE COLUMN FROTH PRODUCT

**Table 3-7. BATCH CATALYZED PFH TEST CONDITIONS AND
CARBON CONVERSIONS WITH BENEFICIATED ALABAMA SHALE
(Presulfided Catalysts)**

Test No.	<u>36-B-24</u>	<u>36-B-19</u>	<u>36-B-25</u>	<u>36-B-22</u>	<u>36-B-20</u>	<u>36-B-26</u>
Average Reactor Temperature, °F	919	945	943	905	1034	928
Reactor Residence Time, min	31	31	32	31	31	31
Pressure, psig	979	986	988	998	1011	983
Shale Particle Size, mesh	----- -20+50 -----					
Superficial Gas Velocity, ft/s	0.075	0.074	0.075	0.074	0.072	0.076
Minimum Fluidization Velocity, ft/s	----- 0.047 -----					
Mixed Catalyst	----- PS-85-765 -----			----- SPS-0674-9 -----		
Pre-Sulfidation	Yes	Yes	Yes	Yes	Yes	Yes
Promoter	No	No	No	No	No	No
Catalyst/Shale, g/g	0.09	0.25	0.47	0.25	0.25	0.25
Product Distribution, % of Feed Carbon						
Residue Shale	19.1	19.2	21.7	18.1	16.0	21.1
Product Gas	14.7	16.9	19.6	17.5	21.5	17.1
Oil	<u>66.2</u>	<u>63.9</u>	<u>58.7</u>	<u>64.4</u>	<u>62.5</u>	<u>61.8</u>
Total	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>

Table 3-8. BATCH CATALYZED PFH TEST CONDITIONS AND
CARBON CONVERSIONS WITH BENEFICIATED ALABAMA SHALE
(Non-Presulfided Catalysts)

Test No.	<u>36-B-15</u>	<u>36-B-23</u>	<u>36-B-16</u>	<u>36-B-17</u>
Average Reactor Temperature, °F	923	944	928	942
Reactor Residence Time, min	19	30	31	31
Pressure, psig	942	980	986	959
Shale Particle Size, mesh	----- -20+50 -----			
Superficial Gas Velocity, ft/s	0.064	0.075	0.075	0.073
Minimum Fluidization Velocity, ft/s	----- 0.047 -----			
Mixed Catalyst	SPS-0674-92	SPS-0674-92	PS-85-765	PS-85-765
Pre-Sulfidation	No	No	No	No
Promoter	No	No	No	W
Catalyst/Shale, g/g	--	--	--	--
Product Distribution, % of Feed Carbon				
Residue Shale	20.2	20.0	22.0	16.8
Product Gas	15.6	18.3	16.6	19.1
Oil	<u>64.2</u>	<u>61.7</u>	<u>61.4</u>	<u>64.1</u>
Total	100.0	100.0	100.0	100.0

oil compositions and properties for the baseline tests are presented in Table 3-9. The average carbon conversion to oil was 65.3 percent, and the average selectivity to oil was 83 percent.

The oil yield corresponded to 260 percent of Fischer Assay. The oil had sulfur and nitrogen contents of 1.95 and 1.56 percent, respectively, and the specific gravity was 1.004 g/mL. The effectiveness of various catalysts was judged by comparing the product oil sulfur and nitrogen contents and the oil specific gravities against the baseline oil. The oil yield was also evaluated relative to the baseline conditions with no catalyst present. Oil quality data for the PFH tests with catalysts are presented in Tables 3-10 through 3-13.

Impregnated Catalysts

The six impregnated throw-away catalysts had no effect on product oil quality (Table 3-10). Sulfur content in the oil decreased by 4 to 22 percent, but no catalyst produced a decrease in the nitrogen content of the oil. The specific gravities of all six product oils were the same as the baseline PFH oil specific gravity. The oil yield was unchanged by any of the six impregnated catalysts. Gas yield was unchanged by three of the catalysts and increased between 17 and 25 percent by the other three catalysts. Increasing the catalyst concentration from 0.1 to 1.0 percent had no effect on carbon conversion to oil or oil quality.

Since none of the impregnated catalysts had any effect on oil quality, all of the remaining tests were conducted using commercially available hydrotreating catalysts. These catalysts were placed either in the PFH reactor exit line or in the reactor with the shale. Catalysts added to the reactor were mixed heterogeneously with the shale in the feed hopper and therefore had the same residence time as the shale itself. Residence times for many of these catalytic PFH tests were 30 minutes instead of the 20 minutes used for the baseline tests. Previous work without catalysts has shown that increasing the residence time above 20 minutes has no effect on oil or gas yield.

Exit Line Catalysts

Six tests were conducted with 25 grams of catalyst in an 18-inch section of heated exit line. The product gas carrying the oil vapor contacted the catalyst upon entering the line at approximately 850°F and exited at a temperature above 550°F. Total oil vapor-catalyst contact time was 1.3 seconds and the catalyst to shale ratio was 0.25.

Four catalysts were used in the exit line, and dramatic improvements in oil quality were achieved (Table 3-11). These catalysts included the commercial Mo and Co catalysts with no pre-sulfidation, pre-sulfided commercial Co catalyst, and the IGT MS-Z1008 catalyst (Mo on ZrO_2).

The catalysts in the exit line caused large reductions of sulfur and nitrogen contents in the oil and decreased the oil specific gravity. They also produced an increase in carbon conversion to gas and a decrease in oil yield.

Table 3-9. QUALITY OF PRODUCTS FROM PFH TESTS WITH
BENEFICIATED ALABAMA SHALE AND NO CATALYST

Test No.	<u>36-B-1</u>	<u>36-B-2</u>	<u>36-B-3</u>	<u>36-B-4</u>	<u>36-B-5</u>	Average* <u>36-B-2, -4</u>
Product Oil						
Composition, wt %						
C	86.34	86.21	86.14	86.05	86.57	86.13
H	9.53	9.71	9.59	9.52	9.61	9.61
S	1.88	1.96	1.88	2.02	1.90	1.95
N	1.64	1.48	1.59	1.62	1.61	1.56
Oil C/H Ratio, g/g	9.06	8.88	8.98	9.04	9.01	8.97
Product Oil sp.gr.	1.016	0.999	1.007	1.006	1.007	1.004
Product Oil Yield						
GPT	56.2	58.6	58.9	58.2	59.0	58.6
% of Fischer Assay	250	260	262	259	262	260

* Average of Tests 2, 3, and 4.

Table 3-10. QUALITY OF PRODUCTS FROM PFH TESTS WITH
BENEFICIATED ALABAMA SHALE AND IMPREGNATED CATALYSTS

Test No.	<u>36-B-6</u>	<u>36-B-7</u>	<u>36-B-8</u>	<u>36-B-9</u>	<u>36-B-10</u>	<u>36-B11</u>
Catalyst	TA-M201	TA-OM202	TA-M203	TA-C204	TA-N205	NA-MC206
Product Oil						
Composition, wt %						
C	85.70	85.86	86.21	86.68	85.87	86.53
H	9.77	9.59	9.45	9.37	9.60	9.70
S	1.57	1.71	1.71	1.65	1.88	1.52
N	1.47	1.59	1.58	1.65	1.54	1.48
Oil C/H Ratio g/g	8.77	8.95	9.12	9.25	8.94	8.92
Product Oil sp.gr.	1.000	1.006	1.005	1.004	1.001	0.995
Product Oil Yield						
GPT	58.5	56.5	56.9	61.6	59.0	56.2
% of Fischer Assay	260	251	253	274	262	250
Decrease in Oil Using						
Catalyst, %						
S	20	13	13	16	4	22
N	6	-2	-1	-6	2	5
C/H	2	0	-2	-3	0	1
Sp.gr.	0	0	0	0	0	1
Carbon Conversion Decrease						
Using Catalyst, %						
Product Gas	20	1	1	25	17	4
Oil	-1	2	1	-8	-2	-1
Oil Yield Decrease (CPT)						
Using Catalyst, %	0	4	3	-5	-1	4

Table 3-11. QUALITY OF PRODUCTS FROM PFH TESTS WITH
BENEFICIATED ALABAMA SHALE AND EXIT LINE CATALYST

Test No.	<u>36-B-12</u>	<u>36-B-13</u>	<u>36-B-14</u>	<u>36-B-29</u>	<u>36-B-27</u>	<u>36-B-28</u>
Mixed Catalyst	No	No	No	No	PS-85-765	PS-85-765
Pre-Sulfidation	--	--	--	--	Yes	Yes
Exit Line Catalyst	PS-85-765	SPS-0674-92	MS-21008	-----	SPS-0674-92	-----
Pre-Sulfidation	No	No	No	Yes	No	Yes
Product Oil						
Composition, wt %						
C	87.08	87.10	85.47	87.63	87.20	86.60
H	10.74	10.71	10.70	10.95	10.70	10.71
S	0.19	0.06	1.39	0.04	0.06	0.05
N	0.61	0.41	1.04	0.41	0.40	0.42
Oil C/H Ratio g/g	8.11	8.13	7.99	8.00	8.15	8.09
Product Oil sp.gr.	0.922	0.916	0.973	0.909	0.907	0.902
Product Oil Yield						
GPT	50.9	53.6	42.8	46.6	51.6	53.7
% of Fischer Assay	226	238	181	207	229	239
Decrease in Oil Using						
Catalyst, %						
S	90	97	29	98	97	97
N	61	74	34	74	74	73
C/H	10	9	11	11	9	10
Sp.gr.	8	9	3	10	10	10
Carbon Conversion Decrease						
Using Catalyst, %						
Product Gas	-31	-34	-12	-58	-49	-44
Oil	20	16	30	27	19	17
Oil Yield Decrease (GPT)						
Using Catalyst, %	13	9	27	20	12	8

**Table 3-12. QUALITY OF PRODUCTS FROM PFH TESTS WITH
BENEFICIATED ALABAMA SHALE MIXED WITH PRE-SULFIDED CATALYSTS**

Test No.	<u>36-B-24</u>	<u>36-B-19</u>	<u>36-B-25</u>	<u>36-B-22</u>	<u>36-B-20</u>	<u>36-B-26</u>
Mixed Catalyst	----- PS-85-765 -----			----- SPS-0674 -----		
Catalyst/Shale, g/g	0.09	0.25	0.47	0.25	0.25	0.25
Temperature, °F	919	945	943	905	1034	928
Product Oil						
Composition, wt %						
C	86.84	88.27	87.46	87.52	88.08	87.21
H	9.55	9.98	9.71	10.09	9.82	9.93
S	1.12	0.63	0.49	0.31	0.62	0.64
N	1.24	0.89	0.75	0.83	0.93	0.81
Oil C/H Ratio g/g	9.09	8.84	9.01	8.67	8.97	8.78
Product Oil sp.gr.	0.985	0.959	0.956	0.952	0.965	0.954
Product Oil Yield						
GPT	60.0	58.5	54.5	60.0	57.0	57.6
% of Fischer Assay	267	260	242	267	253	256
Decrease in Oil Using						
Catalyst, %						
S	43	68	75	84	68	67
N	21	43	52	47	41	48
C/H	-1	1	-1	3	0	2
Sp.gr.	2	5	5	5	4	5
Carbon Conversion Decrease						
Using Catalyst, %						
Product Gas	-9	-26	-46	-30	-60	-27
Oil	-1	2	10	1	4	5
Oil Yield Decrease (GPT)						
Using Catalyst, %	-2	0	7	-2	3	2

**Table 3-13. QUALITY OF PRODUCTS FROM PFH TESTS WITH BENEFICIATED
ALABAMA SHALE MIXED WITH NON-PRE-SULFIDED CATALYSTS**

Test No.	<u>36-B-15</u>	<u>36-B-23</u>	<u>36-B-16</u>	<u>36-B-17</u>
Mixed Catalyst Promoter	-- SPS-0674-92 -- No	-- No	-- PS-85-765 -- No	-- W
Product Oil Composition, wt %				
C	86.72	87.43	87.71	87.47
H	9.90	9.93	9.71	9.80
S	0.59	0.58	0.64	0.62
N	0.92	0.94	0.90	0.95
Oil C/H Ratio g/g	8.76	8.80	9.03	8.93
Product Oil sp.gr.	0.954	0.954	0.970	0.968
Product Oil Yield				
GPT	60.2	57.3	56.0	58.7
% of Fischer Assay	268	255	249	261
Decrease in Oil Using Catalyst, %				
S	70	70	67	68
N	41	40	42	39
C/H	2	2	-1	1
Sp.gr.	5	5	3	4
Carbon Conversion Decrease Using Catalyst, %				
Product Gas	-16	-36	-23	-42
Oil	2	6	6	2
Oil Yield Decrease (GPT) Using Catalyst, %	-3	2	4	0

The commercial catalysts significantly improved the oil quality, but decreased the oil yield and increased the carbon conversion to gas. The Mo and Co catalysts decreased the oil sulfur content to 0.19 and 0.06, respectively, reductions of 90 and 97 percent. Nitrogen contents in the oils were 0.61 and 0.41, reductions of 61 and 74 percent, respectively. Specific gravities of 0.922 and 0.915 g/mL were almost 10 percent lower than the baseline oil specific gravity. Yields of 226 and 238 percent of Fischer Assay were 13 and 9 percent lower than those for the baseline tests. Gas yields were 30 to 35 percent higher than for the baseline tests.

Pre-sulfidation of the Co catalyst (Test 36-B-29) did not effect the quality of the oil produced. Sulfur and nitrogen contents were 0.04 and 0.41 percent, which represent reductions of 98 and 74 percent. The specific gravity was 0.909 g/mL. Oil yield was, however, reduced to 207 percent of Fischer Assay, a reduction of 20 percent. The gas yield of 58 percent was greater than the increase using the catalyst without pre-sulfidation.

The Co catalyst, with and without pre-sulfidation, was also placed in the exit line at the same time the pre-sulfided Mo catalyst was mixed with the feed shale. Oil quality and yield were similar to tests using only the exit line catalysts. Sulfur and nitrogen contents were reduced 97 and 74 percent to 0.06 and 0.42 weight percent. Oil specific gravities were 0.909 and 0.902 g/mL. Carbon conversion to gas was increased by 44 to 49 percent. The oil yields were 229 and 239 percent of Fischer Assay, decreases of 12 and 8 percent from the baseline tests.

The smallest increase in oil quality and greatest decrease in oil yield was produced by the IGT catalyst MS-21008. Product oil using this catalyst had 29 percent lower sulfur and 34 percent lower nitrogen contents than those of the baseline oil. Specific gravity was reduced 3 percent to 0.973 g/mL. The oil yield, however, was 181 percent of Fischer Assay, a reduction compared to baseline tests of 30 percent in carbon conversion to oil and 27 percent in oil yield. Carbon conversion to gas was 12 percent higher with this catalyst present.

Pre-Sulfided Mixed Catalysts

Six batch tests were conducted with pre-sulfided catalysts. The commercial Mo catalyst was used for five tests and one test was conducted using the commercial cobalt catalyst. Test conditions and oil quality data are presented in Tables 3-7 and 3-12.

Both catalysts were tested at a nominal retorting temperature of 925°F with a catalyst-to-shale ratio of 0.25 (Tests 36-B-19 and -26). Both catalysts were effective and improvements in oil quality were almost identical. Product oils contained 0.63 and 0.64 percent sulfur and 0.89 and 0.81 percent nitrogen. The sulfur and nitrogen reductions compared to the baseline tests were approximately 68 and 45 percent. The oils were significantly lighter with specific gravities of 0.954 and 0.959 g/mL.

The mixed catalysts produced a very small decrease in carbon conversion to oil of 2 to 5 percent. Because the product oil was lighter than the base-

line PFH oil, the oil yields of 260 and 256 percent of Fischer Assay were the same as the average baseline oil yield. The exit line catalysts produced a large improvement in oil quality but reduced the oil yield. The mixed catalysts also improved the oil quality to a lesser degree, but oil yield was not affected. The mixed catalysts increased the carbon conversion to gas by about 25 percent.

The mixed catalysts and exit line catalysts have been more effective at decreasing the oil sulfur content than the oil nitrogen content. All of these catalysts produced lighter oil with a lower specific gravity. Previous work has shown that sulfur compounds are fairly evenly distributed over the entire oil boiling point range, while nitrogen compounds are concentrated in the high boiling point fractions of the oil. Elemental analyses on the oil produced by catalytic hydrotreating were outside the scope of this project. However, further study is indicated. The catalysts used have been able to remove almost all of the sulfur (down to 0.04 percent) which is very much lower than the 3.7 percent sulfur in the Fischer Assay oil and 1.95 percent sulfur in the baseline PFH oil. The baseline PFH oil contains three times as much nitrogen as the Fischer Assay oil, which is not surprising since the oil is heavier. The catalysts lighten the oil and reduce the nitrogen content but only to the concentration found in the Fischer Assay oil. Further study would allow investigation of the types of nitrogen present in the catalytic PFH product oil and perhaps lead to catalysts or methods of operation, which would further reduce the nitrogen content in the product oil.

Tests were conducted with the pre-sulfided Mo catalysts to determine the effects of catalyst to shale ratio on oil quality and yield. Catalyst-to-shale ratio was reduced to 0.09 for Test 36-B-24 and increased to 0.47 for Test 36-B-25. Increasing the amount of catalyst improved the oil quality, but decreased the oil yield and increased carbon conversion to gas. Sulfur and nitrogen removal and decrease in specific gravity were significantly higher at a catalyst to shale ratio of 0.25 than at 0.09. Increasing the ratio to 0.47 produced some additional decrease in oil sulfur content (from 0.63 to 0.49 percent) and oil nitrogen content (from 0.89 to 0.75 percent) but had almost no effect on specific gravity. Oil yield decreased slightly to 242 percent of Fischer Assay when the catalyst-to-shale ratio was raised to 0.47. Carbon conversion to gas increased significantly from 9 to 26 to 46 percent as the catalyst to shale ratio was increased.

Retorting temperature was also varied to determine optimum conditions for the pre-sulfided Mo catalyst mixed with the shale. Tests 36-B-22 and -20 had a catalyst-to-shale ratio of 0.25 and average temperatures of 905° and 1034°F, respectively. Oil quality and yield were higher at 905°F than at the higher temperatures. Increased retorting temperature has previously been found to increase carbon conversion to gas, and in these tests the same result was observed. The carbon conversion to gas increased 30 percent in the 900° and 945°F tests. The carbon conversion to gas increased twice as much (60 percent) at 1034°F.

Product oil nitrogen content was similar at 0.88 weight percent for all three temperatures showing an average decrease of 44 percent. Specific gravity was also similar and varied from 0.952 at 905°F to 0.965 g/mL at 1034°F.

Sulfur reduction was greater at 905°F than at the higher temperatures. The product oil contained 0.31 percent sulfur compared to 0.62 and 0.63 percent sulfur for the oil from the higher temperature tests. Oil yield decreased with increasing retorting temperature. At 905°F, the oil yield of 60 GPT or 267 percent of Fischer Assay was 2 percent higher than the baseline PFH oil yield. Oil yields at 945° and 1034°F were slightly lower at 260 and 253 percent of Fischer Assay.

Mixed Catalysts Not Pre-Sulfided

Four PFH tests were conducted with the not pre-sulfided Mo and Co catalysts. The catalysts were mixed with the shale either as-received or after a tungsten promoter was added to the catalyst. The oil quality and yields with not pre-sulfided catalysts were similar to pre-sulfided catalyst oil yields and quality. The tungsten promoter had no effect on oil yield or quality but did increase the carbon conversion to gas.

The Mo and Co catalysts with no pre-sulfidation produced oils with about 0.6 percent sulfur and 0.9 percent nitrogen. These levels were 68 and 41 percent lower than those of oils from the baseline PFH tests. Oil yields were similar to the baseline PFH oil yields with the Co catalyst generating a higher oil yield of 268 percent of Fischer Assay and the Mo catalyst producing an oil yield of 249 percent of Fischer Assay.

The tungsten promoter had no effect on oil quality or yield. The promoter increased carbon conversion to gas. The Co catalyst increased carbon conversion to gas by 16 percent, and the tungsten promoter to 36 percent. The Mo catalyst increased carbon conversion by 23 percent, and the tungsten promoter to 42 percent. The results of the two tests with tungsten promoter added to the catalyst were negative, and no further tests were conducted using this catalyst promoter with the mixed catalysts.

Oil Boiling Point and Product Gas Composition

Simulated boiling point curves of oil produced in Tests 36-B-3 and 36-B-15 and presented in Figure 3-6. Test 36-B-3 was a baseline PFH test using no catalyst. Non-pre-sulfided commercial Co catalyst was mixed with the shale in Test 36-B-15. The boiling point curves show the oil from the catalyzed PFH test is significantly lighter as is apparent by comparing the specific gravities of 0.954 and 1.007 g/mL.

The catalyst increased the fraction of oil in the range usable for transportation fuels. Adding the catalyst increased the oil fraction boiling below 489°F from 21 to 32 percent. The total oil yields for the two tests were similar. Therefore, the catalyst actually produces an increase of almost 40 percent in oil boiling in the transportation fuel range.

Product gas compositions for the catalytic PFH tests are presented in Tables 3-14 through 3-18. Product hydrocarbon gases range from methane to C₆ compounds. Molar concentration of hydrocarbons decreases with increasing carbon number. The catalysts did not affect the distribution of hydrocarbon

Figure 3-6. SIMULATED BOILING POINT CURVES FOR SHALE OIL PRODUCED WITH NO CATALYST (Upper Curve) AND PRE-SULFIDED COMMERCIAL COBALT CATALYST (Lower Curve)

Table 3-14. PRODUCT GAS COMPOSITIONS FROM PFH TESTS
WITH BENEFICIATED ALABAMA SHALE AND NO CATALYST

Test No.	<u>36-B-1</u>	<u>36-B-2</u>	<u>36-B-3</u>	<u>36-B-4</u>	<u>36-B-5</u>	<u>Average**</u>
Product Gas,* mol %						
H ₂	98.66	98.72	98.35	98.80	98.55	98.62
CO	0.00	0.00	0.00	0.00	0.00	0.00
CO ₂	0.00	0.00	0.00	0.00	0.00	0.00
CH ₄	0.70	0.68	0.98	0.62	0.74	0.76
C ₂ H ₆	0.38	0.33	0.60	0.31	0.39	0.41
C ₂ H ₄	0.00	0.00	0.00	0.00	0.00	0.00
C ₃ H ₈	0.20	0.18	0.06	0.18	0.23	0.14
C ₃ H ₆	0.01	0.01	0.00	0.02	0.01	0.01
C ₄ H ₁₀	0.04	0.06	0.00	0.05	0.05	0.04
C ₄ H ₈	0.00	0.00	0.00	0.00	0.00	0.00
C ₅ H ₁₂	0.00	0.01	0.01	0.00	0.00	0.01
C ₆ ⁺	<u>0.01</u>	<u>0.01</u>	<u>0.00</u>	<u>0.02</u>	<u>0.03</u>	<u>0.01</u>
Total	100.00	100.00	100.00	100.001	100.00	100.00
CH ₄ , % of						
Total Hydrocarbons	52.2	53.1	59.4	51.7	51.0	55.1

* H₂S-free basis.

** Average of Tests 2, 3, and 4.

Table 3-15. PRODUCT GAS COMPOSITIONS FROM PFH TESTS
WITH BENEFICIATED ALABAMA SHALE AND IMPREGNATED CATALYSTS

Test No.	<u>36-B-6</u>	<u>36-B-7</u>	<u>36-B-8</u>	<u>36-B-9</u>	<u>36-B-10</u>	<u>36-B-11</u>
Catalyst	TA-M201	TA-M202	TA-M203	TA-C204	TA-N205	TA-MC206
Product Gas,* mol %						
H ₂	98.87	98.72	98.73	98.69	99.02	99.00
CO	0.00	0.00	0.00	0.00	0.00	0.00
CO ₂	0.00	0.00	0.00	0.00	0.00	0.00
CH ₄	0.60	0.71	0.68	0.70	0.52	0.50
C ₂ H ₆	0.30	0.35	0.34	0.36	0.24	0.25
C ₂ H ₄	0.00	0.00	0.00	0.00	0.00	0.00
C ₃ H ₈	0.17	0.17	0.18	0.19	0.12	0.13
C ₃ H ₆	0.01	0.01	0.01	0.01	0.02	0.02
C ₄ H ₁₀	0.04	0.03	0.04	0.04	0.05	0.05
C ₄ H ₈	0.00	0.00	0.00	0.00	0.00	0.00
C ₅ H ₁₂	0.00	0.00	0.00	0.00	0.01	0.02
C ₆ ⁺	0.01	0.01	0.02	0.01	0.02	0.03
Total	100.00	100.00	100.00	100.00	100.00	100.00
CH ₄ , % of Total Hydrocarbons	53.1	55.5	53.5	53.4	53.1	50.0

* H₂S-free basis.

**Table 3-16. PRODUCT GAS COMPOSITIONS FROM PFH TESTS
WITH BENEFICIATED ALABAMA SHALE AND EXIT LINE CATALYSTS**

Test No.	<u>36-B-12</u>	<u>36-B-13</u>	<u>36-B-14</u>	<u>36-B-29</u>	<u>36-B-275</u>	<u>36-B-28</u>
Mixed Catalyst	No	No	No	No	PS-85-765	PS-85-765
Pre-Sulfidation	--	--	--	--	Yes	Yes
Exit Line Catalyst	PS-85-765	SPS-0674-92	MS-21008	SPS-0674-92	SPS-0674-92	SPS-0674-92
Pre-Sulfidation	No	No	No	Yes	No	Yes
Product Gas, * mol %						
H ₂	98.83	98.65	98.95	98.47	98.28	98.20
CO	0.00	0.00	0.00	0.00	0.00	0.00
CO ₂	0.00	0.00	0.00	0.00	0.00	0.00
CH ₄	0.58	0.66	0.54	0.86	0.95	1.06
C ₂ H ₆	0.31	0.39	0.33	0.51	0.51	0.64
C ₂ H ₄	0.00	0.00	0.00	0.00	0.00	0.00
C ₃ H ₈	0.18	0.21	0.12	0.12	0.21	0.07
C ₃ H ₆	0.00	0.00	0.01	0.00	0.00	0.00
C ₄ H ₁₀	0.06	0.06	0.03	0.03	0.04	0.02
C ₄ H ₈	0.00	0.00	0.00	0.00	0.00	0.00
C ₅ H ₁₂	0.01	0.01	0.00	0.00	0.00	0.00
C ₆ ⁺	0.03	0.02	0.02	0.01	0.01	0.01
Total	100.00	100.00	100.00	100.00	100.00	100.00
CH ₄ , % of						
Total Hydrocarbons	49.6	48.9	51.4	56.2	55.2	58.9

* H₂S-free basis.

Table 3-17. PRODUCT GAS COMPOSITIONS FROM PFH TESTS
WITH BENEFICIATED ALABAMA SHALE MIXED WITH PRE-SULFIDED CATALYSTS

Test No.	<u>36-B-24</u>	<u>36-B-19</u>	<u>36-B-25</u>	<u>36-B-22</u>	<u>36-B-20</u>	<u>36-B-26</u>
Mixed Catalyst	----- PS-85-765 -----			----- SPS-0674-92 -----		
Catalyst/Shale, g/g	0.09	0.25	0.47	0.25	0.25	0.25
Temperature, °F	919	945	943	905	1034	928
Product Gas, * mol %						
H ₂	98.69	98.41	98.64	98.41	98.18	98.62
CO	0.00	0.00	0.00	0.00	0.00	0.00
CO ₂	0.00	0.00	0.00	0.00	0.00	0.00
CH ₄	0.69	0.88	0.72	0.91	1.06	0.72
C ₂ H ₆	0.38	0.45	0.36	0.60	0.53	0.39
C ₂ H ₄	0.00	0.00	0.00	0.00	0.00	0.00
C ₃ H ₈	0.19	0.20	0.21	0.06	0.19	0.21
C ₃ H ₆	0.00	0.00	0.00	0.00	0.00	0.00
C ₄ H ₁₀	0.04	0.04	0.05	0.01	0.03	0.04
C ₄ H ₈	0.00	0.00	0.00	0.00	0.00	0.00
C ₅ H ₁₂	0.00	0.00	0.00	0.00	0.00	0.00
C ₆ ⁺	<u>0.01</u>	<u>0.02</u>	<u>0.02</u>	<u>0.01</u>	<u>0.01</u>	<u>0.02</u>
Total	100.00	100.00	100.00	100.00	100.00	100.00
CH ₄ , % of						
Total Hydrocarbons	52.7	55.3	54.4	57.2	58.2	52.2

* H₂S-free basis.

Table 3-18. PRODUCT GAS COMPOSITIONS FROM PFH TESTS
WITH BENEFICIATED ALABAMA SHALE MIXED WITH NON-PRE-SULFIDED CATALYSTS

Test No.	<u>36-B-15</u>	<u>36-B-23</u>	<u>36-B-16</u>	<u>36-B-17</u>
Mixed Catalyst	-- SPS-0674-92 --		-- PS-85-765 --	
Promoter	No	W	No	W
Product Gas,* mol %				
H ₂	98.35	98.60	98.74	98.57
CO	0.00	0.00	0.00	0.00
CO ₂	0.00	0.00	0.00	0.00
CH ₄	0.94	0.75	0.64	0.77
C ₂ H ₆	0.50	0.36	0.34	0.37
C ₂ H ₄	0.00	0.00	0.00	0.00
C ₃ H ₈	0.16	0.20	0.20	0.21
C ₃ H ₆	0.00	0.00	0.00	0.00
C ₄ H ₁₀	0.03	0.06	0.06	0.06
C ₄ H ₈	0.00	0.00	0.00	0.00
C ₅ H ₁₂	0.00	0.01	0.00	0.00
C ₆ ⁺	<u>0.02</u>	<u>0.02</u>	<u>0.02</u>	<u>0.02</u>
Total	100.00	100.00	100.00	100.00
CH ₄ , % of Total Hydrocarbons	57.0	53.6	50.7	53.8

* H₂S-free basis.

gases. Even though carbon conversions to gas often increased significantly with a catalyst present, the hydrocarbon gas distribution was not altered.

Subtask 3.10 Autocatalysis In Hydroretorting

The objective of this subtask was to investigate the effects of potentially catalytic minerals or alkali metal oxides naturally occurring in shale, on the hydroretorting characteristics and product yield. Tests were conducted by the University of Alabama College of Engineering (UA) in a laboratory-scale semi-batch reactor using as-received shale and shale impregnated with potentially catalytic metals.

Equipment Description and Operation

The experiments were performed in a bench-scale unit prepared for hydroretorting. The reactor (Autoclave Engineers Model 79-07117) is capable of operating at 1000°F and 3000 psig. It has a magnetic stirrer and draft tube design to ensure gas mixing throughout the solid sample. Glass wool is used to hold the shale sample in place if less than 100 grams of shale is charged. The reactor is a bolted-closure reactor, consisting of body, cover, closure gasket, cap screws and two retainer screens. All gas-contacted parts are constructed of type 316 stainless steel. The reactor has a volume of 5.9 in³. A schematic diagram of the experimental arrangement is shown in Figure 3-7.

Reactor heating is provided by an electric jacket-type furnace with resistance winding and insulation enclosed in a sleeve-type jacket. The furnace slides over the body of the reactor. It is divided into three heating zones (top, middle and bottom), which are wired into three separate electric circuits. The furnace and reactor temperatures are maintained by separate controllers. The furnace controller input signal is from a type K thermocouple. A 5-channel digital thermometer with type K thermocouples indicates gas temperatures at the reactor top and bottom, gas preheater outlet, reactor inlet line, and the product gas leaving the liquid collector.

Nitrogen is used to purge the system. Hydrogen is fed through a 1/8-inch capillary tube differential pressure (d/p) cell flowmeter. The output of the Foxboro 13-A pneumatic d/p cell flowmeter was calibrated versus hydrogen in standard ft³ per minute at 400 psig. The hydrogen flows through a preheater consisting of a coil of tubing cast in Thermon heat-transfer cement prior to being introduced into the reactor. The gas then passes through a short line to the reactor. The line is wrapped with a heating tape. Inlet gas pressure is measured by a precision Heise pressure gauge. The reactor product gas passes through an in-line filter to collect entrained particles from the reactor. The product gas then was passed through a double-pipe water cooled heat exchanger where it is cooled, and then into the liquid collector. The liquid collector vessel is constructed of Monel and has a volume of 1 liter, an OD of 3.5 inches and a length of 11.5 inches. The product gas exiting the liquid collector passed through a Grove Mighty-Mite back-pressure regulator, and into a tank in which all of the gaseous product was collected. The volume of the gas collection tank is 0.5 ft³.

Figure 3-7. SCHEMATIC DIAGRAM OF EQUIPMENT USED FOR AUTOCATALYSIS TEST

Materials

A batch of about 4 kilograms of moist, beneficiated Alabama shale was dried in a Fisher Isotemp Controlled Atmosphere Moisture Oven, Model 496A at 80°C. Argon was used to provide an inert atmosphere. The moisture content of the as-received sample was determined to be about 44.5 weight percent. The dry cake was then crushed by two methods. In the first, about 100 grams was crushed in air to determine the effect of atmospheric oxygen on the subsequent autocatalytic tests; in the second, about 500 grams were crushed in a glove box purged with nitrogen. A C/H analysis was performed on the shale sample before and after crushing the sample in a LECO analyzer. The result of this analysis is listed in Table 3-19.

Table 3-19. EFFECT OF DRYING ATMOSPHERE ON SHALE SAMPLE ANALYSES

Sample	<u>Before Drying</u>	<u>Air Crushed</u>	<u>Nitrogen Crushed</u>
Component, wt %			
Carbon	29.65	28.22	27.99
Hydrogen	3.19	3.32	3.35
Nitrogen	0.81	0.77	0.80

The analysis shows that there is no appreciable loss of carbon due to atmospheric oxidation while crushing the sample in air. A 1 percent loss of carbon during the drying process is observed.

Experimental Procedure

The experiments are divided into two tasks, namely the baseline experiments and the autocatalytic experiments. The aim of the former set of tests is to obtain a set of operating conditions in which a carbon conversion of about 30 to 60 percent in shale is observed. Also, it is to act as a baseline from which the extent of autocatalytic effect of the four selected metal ions, namely, nickel, copper, iron and potassium, on conversion. A temperature of 900°F and a pressure of 400 psig was selected initially.

Prior to a test, a 10 to 15 gram sample of shale is weighed and charged between layers of glass wool into the reactor. The reactor is bolted down at 60 ft-lb. The system is purged for about 15 minutes with nitrogen. The back pressure is set at 400 psig and then the hydrogen sweep follows. The reactor is heated from ambient to about 900°F at a rate of about 8°F per minute, while the liquid and gaseous products are collected continuously. On reaching the targeted temperature, all heating is stopped and the reactor is cooled slowly to ambient conditions. The amount of gaseous and liquid products thus formed are noted.

Calibration of the d/p Cell Flowmeter

The experimental setup was pressurized to 400 psig with nitrogen and the back-pressure regulator was set to hold this pressure. Hydrogen flow was initiated with its flow rate being varied with a needle valve. The flow rate

of hydrogen was verified using a wet test meter. The calibration results were satisfactory and reproducible.

Autocatalysis Tests

Four metals were tested for their autocatalytic effects in shale hydro-retorting. The additional impregnation of metals was calculated based on the levels in which they naturally occur and also after taking into consideration that during the concentration about 80 percent (by weight) of the inorganic matter was removed as spent shale. These levels are tabulated below.

<u>Sample ID</u>	<u>Metal</u>	<u>Salt</u>
M1	Copper	Cupric Sulfate
M2	Potassium	Potassium Nitrate
M3	Nickel	Nickel(ous) Sulfate
M4	Iron	Ferric Ammonium Sulfate

The amount of each salt added was calculated by using the mass-fraction of the metal ion in the salt and also assuming that 80 percent of the metals occurring naturally were removed from the shale during the process of concentration. The natural occurrence of these metals in shale and the amount of the salt added into a theoretical 100 grams of charge are listed below.

<u>Metal</u>	<u>Occurrence</u>	<u>Salt Added per 100 g of shale, mg</u>
Copper	100 ppm	9.3
Potassium	>1%	8.4
Nickel	100-250 ppm	532.8
Iron	>5%	7856.4

The formation of liquid products in both sets of experiments was negligible. It was suspected that the oil fraction of the product which typically would consist of the C₇ to C₁₄ hydrocarbons would have accumulated in the spent shale itself. Pilot runs, on C/H analysis, showed that there was about the same weight fraction of carbon and hydrogen in the spent shale as in the unreacted samples (typically in the range of 28 to 30 percent carbon and 3 to 4 percent hydrogen). Washing the spent shale in the n-heptane yielded good results. The results available to date are tabulated below.

<u>Sample ID</u>	<u>Mass of Charge</u>	<u>Mass of Spent Shale</u>	<u>Estimated Mass of Gas</u>	<u>Estimated Mass of Liquids</u>
			grams	
B1	14.4763	12.9546	0.4864	1.0353
B2	14.7987	13.8282	0.7054	0.2651
B3	15.2968	12.2609	2.9758	0.0601
M1	14.0522	11.2767	2.7133	0.0642
M2	14.1927	12.4611	1.3811	0.3455
M3	12.7638	11.4895	1.0680	0.2743
M4	15.7891	12.0735	3.6383	0.0773

The C/H data for these samples are not currently available. It can only be estimated that there has been, on an average, 15 percent carbon conversion in the baseline tests.

Conclusion

With the operating conditions at 900°F and pressure at 400 psig and from the baseline tests it can be estimated roughly that two-thirds of the overall carbon conversion has been to the gaseous products. Based on the available data, all the metals distinctly favor the formation of the gaseous fraction of the products.

Subtask 3.11. Shale Oil Upgrading and Evaluation

The objective of this subtask was to investigate conventional and novel methods for upgrading the oil produced by shale hydrotreating. This subtask is divided into two subtasks: 3.11.1. Conventional Upgrading and 3.11.2. Novel Approach to Upgrading.

Discussion

A total of seventeen conventional and novel oil upgrading tests were conducted in this subtask. The oil used for upgrading was produced in a bench-scale PFH test at 925°F and 1000 psig in an earlier program. The oil was stored in a refrigerated room in a sealed container to prevent oxidation. Oil upgrading tests were conducted using the whole shale oil and the shale oil fraction boiling below 650°F. There were several reasons for upgrading the -650°F fraction of the oil as well as the whole oil. First, comparison of upgrading results with the two oils would reveal the effects of the catalysts on the light and heavy ends of the oil. Second, nitrogen compounds tend to be concentrated in the heavy ends of the shale oil. Upgrading the two oil fractions would provide information on the removal of shale oil nitrogen. Finally, if the heavy fraction of the shale oil is recovered without upgrading for use as an asphalt additive, there would be no need to upgrade the whole shale oil.

Analyses of the shale oil samples are presented in Table 3-20. The light fraction of the oil has a significantly lower nitrogen content (0.61 percent) than the whole oil (1.44 percent). The sulfur content is also unexpectedly lower in the light oil fraction, and the specific gravity is also lower, as expected. The light oil fraction has a higher hydrogen to carbon ratio indicating a more aliphatic composition. Both oil samples need to be upgraded before being used as a refinery feedstock.

Experimental

A schematic diagram of the laboratory-scale oil upgrading unit is shown in Figure 3-8. The unit contains a feed gas controller system, a steam pump, an accurate piston-type oil pump, reactor, thermocouples and a temperature recorder, a single-zone furnace and furnace controller, a liquid collection system, a back pressure regulator, a gas sampling manifold, and a dry test meter. All equipment is constructed of type 316 stainless steel and is rated

Figure 3-8. SCHEMATIC DIAGRAM OF THE OIL UPGRADING UNIT

Table 3-20. COMPOSITION OF OIL USED IN OIL
UPGRADING TESTS

Shale	Beneficiated Alabama	
Boiling Point Fraction	<u>Whole Oil</u>	<u>-650°F</u>
Composition, wt %		
Carbon	85.40	83.82
Hydrogen	9.86	11.51
Sulfur	2.75	1.82
Nitrogen	1.44	0.61
Oil H/C, g/g	0.115	0.137
Oil sp. gr., g/mL	0.996	0.872

for operation at 900°F and 2000 psig. Feed gas flow rate is controlled by calibrated mass flow meters capable of operation at pressures up to 4500 psig.

A packed-bed catalyst configuration was utilized for all tests. The reactor was loaded from the bottom by charging alumina tablet "spacers" followed by glass wool, the weighed catalyst, more glass wool, additional alumina "spacers" and more glass wool. The reactor bottom was then sealed. The sealed reactor was connected and the entire unit was pressure checked. Some of the catalysts required pre-sulfidation; these catalysts were pre-sulfided prior to use in the oil upgrading tests.

Catalysts were pre-sulfided using a feed gas containing 1 percent H₂S in hydrogen. The reactor was heated to 482°F (250°C) using a nitrogen purge. The feed gas purge was switched to the sulfiding mixture and the reactor was held at temperature for 30 minutes. The reactor was then heated to 662°F (350°C) and maintained at temperature for two hours. At the end of this period, the reactor was allowed to cool to 230°F (110°C). A hydrogen purge was established in place of the sulfiding mixture, and the reactor was purged over night before conducting the oil upgrading test.

Oil upgrading tests were initiated by pressurizing the system with either methane or hydrogen. The reactor was then heated to the test temperature under a gas purge. After temperature and pressure and the feed gas flow rate were established, the feed oil pump was started. Oil was pumped to the unit at 19.5 mL per hour for all tests. Feed gas and oil enter the reactor from the top and exit from the bottom. Oil is accumulated in a collection system and drained once every 30 or 60 minutes. Product gas passes through the gas sampling manifold and the back pressure regulator.

The volume of the reactor and the flow rates of gas and oil produced an unsteady-state period of approximately two hours for the upgrading tests. During the steady-state period, all operating conditions and flows were constant. Oil inventory in the reactor and oil exit rate were also constant.

Steady-state operation was continued for at least three hours in all tests. All oil and gas samples from the steady-state period were analyzed. After each test, the reactor was disassembled and cleaned.

Catalyst Preparation

Catalysts used in this subtask included two regenerable commercial hydrotreating catalysts, a tungsten-promoted commercial hydrotreating catalyst, and a group of regenerable IGT-MS- series catalysts.

The two commercial hydrotreating catalysts were obtained from Criterion Catalysts, Inc. These catalysts contain either nickel, molybdenum, or phosphorus on an alumina support (PS-85-767) or cobalt, molybdenum, or phosphorus on an alumina support (SPS-0674-92). The pre-sulfiding procedure described in the experimental section was followed each time these catalysts were used in an oil upgrading test. The commercial catalysts were used either with or without the addition of a tungsten promoter.

The tungsten promoter was added to the commercial catalysts by pouring a solution of tungstic acid ($\text{WO}_3 \cdot \text{H}_2\text{O}$) in concentrated ammonium hydroxide over the catalyst. The catalyst was stirred during this procedure to produce uniform coverage. After tungsten addition, the catalysts were dried at 220°F and then calcined at 750°F for two hours.

The IGT-MS- series of catalysts is prepared by decomposing ammonium tetrathio-molybdate (ATM) in the presence of other solid powders. The details of the decomposition, including the temperature, pressure, flow rate, and identity of a stabilizing and enhancing compound, are proprietary to IGT. The first step in preparing these catalysts is to mix all the solids in a ball mill mixer. Solids include ATM, a support material that is usually a mixed oxide including zirconium oxide, a stabilizing and enhancing compound, and any promoter oxides, such as cobalt oxide. The powders are well mixed and then placed in a reactor for the ATM decomposition. After the ATM decomposition, the catalyst powder is formed into wafers at 12,000 to 18,000 psi. The wafers are broken apart and sieved to -8+20 mesh.

A group of metal oxide promoters were included in the IGT-MS- catalysts studied. The metals, including tungsten, niobium, chromium, and nickel, were added in the oxide forms WO_3 , Nb_2O_5 , Cr_2O_3 , and NiO . The methods used to add the promoters are proprietary to IGT.

Subtask 3.11.1. Conventional Upgrading

The objective of this subtask was to evaluate conventional hydrotreating technology for upgrading shale oil produced from the PFH process to transportation fuel.

Discussion

A number of catalysts were evaluated as conventional and unconventional shale oil upgrading catalysts. A list of the catalysts is presented in Table 3-21. Three of the catalysts, the two commercial catalysts and MS-Z100, were used in this subtask as conventional hydrotreating catalysts. The other five catalysts were designed specifically for oil upgrading in methane and were used in Subtask 3-11-2.

Table 3-21. CATALYSTS EVALUATED FOR SHALE OIL UPGRADING

Catalyst	Source	Description
PS-85-767	Commercial*	Ni/Mo/P on Al ₂ O ₃
SPS-0674-92	Commercial*	Co/Mo/P on Al ₂ O ₃
MS-Z100	IGT	MoS _x on CaO·ZrO ₂
MS-T101	IGT	MoS _x on CaO·TiO ₂
MS-Y103	IGT	MoS _x on Y ₂ O ₃ ·ZrO ₂
MS-200	IGT	MoS _x /Nb ₂ O ₅ /Cr ₂ O ₃ on CaO·ZrO ₂
MS-201	IGT	MoS _x /WO ₃ on CaO·ZrO ₂
MS-202	IGT	MoS _x /WO ₃ /NiO on CaO·ZrO ₂

* Criterion Catalysts, Inc.

Six conventional hydrotreating tests were conducted. The whole oil was upgraded in the first three tests at a temperature of 750°F and a pressure of 2000 psig. Catalysts for these tests included the two commercial catalysts and MS-Z100. The other three tests were conducted with commercial catalyst PS-85-767 containing nickel. One test was conducted using the catalyst as received. A tungsten promoter was added to the catalyst for the last two tests. The pressure was 2000 psig for the tests. Temperature was 750°F for the first two tests and 700°F for the final test. A summary of the test operating conditions and results is presented in Table 3-22.

Conventional upgrading was effective on the whole oil. The commercial catalysts reduced the shale oil sulfur content by 89 and 84 percent and reduced the nitrogen content by 72 and 57 percent. Product oil and sulfur content were as low as 0.29 and 0.41 percent, respectively. The oil hydrogen-to-carbon ratio was increased using the commercial catalysts, and the specific gravity decreased by about 10 percent. The IGT catalyst MS-Z100 reduced the oil sulfur and nitrogen contents and produced a lighter oil, but this catalyst was not as effective as the commercial catalysts.

More sulfur and nitrogen were removed from the oil using the nickel catalyst than using the cobalt catalyst. Therefore, PS-85-765 was chosen as the catalyst for upgrading the -650°F shale oil fraction.

Product oil and gas flows were measured over the steady-state period, and these flows were compared with the oil feed rate. About 1 percent of the carbon in the feed oil formed gas. Estimates for the whole oil upgrading recovery was greater than 90 percent.

Table 3-22. OPERATING CONDITIONS AND RESULTS OF
OIL UPGRADING TESTS WITH HYDROGEN

Test No.	<u>38-0-2</u>	<u>38-0-3</u>	<u>38-0-4</u>	<u>38-0-9</u>	<u>38-0-10</u>	<u>38-0-11</u>
Temperature, °F	770	740	725	755	740	700
Pressure, psig	2000	2000	2000	2000	2000	2000
Feed Gas	H ₂	H ₂	H ₂	H ₂	H ₂	H ₂
Steam	No	No	No	No	No	No
Feed Oil	Whole	Whole	Whole	-650°F	-650°F	-650°F
Feed Gas Rate, SCFH	1.1	1.1	1.1	1.1	1.1	0.9
Feed Oil Rate, mL/h	----- 19.5 -----					
Feed Oil Space Velocity, V _{oil} /V _{cat.} ·h	----- 1.0 -----					
Catalyst	PS-85-767	SPS-0674-92	MS-Z100	-----	PS-85-767	-----
Catalyst Sulfidation	Yes	Yes	No	Yes	Yes	Yes
Catalyst Promoter	No	No	No	No	W	W
Product Oil Composition, wt %						
Carbon	86.68	86.95	86.04	81.56	86.04	86.43
Hydrogen	11.88	11.42	10.36	13.27	13.78	13.18
Sulfur	0.29	0.43	1.28	0.12	0.05	0.06
Nitrogen	0.41	0.62	1.22	0.09	0.01	0.02
Product Oil H/C, g/g	0.137	0.131	0.120	0.163	0.160	0.152
Product Oil Sp. Gr.	0.896	0.920	0.964	0.798	0.813	0.829
Upgrading Results						
Sulfur Removal, %	89	84	53	93	97	97
Nitrogen Removal, %	72	57	15	85	98	97
H/C Change, %	19	14	4	18	17	11
Sp. Gravity Change, %	-10	-8	-3	-8	-7	-5
Carbon Recovery*, %						
Product Oil	92	76	90	96	84	99
Product Gas	1	1	1	2	1	1

* % of carbon in feed oil.

The commercial nickel catalyst was even more effective at upgrading the -650°F shale oil fraction. Sulfur and nitrogen were reduced by 93 and 85 percent producing a product oil with 0.12 percent sulfur and 0.09 percent sulfur. Adding a tungsten promoter to the catalyst and upgrading the oil at the same conditions of 750°F and 2000 psig improved the sulfur and nitrogen removal to 97 and 98 percent, respectively. The product oil contained only 0.05 percent sulfur and 0.01 percent nitrogen. In both of these tests, the hydrogen-to-carbon ratio was increased. The specific gravities decreased 7 percent to 0.80 and 0.81 g/mL.

The final conventional upgrading test was conducted with the tungsten-promoted commercial nickel catalyst. A pressure of 2000 psig was again used, but the temperature was reduced to 700°F. The upgrading results were almost identical to the results of the test at 740°F (Test 38-O-10). Sulfur and nitrogen were both reduced by 97 percent, the hydrogen-to-carbon ratio was increased, and the oil specific gravity was decreased 5 percent. Only 1 percent of the feed carbon was converted to gas which is the same fraction measured in all six conventional upgrading tests.

Average product gas compositions for the conventional upgrading tests are presented in Table 3-23. Product gases included aliphatic hydrocarbons from methane through C₆ and H₂S. No carbon oxides or unsaturated hydrocarbons were observed. The largest components of the product gas in descending quantity were propane, methane, and ethane.

Table 3-23. PRODUCT GAS COMPOSITIONS FROM OIL
UPGRADING TESTS IN HYDROGEN

Test No.	<u>38-O-2</u>	<u>38-O-3</u>	<u>38-O-4</u>	<u>38-O-9</u>	<u>38-O-10</u>	<u>38-O-11</u>
Product Gas, mol %						
Hydrogen	98.38	98.73	99.09	99.20	99.22	99.37
Carbon Dioxide	0.00	0.00	0.00	0.00	0.00	0.00
Methane	0.40	0.50	0.18	0.19	0.14	0.07
Ethane	0.27	0.34	0.12	0.14	0.09	0.07
Propane	0.58	0.21	0.20	0.40	0.29	0.12
Butane	0.05	0.06	0.03	0.04	0.04	0.02
Pentane	0.01	0.01	0.01	0.02	0.01	0.01
C ₆ +	0.02	0.02	0.03	0.01	0.02	0.02
Hydrogen Sulfide	<u>0.29</u>	<u>0.13</u>	<u>0.34</u>	<u>0.00</u>	<u>0.19</u>	<u>0.32</u>
Total	100.00	100.00	100.00	100.00	100.00	100.00

Subtask 3.11.2. Novel Upgrading

The objective of this subtask was to determine if the whole product oil can be hydrotreated in a one-step catalytic process without the use of hydrogen or severe operating conditions.

Discussion

Eleven shale oil upgrading tests were conducted in this subtask. Three tests were performed to upgrade the whole shale oil, and the other eight tests were performed to upgrade the -650°F fraction of the oil. Descriptions of the catalysts used for these tests was provided in Table 3-21. In these tests, the upgrading atmosphere was methane. The pressure was reduced from 2000 to 1000 psig and the temperature was 750°F for most tests. The novel upgrading conditions are significantly milder than conventional hydrotreating conditions. Operating conditions and results of the novel upgrading tests are shown in Tables 3-24 and 3-25.

Ten of the eleven upgrading tests were conducted with MS series catalysts produced at IGT. These catalysts are designed to be non-coking during oil upgrading in methane. One test was conducted using the tungsten-promoted commercial nickel catalyst. This test was conducted to provide a comparison of results between a commercial catalyst and the MS series catalysts.

Three upgrading tests were conducted with the whole oil. Catalysts MS-T101 and MS-Y103 were used at reactor conditions of 750°F and 1000 psig. In the third test, steam was added to the feed gas along with the methane and catalyst MS-T101 was used.

The MS catalysts removed approximately 40 percent of the sulfur from the oil but only removed 10 and 5 percent of the shale oil nitrogen. The hydrogen to-carbon ratio was slightly higher (6 percent) after upgrading. The specific gravity was almost identical before and after upgrading.

When no steam was added to the reactor, the catalyst remained clean with no apparent coking taking place. Steam addition resulted in significant coke formation and a near plugging of the reactor tube. The temperature rose from 750° to 970°F and could not be controlled. Sulfur removal (35 percent) was slightly lower than in the tests with no steam present. Nitrogen removal was 30 percent, which is much higher than with no steam present. Steam addition produced a lighter oil with a decrease of 5 percent in the specific gravity.

Test 38-O-8 was the only test conducted with steam addition. Although steam produced an oil with a slightly improved (reduced) specific gravity, the product oil still contained 1.8 percent sulfur and 1.0 percent nitrogen. Also, the large amount of oil coking on the catalyst indicated that operating procedures and conditions would have to be modified to utilize MS-T101 as a possible upgrading catalyst.

The last eight oil upgrading tests (including replicate Tests 38-O-14 and 38-O-15) were conducted with the -650°F shale oil fraction. Catalysts included the tungsten-promoted commercial nickel catalyst, MS-T101 containing MoS_x , and MS catalysts containing MoS_x and several different promoters.

The tungsten-promoted PS-85-767 catalyst produced sulfur and nitrogen reductions of 46 and 31 percent and had no effect on hydrogen-to-carbon ratio or specific gravity. The product oil contained 1.0 percent sulfur and 0.4 percent nitrogen. Some coking occurred in this test. Further tests were

**Table 3-24. OPERATING CONDITIONS AND RESULTS OF OIL
UPGRADING TESTS WITH METHANE AND WHOLE OIL**

Test No.	<u>38-0-5</u>	<u>38-0-6</u>	<u>38-0-8</u>
Temperature, °F	740	745	970
Pressure, psig	1000	1000	1000
Feed Gas	CH ₄	CH ₄	CH ₄
Steam	No	No	Yes
Feed Oil	Whole	Whole	Whole
Feed Gas Rate, SCFH	0.8	0.9	0.9
Feed Oil Rate, mL/h	-----	19.5	-----
Feed Oil Space Velocity, V _{oil} /V _{cat.} ·h	-----	1.0	-----
Catalyst	MS-T101	MS-Y103	MS-T101
Catalyst Sulfidation	No	No	No
Catalyst Promoter	No	No	No
Product Oil Composition, wt %			
Carbon	86.47	86.58	84.17
Hydrogen	9.45	9.28	9.97
Sulfur	1.56	1.70	1.79
Nitrogen	1.29	1.37	1.01
Product Oil H/C, g/g	0.109	0.107	0.118
Product Oil Sp. Gr.	1.007	1.012	0.942
Upgrading Results			
Sulfur Removal, %	43	38	35
Nitrogen Removal, %	10	5	30
H/C Change, %	-5	-7	3
Sp. Gravity Change, %	1	2	-5
Carbon Recovery*, %			
Product Oil	73	90	101
Product Gas	8	6	NA

* % of carbon in feed oil

NA Not available

Table 3-25. OPERATING CONDITIONS AND RESULTS OF OIL UPGRADING
TESTS WITH METHANE AND THE OIL BOILING BELOW 650°F

Test No.	38-O-12	38-O-14	38-O-15	38-O-16
Temperature, °F	740	730	730	775
Pressure, psig	1000	1000	1000	1000
Feed Gas	CH ₄	CH ₄	CH ₄	CH ₄
Steam	No	No	No	No
Feed Oil	-650°F	-650°F	-650°F	-650°F
Feed Gas Rate, SCFH	0.9	0.9	0.9	0.9
Feed Oil Rate, ml/h	----- 19.5 -----			
Feed Oil Space Velocity, $V_{oil}/V_{cat.} \cdot h$	----- 1.0 -----			
Catalyst	PS-85-767	MS-T101	MS-T101	MS-T101
Catalyst Sulfidation	Yes	No	No	No
Catalyst Promoter	W	No	No	No
Product Oil Composition, wt %				
Carbon	86.89	83.80	85.84	86.05
Hydrogen	11.96	11.28	11.59	11.66
Sulfur	0.98	1.45	1.72	1.67
Nitrogen	0.42	0.48	0.54	0.56
Product Oil H/C, g/g	0.138	0.135	0.135	0.136
Product Oil Sp. Gr.	0.861	0.865	0.876	0.875
Upgrading Results				
Sulfur Removal, %	46	20	5	8
Nitrogen Removal, %	31	21	11	8
H/C Change, %	0	-2	-1	-1
Sp. Gravity Change, %	-1	-1	0	0
Carbon Recovery*, %				
Product Oil	104	93	105	114
Product Gas	-17	1	4	3

* % of carbon in feed oil

Table 3-25 Cont. OPERATING CONDITIONS AND RESULTS OF OIL UPGRADING
TESTS WITH METHANE AND THE OIL BOILING BELOW 650°F

Test No.	38-O-17	38-O-18	38-O-19	38-O-20
Temperature, °F	745	735	815	745
Pressure, psig	1000	1000	1000	1000
Feed Gas	CH ₄	CH ₄	CH ₄	CH ₄
Steam	No	No	No	No
Feed Oil	-650°F	-650°F	-650°F	-650°F
Feed Gas Rate, SCFH	0.9	0.9	0.9	0.9
Feed Oil Rate, ml/h	----- 19.5 -----			
Feed Oil Space Velocity, V _{oil} /V _{cat.} ·h	----- 1.0 -----			
Catalyst	MS-200	MS-201	MS-201	MS-202
Catalyst Sulfidation	No	No	No	No
Catalyst Promoter	Nb,Cr	W	W	W,Ni
Product Oil Composition, wt %				
Carbon	86.30	86.17	85.74	85.95
Hydrogen	11.69	11.75	11.40	11.59
Sulfur	1.53	1.53	1.62	1.44
Nitrogen	0.47	0.52	0.55	0.51
Product Oil H/C, g/g	0.135	0.136	0.133	0.135
Product Oil Sp. Gr.	0.865	0.868	0.874	0.869
Upgrading Results				
Sulfur Removal, %	16	16	11	21
Nitrogen Removal, %	23	15	10	16
H/C Change, %	-1	-1	-3	-2
Sp. Gravity Change, %	-1	0	0	0
Carbon Recovery*, %				
Product Oil	96	97	101	99
Product Gas	0	-2	-1	-7

* % of carbon in feed oil

conducted to find a catalyst giving higher removal of sulfur and nitrogen without coking.

Seven tests were conducted with four MS catalysts. Five of the tests were performed at 750°F and 1000 psig. The temperature was increased to 775°F for one test and to 815°F for the seventh test. The four MS catalysts included MoS_x , MoS_x promoted with Nb and Cr, MoS_x promoted with W, and MoS_x promoted with W and Ni.

Sulfur and nitrogen removals were between 5 and 21 percent in all seven methane tests with the MS catalysts. The oil hydrogen-to-carbon ratio and specific gravity was unchanged by the catalysts. The promoters had no apparent effect on oil composition or quality. Increasing the reactor temperature to 775°F or 815°F did not improve the upgrading of the oil.

The oil upgrading mechanism for conventional hydrotreating appears to be different from that for oil upgrading in methane. In a hydrogen atmosphere, all of the gas phase hydrocarbons were saturated with propane present in the highest concentration. Tables 3-26 and 3-27 show the hydrocarbons produced during upgrading in a methane atmosphere include both saturated and unsaturated hydrocarbons. Propane is not the largest volume product. Instead, product hydrocarbons decrease with increasing molecular size. A small amount of carbon dioxide is produced in methane where none was formed in hydrogen upgrading.

GC simulated boiling point curves were determined for the two feed oils and the seventeen upgraded oil samples from this subtask and Subtask 3.11.1. Comparisons of some of these boiling point curves are presented in Figures 3-9 through 3-12. Data is not presented for all seventeen tests, but the test data is generally representative of all of the oils.

Figure 3-9 shows the boiling point curves for the whole oil, the whole oil upgraded in hydrogen with catalyst PS-85-767 (Test 38-O-2), the whole oil upgraded in methane with catalyst MS-T101 (Test 38-O-5), and the -650°F fraction of the shale oil. The upgraded oils have larger fractions boiling at lower temperatures than the whole oil, but then still have components boiling over the entire temperature range represented by the whole oil. The boiling point curves of the two upgraded oils are similar and are between the curves for the whole oil and the -650°F oil. The similarity of the upgraded oil boiling point curves is interesting because the sulfur and nitrogen removals were different and the specific gravities of the two oils are very different.

Conventional hydrotreating results are shown in Figure 3-10. Product oils from both Tests 38-O-2 and 38-O-9 are lighter and boil at lower temperatures than the feed oils.

Figure 3-11 includes boiling point curves for the -650°F oil and for this oil after upgrading in hydrogen and methane. Conventional hydrotreating produces a larger increase in the fraction of oil boiling at lower temperatures. Figure 3-12 compares the boiling point curve of the -650°F oil with the boiling point curves for this oil after upgrading with several catalysts in methane. The curves show only a small decrease in the average boiling point of the oil. This is in agreement with the oil specific gravity data from these tests which showed no change in oil density using the MS catalysts with various promoters in methane.

Table 3-26. PRODUCT GAS COMPOSITIONS FROM OIL UPGRADING TESTS WITH METHANE AND THE WHOLE OIL

Test No.	<u>38-O-5</u>	<u>38-O-6</u>	<u>38-O-8</u>
Product Gas, mol %			
Hydrogen	2.30	2.35	4.94
Carbon Dioxide	0.03	0	0.92
Methane	96.52	96.55	90.71
Ethane	0.23	0.16	1.12
Ethene	0.00	0.00	0.11
Propane	0.17	0.10	0.59
Propene	0.05	0.04	0.20
Butanes	0.06	0.05	0.24
Butenes	0.02	0.04	0.17
Pentanes	0.02	0.03	0.11
Pentenenes	0.00	0.00	0.02
C ₆ ⁺	0.09	0.18	0.39
Hydrogen Sulfide	<u>0.51</u>	<u>0.50</u>	<u>0.48</u>
Total	100.00	100.00	100.00

Table 3-27. PRODUCT GAS COMPOSITIONS FROM OIL UPGRADING TESTS WITH METHANE AND THE OIL BOILING BELOW 650°F

Test No.	<u>38-O-12</u>	<u>38-O-14</u>	<u>38-O-15</u>	<u>38-O-16</u>
Product Gas, mol %				
Hydrogen	63.77	1.22	0.74	0.79
Carbon Dioxide	0.00	0.04	0.05	0.02
Methane	35.54	98.18	98.83	98.80
Ethane	0.10	0.09	0.07	0.07
Ethene	0.00	0.00	0.00	0.00
Propane	0.16	0.13	0.03	0.04
Propene	0.01	0.10	0.03	0.03
Butanes	0.03	0.04	0.02	0.02
Butenes	0.00	0.01	0.00	0.00
Pentanes	0.01	0.02	0.02	0.01
Pentenenes	0.05	0.00	0.00	0.00
C ₆ ⁺	0.00	0.09	0.11	0.10
Hydrogen Sulfide	<u>0.33</u>	<u>0.08</u>	<u>0.10</u>	<u>0.12</u>
Total	100.00	100.00	100.00	100.00

Table 3-27 (Cont). PRODUCT GAS COMPOSITIONS FROM OIL UPGRADING TESTS
WITH METHANE AND THE OIL BOILING BELOW 650°F

Test No.	<u>38-0-17</u>	<u>38-0-18</u>	<u>38-0-19</u>	<u>38-0-20</u>
Product Gas, mol %				
Hydrogen	1.46	1.06	1.27	1.20
Carbon Dioxide	0.06	0.06	0.04	0.06
Methane	97.89	98.48	98.07	98.12
Ethane	0.11	0.06	0.12	0.09
Ethene	0.00	0.00	0.00	0.00
Propane	0.07	0.04	0.06	0.12
Propene	0.03	0.03	0.04	0.08
Butanes	0.04	0.02	0.03	0.03
Butenes	0.01	0.01	0.02	0.02
Pentanes	0.02	0.02	0.02	0.02
Pentenenes	0.00	0.00	0.00	0.00
C ₆ ⁺	0.11	0.10	0.11	0.12
Hydrogen Sulfide	<u>0.20</u>	<u>0.12</u>	<u>0.22</u>	<u>0.14</u>
Total	100.00	100.00	100.00	100.00

Figure 3-9. EFFECT OF CATALYST TYPE AND ATMOSPHERE ON BOILING POINT CURVES FOR WHOLE OIL AND OIL BOILING BELOW 650°F

Figure 3-10. EFFECT OF CATALYST TYPE ON BOILING POINT
CURVES FOR WHOLE OIL AND OIL BOILING BELOW 650°F

Figure 3-11. EFFECT OF CATALYST TYPE AND ATMOSPHERE ON BOILING POINT CURVES FOR OIL BOILING BELOW 650°F

Figure 3-12. EFFECT OF CATALYST AND PROMOTER TYPE ON BOILING POINT CURVES FOR OIL BOILING BELOW 650°F

Task 4. Beneficiation Research

The Mineral Resources Institute (MRI) at The University of Alabama was responsible for the overall task on shale beneficiation research. The objective of the task was to test new concepts for improving the oil shale beneficiation system. MRI conducted work in five individual subtasks. Three were in the area of grinding research: 4.1.3. Stirred Ball Mill Grinding, 4.1.5. Alternative Technology Evaluation, and 4.1.6. Ultrafine Size Separation. The fourth - Subtask 4.2.1.1 (Column Flotation Modeling) - was a part of the general category of kerogen/mineral matter separations. Subtask 4.7 was on Economic Analysis. A sixth subtask on Circuit Evaluation of Indiana Shales, was eliminated when the program funding was reduced.

The University of Kentucky Center for Applied Energy Research (UK-CAER) was a subcontractor to MRI on the project and conducted Subtask 4.4 (Integrated Grinding and Flotation).

The results of the work conducted in Task 4 are described below.

Subtask 4.1.3. Stirred Ball Mill Grinding

The objective of this subtask was to assess the grindability behavior of three particle types: raw shale feed, concentrate (kerogen-rich fraction), and tailings (mineral-matter-rich fraction).

MRI fabricated a polyurethane-lined attrition grinder dimensionally similar to the LME-4 Netzsch mill. The working volume of the attrition grinder was 1.8 liters. The major difference between the attrition grinder and the mill is that the former is in a vertical configuration whereas the mill is in a horizontal configuration. The reasons for fabricating the small-scale grinder were 1) to avoid mill wear by sand media and 2) to minimize the quantity of material needed for test runs. This unit could not be operated with the existing Denver cell agitation unit because the motor horsepower was too low ($\frac{1}{4}$ HP). Therefore, a drill press with a larger capacity motor ($\frac{1}{4}$ HP) was procured anticipating that this press could be suitably modified and the required rpm could be achieved. With no load, the drill press operate at up to 4000 rpm, but when the drill press shaft was operated in conjunction with the grinder unit under normal operating conditions (e.g. 80 percent sand media filling), the rpm was reduced to 500 rpm. The level of sand media loading that could be used with this motor was limited to 40 percent, which is practically ineffective in stirred ball milling. Therefore, the mechanical and electrical circuitry were modified to overcome the resistance offered by media loading in achieving the rotor speed range of 2500 to 3000 rpm. This included the installation of a 1.5-HP motor. None of these efforts were successful. Therefore, plans to test shale grinding with this unit were abandoned and a batch polyurethane unit was used instead to evaluate the relative grindability of oil shale feed, concentrate, and tailings.

In these batch tests, the feed material finer than 400 mesh was prepared by grinding Alabama shale for 20 minutes at 40 percent solids in a rod mill. Concentrate and tails were prepared by a series of flotation runs in a conventional Denver cell. The overall particle size distribution of concentrate was

finer than tailings and is shown in Figure 4-1. Table 4-1 lists the carbon, hydrogen, and nitrogen contents and Fischer assay of these fractions. These products were sized by microsieves into three fractions (-37+30, -30+20, and -20 micrometer [μm]). Two series of grinding tests were conducted. In the first, the -20 μm particles of each product type were used. In the second, equal amounts of particles from each fraction of each product type (synthetic particle size distribution) were used. The grinding tests were performed with 15 grams of dry material and 23 milliliters of water. One hundred and fifty grams of -12+20 mesh sand media was used in these runs and the grinder was operated at 2300 rpm for 5 minutes. The power draw did not vary from run to run and, therefore, the degree of fineness was used as a direct indicator of relative grindability.

Table 4-1. ANALYSIS OF SAMPLES USED FOR GRINDABILITY COMPARISON

Sample Type	<u>Feed</u>	<u>Concentrate</u>	<u>Tailings</u>
Analysis, wt %			
Carbon	3.19	18.74	2.34
Hydrogen	1.63	2.15	0.59
Nitrogen	0.39	0.48	0.09
Fischer Assay, GPT	9.0	30.0	0.6

The first series of grinding tests was made using 15 grams of -20 μm material of feed (median size 7.1 μm), concentrate (median size 5.1 μm), and tailings (median size 9.1 μm). Even though there was a significant difference between the size distribution of feed and tailings (compare Figures 4-2 and 4-3), the ground feed and ground tailings size distribution did not differ much but did differ from ground concentrate. This was expected from the earlier observation because the concentrate size distribution was finer than that of the tails indicating that the concentrate was easier to grind. But it also raised the possibility that the finer distribution of ground concentrate was possibly due to already finer particles present in the concentrate. To confirm this observation, a sample with a synthetic particle size distribution was made by using 5 grams of material from each fraction of feed, concentrate and tailings. The results of grinding were identical to that of -20- μm material, in other words ground concentrate showed finer distribution confirming the high grindability of concentrate. This is shown in Figure 4-4.

The following conclusions can be made:

1. The kerogen-rich fraction (concentrate) is relatively easier to grind than the mineral matter-rich fraction (tailings). The concentrate has higher grindability.
2. The power consumption was independent of the nature of the feed material.

Figure 4-1. OVERALL SIZE DISTRIBUTION OF RAW SHALE, CONCENTRATE AND TAILINGS

Figure 4-2. PARTICLE SIZE DISTRIBUTION OF -20 MICROMETER MATERIAL PREPARED FROM RAW FEED, CONCENTRATE, AND TAILINGS

Figure 4-3. SIZE DISTRIBUTION OF GROUND PRODUCTS FROM -20 MICROMETER RAW FEED, CONCENTRATE, AND TAILINGS

Figure 4-4. PARTICLE SIZE DISTRIBUTIONS OF GROUND PRODUCTS RESULTING FROM THE IDENTICAL SYNTHETIC PARTICLE SIZE DISTRIBUTION COMPRISED OF RAW FEED, CONCENTRATE AND TAILINGS

3. Sand media can be used effectively in regrinding mode in the stirred ball mill.

Subtask 4.1.5. Alternative Technology Evaluation

Background and Objectives

Comminution, or grinding, is the largest single cost in the beneficiation process for oil shale. It is of major interest, therefore, to examine new or emerging technologies that may have the potential to reduce capital or operating costs. Two technologies were selected for evaluation in this program - roller mills and roller presses. Two additional technologies (semi-autogenous grinding and vibratory milling) had been selected for study in the original program, but were eliminated in the reduced program.

The objective of the evaluation was to determine if roller mills or roller presses should be included in future test programs.

Roller Mills

The Lafarge Corporation operates a cement plant at Demopolis, Alabama. The plant produces cement from a local chalk formation. The so-called chalk is actually a weakly consolidated, siliceous limestone that approximates, in composition, a natural cement rock. Only a minor amount of iron ore and clay, about 3 percent, are added to the chalk to adjust the composition to that desired for cement making.

The raw natural mix is ground to 90 percent passing 200 mesh (74 μ m) in a single roller mill. The roller mill consists of three steel faced rollers rotating in an annular track about a central cone. The roller mill is enclosed and is constantly swept by heated air. The air acts both to dry the feed and to convey the product through a series of air classifiers (cyclones).

The apparent energy consumption, attributable to comminution, in this process is quite low. The roller mill consumes some 500 kW in grinding an average of 220 tons of raw material per hour. The fans, however, that provide the air sweep through the mill and power the air classifiers consume 2500 kW. In addition, a substantial amount of energy is consumed in heating the air to dry the raw material. Drying is critical to the process in that it weakens the rock structure and prevents agglomeration due to compaction during crushing.

When the power to the fan and the thermal energy are added to the power consumption in the roller mill, it appears that the total energy consumption in the system is on the order of 15 to 20 kWh/ton. When one considers that the raw material at the Demopolis plant is substantially softer than a typical oil shale, there is no apparent opportunity to reduce the cost of grinding oil shale by the application of roller mill technology.

This conclusion is supported by the action of the Lafarge Corporation plant at Alpena, Michigan. That plant has converted from roller mills to

roller presses in their raw-grind section, which processes a more competent limestone.

No further consideration of roller mills in the oil shale beneficiation system is recommended.

Roller Presses

Roller presses are a relatively recent adaptation of the long established roll crusher. The roll crusher consists of two counter-rotating horizontal cylinders (rolls) that nip and break rock fragments between them. The size of a roll crusher product is fixed by adjusting the gap between the rolls. Fragments smaller than the gap pass through untouched. An important attribute of roll crushers is the tendency to produce a minimum amount of fines.

Roller presses, in contrast to roll crushers, are designed and operated to maximize the production of fines. Roller presses differ from roll crushers in that there is no fixed gap between the rolls, instead hydraulic cylinders maintain a high constant pressure on the rock between the roll faces. Typically, the roller presses are "choke fed" to maintain multiple layers of rock fragments between the rolls. The high applied pressure causes a high degree of rock-upon-rock breakage and a resulting high rate of production of fines. The high pressures between the rolls also force the broken rock to re-consolidate as rather friable flakes.

The Lafarge Corporation cement plant at Alpena, Michigan uses roller presses in its raw-grind circuit. The raw material mix, consisting of 82 percent limestone and 18 percent Antrim shale enters the plant at a nominal -3-inch size. It is blended and fed to the roller presses. Each roller press is driven by two 1200-HP motors. The roller press discharges into a 500-HP hammer mill where it is deagglomerated and dried. The deagglomerated product of the hammer mills is classified and the finished product is sent directly to the homogenizing silos. Classifier oversize is further ground in a 12-foot x 24-foot ball mill driven by a 2250-HP motor. A portion of the oversize is normally returned to the roller presses to provide bridging material that enhances the rock-upon-rock crushing action.

The raw grinding circuit used in the Alpena plant consists of two parallel circuits, each having a roller press, hammer mill, and ball mill operating series. Operating in the normal mode, the capacity of each circuit is about 200 ton/h with a power consumption including thermal energy, in the range of 15 to 19 kWh/ton.

About 10 percent of the power is consumed in the hammer mills with the balance about equally divided between the roller press and the ball mill (i.e., 6.75 to 8.7 kWh/ton each). It is interesting to note that this is a slightly higher power consumption in the roller press than in a tertiary crusher that it might replace. The ball mill power consumption, however, is substantially lower than MRI estimated for the primary ball mill in a shale grinding circuit. This is probably due to the high concentration of fines produces by the roller press.

The roller press system exhibits a high wear rate, and consequently, there are high maintenance costs associated with the hammer mills. In the cement industry this is an acceptable consequence of their need to grind dry.

In summary it appears that roller presses, like roller mills, are a specialty application in the cement industry and show no inherent advantages in the processing of oil shales. No further consideration of roller presses is recommended.

Subtask 4.1.6. Ultrafine Size Separations

The overall task under the present contract calls for a concentrated effort to develop a minimum cost system for the delivery of shale concentrates of suitable form to the PFH system. Past studies have indicted the capital and operating costs of the stirred ball milling circuit, required to reduce the oil shale to a size consist compatible with the production of high grade oil shale flotation concentrates, represented the highest unit costs of the beneficiation system. Reduction of the number of stirred ball mill units required, or perhaps the elimination of the total stirred ball milling circuit, would therefore represent the most effective method of reducing costs. On this basis, the results of past studies of the primary grinding circuit, the ground pulp sizing circuit, and column cell flotation results were reviewed for potential methods of cost reduction.

Review of Past Studies

In the early phases of the oil shale beneficiation program, all grinding and subsequent flotation studies were based on grinding all of the shale to a d_{90} of 10 μm for effective recovery of the kerogen values by flotation.

As the program progressed, a number of other options were investigated as methods of reducing the grinding costs. A summary of these options are tabulated below:

1. Grind the entire sample to a d_{90} of about 20 μm , followed by flotation, regrinding of the concentrate and re-flotation to produce a high grade (40 to 45 gal/ton) concentrate. This option probably would have increased the capital costs of the stirred ball milling circuit because of the additional mills required to regrind the concentrate.
2. Removal of the flotation ready sized material, i.e., finer than about 10 μm from the primary grinding circuit at the earliest possible opportunity. Studies during 1991-92 showed that a primary grinding circuit, close circuited with a 100 mesh screen, would give a screen undersize product containing about 30 percent by weight of -12 μm material. Efforts to isolate the -12 μm size fraction by three stages of hydrocycloning failed to yield an effective recovery of this flotation ready sized material.
3. Studies during 1991-92 also indicated that certain hydrocycloning parameters might yield a relatively coarse flotation feed, i.e., in the 20 to 24 μm size range, that could be treated by column cell flotation

to yield high recovery of the kerogen. These studies also indicated that a rougher flotation concentrate could be recleaned to yield an improved concentrate grade.

On the basis of previous results, the program for the current work was designed to 1) determine the most effective method of removing flotation ready sized material from a primary grinding circuit, close-circuited at 150 mesh, and 2) determine the potential benefits of recleaning a column cell rougher concentrate under variable flotation conditions.

Primary Grinding Circuit

About 1000 pounds of Alabama oil shale was jaw and roll crushed to pass 10 mesh and thoroughly mixed for feed to the grinding circuit. The -10 mesh material was fed by a constant weight feeder at 50 percent solids to a Denver 18-inch x 30-inch ball mill, in closed circuit with a 150-mesh Sweco screen.

Size analyses of the ball mill feed and ball mill discharge at two feed and circulating load rates are given in Table 4-2. Normal milling practices utilize circulating loads of 200 to 500 percent for two primary purposes (1) increased production, and (2) prevention of overgrinding. However, in the case of oil shale, which requires grinding to extremely fine sizes for both liberation and flotation efficiency, the use of high circulating loads may not be the most effective grinding method. Table 4-3 shows the effect on production of -24 μm material in the ball mill discharge. Table 4-4 shows that the increased circulating load also affects the size distribution of the -150 mesh screen undersize product.

Total -150 mesh screen undersize production during the course of the grinding studies was 770 pounds averaging 34.3 percent +24 μm and 65.7 -24 μm material. This screen undersize product represented feed for subsequent hydrocyclone studies.

Hydrocyclone Studies

Previous hydrocyclone studies had been conducted using a 2-inch Mozley cyclone with a fixed vortex finder of 11 mm and an apex spigot of 6.4 mm. Targeted d_{90} in these earlier studies, using -100 mesh feed slurry, at three cyclone feed solids and 3 cyclone feed pressures are presented in Figure 4-5. The data in Figure 4-5 indicate that a targeted d_{90} of 20 to 24 μm would require low feed pressures and high feed solids.

A factorially designed series of hydrocyclone tests was conducted to determine the effects of variable vortex finder and apex spigot size, and cyclone feed pressure at a constant feed solids of about 30 percent. Table 4-5 summarizes the results of this test series. Figures 4-6 through 4-9 present the results of some of the various parameters evaluated.

During the course of the hydrocyclone studies, it was determined that feed pulp temperature appeared to have a rather significant effect upon the separation results obtained. To determine the effect of feed pulp temperature on the cyclone products over a wide temperature range at constant feed solids,

Table 4-2. EFFECT OF INCREASED FEED RATE AND CIRCULATING LOAD ON MILL DISCHARGE SIZE

Size μm	Ball Mill Feed (minus 10 mesh)		Ball Mill Discharge (1.84 lbs/min, 16% C.L. *)		Ball Mill Discharge (2.97 lbs/min, 77% C.L. *)	
	Wt. %	Cum. Wt. %	Wt. %	Cum. Wt. %	Wt. %	Cum. Wt. %
plus 1,180	14.1	xxx	----	----	----	----
1,180/850	23.9	38.0	----	----	0.2	----
850/600	17.5	55.5	0.2	----	1.1	1.3
600/425	13.5	69.0	0.9	1.1	3.0	4.3
425/300	8.0	77.0	2.7	3.8	3.4	7.7
300/212	6.6	83.6	3.3	7.1	4.8	12.5
212/150	3.2	86.8	4.6	11.7	6.9	19.4
150/106	3.4	90.2	11.6	23.3	12.3	31.7
106/64	9.8	----	14.0	37.3	22.4	54.1
64/24	----	----	18.8	56.1	14.6	68.7
24/12	----	----	14.9	71.0	10.6	79.3
minus 12	----	----	29.0	----	20.7	----
Total	100.0	100.0	100.0	100.0	100.0	100.0

* C.L. = circulating load

Table 4-3. EFFECT OF INCREASED CIRCULATING LOAD ON SIZE CONSIST OF BALL MILL DISCHARGE

Feed Rate lbs./min.	Circulating load, %	Mill Discharge Size, μm		Minus 24 Micrometers	
		d90	d50	%	lbs./min.
1.84	16	172.9	37.0	43.9	.81
2.97	77	257.8	71.7	31.3	.93

Table 4-4. EFFECT OF INCREASED CIRCULATING LOAD ON SIZE CONSIST OF SCREEN UNDERSIZE

Feed Rate lbs./min.	Circulating load, %	Screen Undersize Size, μm				Micrometer	
		+64	64/24	24.12	-12	d90	d50
1.84	16	8.8	24.3	21.3	45.6	58.9	13.7
2.97	77	10.0	24.8	21.0	44.2	63.6	14.2

Figure 4-5. EFFECT OF CYCLONE FEED PRESSURE AND FEED SOLIDS CONTENT WITH -100 Mesh FEED

Table 4-5. SUMMARY OF FACTORIAL HYDROCYCLONING TESTS

Vortex finder, mm Apex spigot, mm		8			11			14		
		4.5	6.4	9.4	4.5	6.4	9.4	4.5	6.4	9.4
Cyclone feed rate liters/min	psig 10	13.1	14.2	14.0	19.7	19.2	19.6	22.5	23.4	20.4
	psig 15	17.8	15.9	19.0	22.9	24.6	24.7	32.2	30.8	35.1
	psig 20	18.9	19.4	20.6	29.9	27.7	28.4	35.7	38.9	39.3
Cyclone overflow solids %	psig 10	21.0	17.3	15.7	22.3	19.0	16.6	25.2	22.7	21.2
	psig 15	19.2	15.6	13.4	21.2	17.8	15.1	25.9	22.0	18.4
	psig 20	18.6	14.7	12.4	20.2	17.0	14.1	26.4	21.7	18.0
Cyclone overflow solids, dist. %	psig 10	49.1	29.8	15.5	59.8	43.8	28.9	70.5	59.7	46.6
	psig 15	46.9	27.9	14.0	55.8	40.8	27.2	65.1	58.3	42.4
	psig 20	43.3	26.5	12.9	52.0	39.8	25.1	66.1	55.4	41.1
Cyclone overflow slurry, dist. %	psig 10	72.9	54.5	31.5	82.0	72.2	55.1	87.6	81.9	68.6
	psig 15	75.0	57.1	33.9	81.4	73.0	57.9	87.8	82.9	74.0
	psig 20	73.9	58.1	34.0	80.2	74.1	58.3	85.7	82.0	73.9
Cyclone overflow d ₉₀	psig 10	31.8	23.2	22.0	36.3	26.7	22.3	38.8	31.6	27.8
	psig 15	27.8	21.2	18.6	32.0	23.4	19.8	39.3	31.9	22.9
	psig 20	25.4	19.8	16.4	29.9	22.9	18.6	41.3	31.2	21.8
Cyclone overflow minus 24 μ m dist. %	psig 10	61.4	40.6	21.4	71.9	57.7	40.0	83.1	74.9	61.1
	psig 15	61.2	39.1	19.9	69.3	55.5	38.7	76.4	73.0	58.1
	psig 20	57.7	37.7	18.6	66.5	54.6	36.1	70.1	69.9	57.2

Figure 4-6. RESULTS ACHIEVED WITH MOZLEY 2-INCH HYDROCYCLONE
WITH 8-mm VORTEX FINDER

Figure 4-7. RESULTS ACHIEVED WITH MOZLEY 2-INCH HYDROCYCLONE
WITH 11-mm VORTEX FINDER

Figure 4-8. RESULTS ACHIEVED WITH MOZLEY 2-INCH HYDROCYCLONE WITH 14-mm VORTEX FINDER

Figure 4-9. EFFECT OF FEED RATE ON THE RESULTS ACHIEVED WITH THE MOZLEY 2-INCH HYDROCYCLONE

feed pressure, vortex size and apex size, a sample of the -150 mesh slurry was recirculated in the cyclone system for about 2 hours. During this period the cyclone overflow and underflow products were sampled at 15-minute intervals and feed pulp temperature measurements were taken. Initially the -150 mesh feed was cooled down to 7°C using ice. Results of these studies are presented in Table 4-6.

These data show that feed pulp temperature has a very significant effect on the size of the cyclone overflow; however, there is no apparent effect on the solids distribution to the cyclone products. In all probability the increase in pulp temperature yields a decrease in pulp viscosity.

Based on the results of the factorially designed hydrocycloning studies, the bulk screen undersize product from the primary grinding circuit was cycloned to yield the results shown in Table 4-7.

The primary hydrocyclone underflow product shown in Table 4-7 had a solids content of 56 percent. This product was diluted to 27 percent solids and retreated in the cyclone under the same conditions as shown in Table 4-7 to yield the results shown in Table 4-8.

Table 4-9 presents the results of overall hydrocycloning based on the response of the -24 μm fraction in the -150 mesh screen underflow from the primary grind. Table 4-10 show the results of the cyclone products based on the chemistry of the separation. Table 4-9 shows that 61.4 percent by weight of the -150 mesh screen undersize from the primary grind was isolated by hydrocycloning to yield a product having a d_{90} of 22.9 μm , which met the target size for coarse flotation studies. The secondary cyclone underflow product (38.6 percent of the solids) would require further grinding, either in a stirred ball mill circuit, or, it could be returned to the primary grinding circuit. The secondary cyclone underflow product shown in Table 4-10 was subsequently batch ground in a laboratory rod mill to a d_{90} of 23 μm and combined with the cyclone overflow product to represent column cell flotation feed.

Column Cell Flotation

A review of past column cell flotation studies of Alabama oil shale ground to a d_{90} of 23 μm is presented in Figure 4-10. In this case flotation variables such as air flow rate, tailings discharge height, etc., were reduced to a simple mass balance of the response of flotation slurry to the conditions of trial. The mass balance in this case represents the percentage of total slurry reporting as flotation concentrate which, as a rule, is a function of the air flow rate.

Past flotation studies of Alabama oil shale have shown that oil recovery, based on Fischer Assay, generally is 4 to 5 percent higher than carbon recovery. Hence, the data shown in Figure 4-10 indicate that oil recoveries of greater than 95 percent could be expected when the air flow rate was adjusted to yield concentrate slurries containing 30 to 40 percent of the feed slurry weight.

Table 4-6. EFFECT OF PULP TEMPERATURE ON CYCLONE OVERFLOW
WHEN TREATING -150 Mesh ALABAMA OIL SHALE

Feed Pulp temp. °C	Solids Dist. % Cyclone Overflow	<u>µm size, wt. %</u>		<u>µm size, dist. %</u>		d90	d50
		+24	-24	+24	-24		
7	56.9	19.6	80.4	33.3	68.8	36.6	9.9
17	59.5	16.6	83.4	29.5	74.6	31.7	9.1
23	58.0	14.2	85.8	24.6	74.8	29.5	8.4
30	59.0	12.7	87.3	23.4	77.5	27.8	8.0
35	58.6	11.5	88.5	20.1	78.0	26.2	7.6
42	58.4	10.2	89.8	17.8	78.9	24.3	7.4

Operating Conditions: Mozley cyclone 2"
Vortex Finder: 14.3 mm
Apex Spigot: 6.4 mm
Feed Solids, % 30
Feed Pressure, psig: 15

Table 4-7. RESULTS OF PRIMARY HYDROCYCLONING OF BULK SAMPLE
FOR PRODUCTION OF COLUMN CELL FLOTATION FEED

Cyclone Product	Solids Dist. %	<u>µm size, wt. %</u>		<u>µm size, dist. %</u>		d90
		+24	-24	+24	-24	
O'flow	49.0	6.5	93.5	9.3	69.7	21.5
U'flow	51.0	61.0	39.0	90.7	30.3	----
Feed	100.0	34.3	65.7	100.0	100.0	----

Operating Conditions: Mozley Cyclone, 2"
Vortex Finder: 14.3 mm
Apex Spigot: 9.4 mm
Feed Solids, %: 27
Feed Pressure, psig: 25

Table 4-8. RESULTS OF RETREATMENT OF PRIMARY CYCLONE UNDERFLOW PRODUCT

Cyclone Product	Solids Dist. %	TOB* Dist. %	<u>µm size, wt. %</u>		<u>µm size, dist. %</u>		d90
			+24	-24	+24	-24	
O'flow	24.3	12.4	13.6	86.4	5.4	53.8	28.6
U'flow	75.7	38.6	76.2	23.8	94.6	46.2	----
Feed	100.0	51.0	61.0	39.0	100.0	100.0	----

* Total Ore Basis

Operating Conditions: same as in primary separation

Table 4-9. COMPOSITE RESULTS OF HYDROCYCLONING BULK SAMPLE

Cyclone Product	Solids Dist. %	<u>µm size, wt. %</u>		<u>µm size, dist. %</u>		d90
		+24	-24	+24	-24	
Primary O'flow	49.0	6.5	93.5	9.3	69.7	21.5
Secondary O'flow	12.4	13.6	86.4	4.9	16.3	28.6
Composite O'flow	61.4	7.9	92.1	14.2	86.0	22.9
Secondary U'flow	38.6	76.2	23.8	85.8	14.0	----
Composite Feed	100.0	34.3	65.7	100.0	100.0	----

Table 4-10. RESULTS OF CONTINUOUS HYDROCYCLONING STUDIES BASED ON PRODUCT CHEMISTRY

Cyclone Product	Wt. %	F.A. oil, g/t	<u>Analysis, %</u>				<u>Distribution, %</u>				
			C	H	N	S	Oil	C	H	N	S
Primary & Secondary O'flow	61.4	11.2	16.32	2.02	0.51	6.94	63.8	65.7	66.7	61.9	51.6
Secondary U'flow	38.6	10.1	13.56	1.60	.50	10.33	36.2	34.3	33.3	38.1	48.4
Hydrocyclone Feed	100.0	10.8	15.25	1.86	.51	8.25	100.0	100.0	100.0	100.0	100.0
Head Sample	----	11.5	15.25	1.79	.44	8.25	----	----	----	----	----

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Figure 4-10. MASS BALANCE OF COLUMN CELL FLOTATION RESULTS ON ALABAMA OIL SHALE GROUND TO A d_{90} OF 23 μm

Rougher Column Cell Flotation

To verify the mass balance data on the column cell feed produced in the hydrocycloning studies, three tests were made prior to initiating the bulk separation. The column cell used in these tests was identical to that described previously for flotation of Alabama oil shale. The results of these studies (Table 4-11) show that good carbon recoveries could be expected from the bulk sample in a mass balance range of 23 to 37 percent. On the basis that Fischer Assay oil recovery would be 4 to 5 percent higher than carbon recovery, then an overall oil recovery from the bulk sample should be about 96 percent.

To expedite flotation of the bulk sample, two identical column cells, operated in parallel, were used. Flotation conditions were the same as those in the preliminary studies, i.e., 3.5 percent feed solids and 35 ppm Dowfroth 250. Mass balance of the concentrate slurry from each column cell was maintained at about 32 percent. Results of the production run used to produce sufficient material for cleaner froth flotation studies are shown in Table 4-12. Size analyses of the column cell feed, concentrate and tailings gave the results shown in Table 4-13. These data indicate that, under the test conditions, the coarse carbon and/or kerogen responds to the flotation conditions much better than the very fine carbon.

Cleaner Column Cell Flotation

In any column flotation system, the froth tends to have a higher solids content than that of the feed. This is demonstrated in Table 4-11, which also shows that low froth volumes (slurry balances) tend to produce froths with higher solids contents. To determine whether cleaner flotation should be conducted at the increased solids content, of the rougher froth, or whether it should be diluted to a normal solids level, tests were conducted with slurries containing 7.6 and 3.7 percent solids. The results of these studies, presented in Figure 4-11, show that higher solids are already preferable for cleaner flotations.

A review of the mass balance versus concentrate grade and recovery is shown in Table 4-14. Because these data indicated that the lowest mass balance at either feed solids level gave the highest grade concentrate, the remainder of the rougher concentrate was retreated in the column cell using an average concentrate mass balance of 9.2 percent. Results of the recleaning studies are given in Table 4-15.

Results of the bulk recleaning of the rougher column cell concentrate shown in Table 4-15 indicate that a concentrate grade of about 31 gal/ton of oil will be the maximum grade obtainable by floating shale ground to a d_{90} of about 23 μm . Results of the overall roughing and cleaning operations for the continuous column cell tests are given in Table 4-16. Size analyses of the rougher tails, cleaner concentrate and middling products are shown in Table 4-17.

The size analyses presented in Table 4-17 show that the clay wastes rejected by rougher flotation is considerably finer than the kerogen. The

Table 4-11. COLUMN CELL FLOTATION STUDIES OF BULK FEED PRODUCT

Column Cell Product	Air SLPM	Solids %	Mass bal. %	Wt. %	Analysis, %				Distribution, %			
					C	H	N	S	C	H	N	S
Concentrate	5.3	9.1	23.0	50.0	28.63	2.99	0.71	10.32	91.3	83.3	89.9	66.5
Concentrate	5.6	8.3	25.0	51.1	28.45	3.00	.86	9.91	91.3	83.7	87.3	65.9
Concentrate	5.8	6.0	36.8	55.3	26.54	2.81	.74	9.57	93.0	85.7	93.0	70.3

Flotation conditions: Feed solids, % = 3.5
Dowfroth 250, ppm = 35

Table 4-12. PRODUCTION OF BULK CONCENTRATE FOR CLEANER FLOTATION STUDIES

Flotation Product	Wt. %	F.A. oil, g/t	Analysis, %				Oil	Distribution, %			
			C	H	N	S		C	H	N	S
Concentrate	55.0	21.3	25.55	2.75	0.83	10.54	96.7	92.2	82.1	78.4	73.0
Tailings	45.0	0.9	2.66	.73	.28	4.76	3.3	7.8	17.9	21.6	27.0
Feed	100.0	12.1	15.25	1.84	.58	7.94	100.0	100.0	100.0	100.0	100.0

Table 4-13. SIZE ANALYSIS OF BULK COLUMN CELL FLOTATION PRODUCTS

Flotation Product	Wt. %	μ m size, wt. %			μ m size, dist. %			d90	d50
		+24	24/12	-12	+24	24/12	-12		
Concentrate	55.0	12.1	29.7	58.2	88.1	67.6	46.8	26.4	9.8
Tailings	45.0	2.0	17.3	80.7	11.9	32.4	53.2	15.8	5.8
Feed	100.0	7.6	24.1	68.3	100.0	100.0	100.0	23.0	7.8
Heads (Analysis)	-----	8.4	24.9	66.7	-----	-----	-----	-----	-----

Figure 4-11. GRADE-RECOVERY CURVES FOR CLEANER CONCENTRATE AT 7.6 AND 3.7 PERCENT SOLIDS WITH 35 ppm DOWFROTH 250

Table 4-14. COMPARISON OF CONCENTRATE MASS BALANCE AND CLEANER GRADE AND RECOVERY IN CLEANER COLUMN CELL FLOTATION STUDIES

Flotation Product	Feed Solids, %	Mass Balance, %	Solids Wt., %	F.A. Oil	
				G/T	Dist. %
Cl. Conc.	7.6	26.5	21.0	31.0	54.3
Cl. Conc.	7.6	30.6	28.2	29.6	68.6
Cl. Conc.	7.6	35.6	32.6	28.5	74.9
Cl. Conc.	3.7	19.4	30.4	28.8	71.3
Cl. Conc.	3.7	25.8	36.6	27.0	81.0
Cl. Conc.	3.7	32.1	40.9	25.7	85.7

Table 4-15. RESULTS OF RE-CLEANING ROUGHER COLUMN CELL CONCENTRATE

Flotation Product	Wt. %	F.A. oil, g/t	Analysis, %			Distribution, %			
			C	H	N	Oil	C	H	N
Cleaner Concentrate	42.0	31.0	36.63	3.91	1.13	63.4	57.0	55.8	55.0
Middlings	58.0	14.7	20.04	2.24	.67	36.6	43.0	44.2	45.0
Feed	100.0	21.5	27.01	2.94	.86	100.0	100.0	100.0	100.0

Table 4-16. OVERALL RESULTS OF ROUGHING AND RE-CLEANING
ALABAMA OIL SHALE AT d_{90} OF 23 μm

Column Cell Product	Wt. %	F.A. Oil, g/t	Analysis, %			Distribution, %			
			C	H	N	Oil	C	H	N
Cleaner Concentrate	23.1	31.0	36.63	3.90	1.13	58.4	52.7	46.0	43.2
Middlings	31.9	14.7	20.04	2.28	.68	38.3	39.8	37.2	35.9
Rougher Concentrate	55.0	21.5	27.01	2.96	.87	96.7	92.5	83.2	79.1
Rougher Tailings	45.0	0.9	2.66	.73	.28	3.3	7.5	16.8	20.9
Column Cell Feed	100.0	12.3	16.05	1.96	.60	100.0	100.0	100.0	100.0

Table 4-17. SIZE ANALYSES OF BULK ROUGHER AND
CLEANER FLOTATION PRODUCTS

Flotation Product	Wt. %	μm size, wt. %			μm size, distribution %			d_{90}	d_{50}
		+24	24/12	-12	+24	24/12	-12		
Cleaner Concentrate	23.1	7.1	25.1	67.8	23.4	24.4	22.7	22.3	7.5
Middlings	31.9	15.0	32.0	53.0	65.3	42.9	24.6	28.9	11.3
Rougher Concentrate	55.0	11.7	29.1	59.2	87.7	67.3	47.3	26.1	9.7
Rougher Tails	45.0	2.0	17.3	80.7	12.3	32.7	52.7	15.8	5.8
Flotation Feed	100.0	7.3	23.8	68.9	100.0	100.0	100.0	21.5	7.9

middling fraction is shown to have a much coarser size consist than the cleaner concentrate indicating the probability that this material is present as a true unliberated middling fraction.

Scavenger Flotation Studies of Column Cell Middlings

Scavenger flotation studies of the column cell middling product having a d_{90} of 28.9 μm failed to show any appreciable upgrading under a number of various test conditions; again, tending to confirm that this product represented true unliberated middlings. Based on these studies, this product, representing about 32 percent of the original feed to the column cells, would require regrinding to a finer size prior to further treatment.

Subtask 4.2.1.1. Column Flotation Modeling

Modeling Studies

This subtask was divided into two parts. The objective of the first part was to quantitatively describe column flotation of oil shale. The objective of the second part was to develop an on-line procedure for measuring the oil content of a shale sample on the basis of back scattered intensity for quality control purposes.

A phenomenological model, based on plug flow with axial dispersion has been successful for predicting mineral recovery in flotation columns. In this project, the dispersed plug flow model was chosen and modified to suit the oil shale beneficiation system. This model essentially combines a steady-state residence time distribution (RTD) with first-order flotation kinetics, that is, the recovery is a function of K_i , τ_p , and N_d , as follows:

$$R_i = f(K_i, \tau_p, N_d) \quad (1)$$

where R_i is the recovery of species i ; K_i is the first-order flotation coefficient for species i (min^{-1}), τ_p is the mean particle residence time (min), and N_d is the dispersion number, which is a measure of the axial dispersion in the collection zone of the flotation column.

In general, the mass transport phenomena in a flotation column is described by the following equations for axial dispersion and convection:

$$\frac{\partial c}{\partial \theta} = N_d \frac{\partial^2 c}{\partial \lambda^2} - \frac{\partial c}{\partial \lambda} \quad (2)$$

where c is the dimensionless concentration of solid particles, N_d is the dispersion number, θ is dimensionless time, and λ is dimensionless distance.

According to Equation 2, the change in concentration of a specific mineral species along the column with time is a function of three factors: transport due to turbulent eddies and diffusion (i.e., dispersion), transport due to bulk or plug flow (i.e., convection), and disappearance due to collection by air bubbles. This is a one-dimensional model; hence, radial dispersion and

nonuniform velocity profiles are not considered. The collection of solid particles by the air phase can be described by the first-order flotation kinetic equation, as follows:

$$\frac{\partial c}{\partial \theta} = -Kc \quad (3)$$

Where K is the flotation rate constant, given by

$$K = \frac{1.5 V_g E_K}{d_b} \quad (4)$$

where V_g is the superficial gas velocity, d_b is the average bubble diameter, and E_K is the collection efficiency, which is related to the probabilities of collision, attachment and detachment of air bubbles and solid particles.

As described by Equation 1, the mineral recovery in a flotation column is related to flotation kinetic rate constant and the steady-state RTD, then the study of this model can be divided into two portions. The first part is the measurement and modeling of the RTD, which can be described with two parameters: the mean residence time, τ , and the dispersion number, N_d . The second part is the determination of the first-order flotation kinetic rate constant, K, of the oil shale.

To obtain the RTD, Equation 2 is solved in the Laplace domain. The impulse response of Equation 2 is

$$C = \sqrt{\frac{\tau}{4\pi N_d t^3}} \exp\left[\frac{1}{4N_d}\left(2 - \frac{t}{\tau} - \frac{\tau}{t}\right)\right] \quad (5)$$

This is the theoretical RTD model, derived from the principle model equation. Experimental measurements of RTD with tracers in a deep froth flotation column were conducted that will be described later. The two parameters, the mean residence time and the vessel dispersion number, were estimated using Equation 5 by fitting experimental data to the equation.

Based on the published literature, it is anticipated that the RTD of solid particles is similar to that of the liquid if the particles are very small. Also, because the RTD of fine shale particles is very difficult to measure experimentally (generally radioactive tracers are used), hence, the RTD measurements focused on liquid tracer mainly, though some experiments using solid tracer were also conducted.

A series of experiments to measure the liquid mixing characteristics in a deep froth flotation column were conducted with potassium chloride, KCl, as tracer. In the tests, the RTD of the liquid was estimated by measuring the KCl concentration at the tailings outlet of the column as a function of time. Figures 4-12 and 4-13 show the experimental RTD (measured in terms of KCl concentration) and conductivity. The experimental data was fitted to the theoretical model (Equation 5), to estimate τ and N_d by a direct fitting procedure with a non-linear least square optimization subroutine. The mean

Figure 4-12. EXPERIMENTAL RESIDENCE TIME DISTRIBUTION WITH THE TRACER KCl

Figure 4-13. EXPERIMENTAL RTD MEASURED WITH KCl CONCENTRATION AND CONDUCTIVITY

residence time and vessel dispersion number were estimated as 12.79 minutes and 0.14, respectively. Because the value of the mixing parameter is small and close to zero, the mixing is plug-flow. This result is in agreement with other reported studies. The experimental and fitted RTD data is plotted in Figure 4-14 and are in good agreement.

Estimated = 12.79 minutes
Experimental = 12.76 minutes

In addition, experiments to measure the liquid RTD under different conditions were also used to determine the model's suitability by estimating the RTD of the deep froth flotation column. Figure 4-15 shows the normalized results of liquid RTD measurements conducted at different conditions. When the feed flow rates are 250 and 105 mL/min, the liquid mixing behavior follows the same rules under different conditions and both experimental RTD curves overlapped. Also, the data can be successfully fitted with the model (Figure 4-16), indicating that the axial dispersion model is suitable for describing deep froth flotation column.

The RTD measurements with solid particles were used to determine the dispersion number. Because the particles are very fine, it may well be that the two parameters are the same. Since it is more difficult to measure the RTD of solid particles, this will result in a convenient method to determine the solid dispersion number, which is used in the model for the ultra-fine particles of the deep froth column flotation. In the test, the column was filled with tap water mixed with frother before the tracer was injected. When the conditions were at steady state, 15 grams of silica sand tracer were injected into the column. Samples from the exit of the column were taken at specific time intervals. The samples collected were filtered, dried, and weighed. The concentration of sand was calculated and data was plotted as illustrated in Figure 4-17. The experimental conditions for the measurement of the RTD of solid particles are listed in Table 4-18.

Table 4-18. EXPERIMENTAL CONDITIONS FOR SOLID RTD MEASUREMENT

Air Flow Rate, SLPM	4.5	Feed Flow Rate, mL/min	250
Tailings Rate, mL/min	250	Solids Particle Size, μm	3.70
Solids Weight, g	15.08	Frother Concentration, ppm	60
(Dowfroth 250)			

The first-order flotation kinetic rate constant (K) of the oil shale was also estimated. The estimation procedure is complicated because it is related to flotation hydrodynamics. Nevertheless, it can be obtained with several mathematical equations as well as the experimental measurement of the induction time of the specific mineral species being treated. The induction time of a samples correlates with its hydrophobicity, which indicates the relative floatability of the specific mineral. Researchers at UK determined the induction time of the shale concentrate and tailings to be 10.07 and 23.07 milliseconds, respectively. Thus, there is a significant difference between the hydrophobicities of oil shale concentrate and tailings.

Figure 4-14. EXPERIMENTAL AND MODEL RTD ($N_d = 0.14$, $\tau = 12.79$ min)

Figure 4-15. EXPERIMENTAL RTDs WITH DIFFERENT FEED FLOW RATES

Figure 4-16. EXPERIMENTAL AND MODEL RTDs

Figure 4-17. EXPERIMENTAL RTD OF SOLID PARTICLES

Once the parameters were determined, the computer simulation based on this model was run for various experimental conditions. The computer program was based on the analytical solution of Equations 2 and 3 as follows:

$$R = 1 - \frac{4a \exp\left(-\frac{1}{2N_d}\right)}{(1+a)^2 \exp\left(-\frac{a}{2N_d}\right) - (1-a)^2 \exp\left(-\frac{-a}{2N_d}\right)}$$

where

$$a = \sqrt{1 + 4K \cdot \tau N_d}$$

In the simulation, shale was considered to be a two-component (valuable and gangue) system for simplicity. As illustrated in Figure 4-18, the simulation recovery of the non-ash component present in oil shale changes with air flow rate and solid particle size. As the figure shows, it is difficult to recover particles less than 5 μm in size. The optimum range of air velocity should be from 1.2 to 1.8 cm/s for deep froth column flotation. Figure 4-19 indicates the change in recovery of non-ash component in oil shale with particle sizes. It is clear that the optimum particle size range is from 35 to 55 μm in deep froth column flotation, which is to be tested. The conditions and parameters used in the simulation are listed in Table 4-19.

Table 4-19. EXPERIMENTAL CONDITIONS AND PARAMETERS USED IN SIMULATION

Slurry Feed Rate, mL/min	250
Solids Content, wt %	5
Solids Density, g/cm ³	2.4
Solid Flow Rate, g/min	12.5
Column Length, cm	160
Diameter, cm	7.63
Induction Time for Non-Ash Component, ms	0.214
Slip Velocity of Liquid and Solid, cm/s	0.1
Bias Rate, cm/s	0.1

The following conclusions can be drawn:

1. The RTD measurement and the model fitting results show that the axial dispersed plug flow model is suitable for deep froth column flotation. This is the typical procedure to determine if the model suits a flotation column according to the literature in this area.
2. The two RTD parameters, the mean residence time, τ , and the vessel dispersion number, N_d , for deep froth flotation column, were 12.79 minutes and 0.14, respectively. The value of N_d indicates that the flow behavior was plug flow.

Figure 4-18. MODEL RECOVERY OF NON-ASH IN OIL SHALE
VERSUS AIR VELOCITY

Figure 4-19. MODEL RECOVERY OF NON-ASH IN OIL SHALE
VERSUS PARTICLE SIZE CHANGE

3. The first-order flotation rate constant of oil shale with deep froth column flotation can be determined with several additional mathematical equations (not included totally in this report) and the experimental measurements of the induction time of oil shale samples. The induction time of concentrate and tailings of oil shale were 10.07 and 23.07 ms, respectively. The results indicated a significant difference between the hydrophobicities of oil shale concentrate and tailings.
4. The simulation results showed that the optimum range of air flow rate for deep froth flotation should be from 1.2 to 1.8 cm/s, the optimum particle size range is from 35 to 55 μm , and it is difficult to recover particles less than 5 μm in size.

X-ray Back-Scattering Tests

Determination of oil yield in a shale sample by Fischer Assay is time consuming, and, therefore, unsuitable for on-line analysis. Attempts have been made to find an alternate procedure for Fischer Assay. Correlations of the oil yield with specific gravity, carbon content, H/C ratio, etc. have been developed previously by MRI. In this subtask, a method developed for on-line measurement of the ash content of coal tailings was applied for the purpose of measuring the oil yield of oil shale slurries. Optical activity of the oil shale modeled in terms of the scattering intensity was correlated with the oil yield. This approach is more generic because the major elements (carbon, hydrogen, and nitrogen) present in kerogen are simultaneously used as an indicator of the oil yield.

The Fischer Assay is the standard method to evaluate the oil yield of oil shale and products.¹ Though this method is accurate and reproducible, it suffers from the following shortcomings: 1) it is time consuming and labor intensive, 2) it requires a relatively large amount of sample (100 grams), and 3) the analysis is unsuitable for on-line control and pilot plant testing purposes where the results are often required within a short time with a small amount of wet sample.

These shortcomings have compelled researchers to develop alternate rapid and accurate methods of estimating oil yield of shale samples. The methods have been: 1) to correlate the carbon and hydrogen present in shales in the form of H/C and O/C ratio with oil yield,² 2) to correlate the rock density to volume of organic matter in oil shales,³ and 3) to correlate specific gravity of shale with carbon and then correlate carbon to oil yield.⁴

While these efforts have given quite consistent results, these methods also have drawbacks. For example, two shale samples with similar carbon contents or H/C ratio or O/C ratio will predict equal oil yields. In reality, the actual oil yield could be quite different, because of variations in nitrogen or sulfur content. If raw shale and its beneficiated products were used to develop correlations, then it is likely that those may not apply to thermally and chemically treated materials⁴ and vice-versa.

The objective of this subtask was to describe a technique that has potential to ensure faster and more reliable predictions of oil yield. This

was accomplished by modeling the backscattering intensity equation along the lines of a potential and proven technique, thus overcoming the shortcomings that have been previously outlined. The scientific rationale for choosing such a technique is discussed, along with the analysis of some experimental data from Alabama, Indiana, and Tennessee shales and their beneficiated products.

Boyce⁵ proposed an x-ray back scatter technique to measure the ash content of coal in tailing streams. He used back scattered x-rays for coal analysis and found a strong dependence between the incoherent (Compton) to coherent (Rayleigh) intensity ratio (C/R) and ash content. An ash range from 48 to 65 percent was tested with solids content from 18 to 35 percent and the accuracy was within 4 percent at the 95 percent confidence level. He considered the coal slurry as a three-component system consisting of carbon representing the coal phase, aluminum representing the mineral phase, and water. The scattering intensity in general is defined as n (or C/R):

$$n = k \frac{\sum \sigma_i I_i}{\sum \mu_i I_i}$$

For the coal slurry, n is defined as:

$$n = k \frac{\sigma_a I_s + \sigma_c(1-r)s + \sigma_w(1-s)}{\mu_a I_s + \mu_c(1-r)s + \mu_w(1-s)}$$

Where k is the shape factor, σ is mass scattering coefficient μ is total mass absorption coefficient, r is the weight fraction of ash and s is the weight fraction of solids in slurry. Subscripts a, c and w refer to aluminum, coal and water phases, respectively. It was found that n varied inversely proportional to ash in a linear mode.

Analysis of the work by Boyce on coal tailings to measure its ash content indicated a potential application for measuring the ash content of oil shales. With respect to mineral matter content, coal tailings and oil shales are similar. But which constituent of oil shale would scatter x-rays? Since the primary focus of shale is oil yield, the oil bearing constituent (kerogen) was a natural structural choice. Also, kerogen is the least insoluble phase that forms the nucleus of the oil shale and contributes more to backscattering than loosely held inorganic and mineral matter. The scattering of x-rays is due mainly to the kerogen and that any attenuation or absorption is due to the presence or absence of kerogen, because it is usually harder than mineral matter.⁶ Therefore, it was decided to model the scattering intensity equation with respect to only kerogen, which was in-turn described as a four-component system (carbon, hydrogen, nitrogen, and sulfur). The model and procedure are described below.

The fractional decrease in the intensity I of an x-ray beam as it passes through any homogeneous substance is proportional to the distance traversed x that the mass per square cm penetrated is m and is given by:⁷

$$I_x = I_0 e^{-(\mu/d)m}$$

Where I_0 = Intensity of incident x-ray beam
 I_x = intensity of transmitted beam after passing through a thickness x
 d = density of the substance
 μ = total absorption coefficient
 μ/d = total mass absorption coefficient = μ

The total mass absorption coefficient (μ/d) is usually considered as the sum of two parts:

$$\mu/d = \mu_0/d + \sigma/d$$

Where μ_0/d is the true or fluorescent mass absorption coefficient and
 σ/d is the mass scattering coefficient = σ

The total mass absorption coefficients for the components at the desired wavelength are listed in the literature.⁸ The mass scattering coefficients are independent of the wavelength and were calculated for respective components by the expression:⁷

$$\sigma = \sigma/d = 0.4019 N/A$$

Where N is that atomic number of the scattering component
 A is the atomic weight of the scattering component

Considering the kerogen to be a four-component system, the scattering intensity n can be defined as:

$$n\left(\frac{C}{R}\right) = k \frac{\sigma_C I_C + \sigma_H I_H + \sigma_N I_N + \sigma_S I_S}{\mu_C I_C + \mu_H I_H + \mu_N I_N + \mu_S I_S}$$

Where k is the shape factor (1.15),⁹ s is the scattering coefficient, σ is the total mass absorption coefficient, and r is the weight fraction. Subscripts C, H, N, and S represent carbon, hydrogen, nitrogen, and organic sulfur, respectively.

The wavelengths used were 0.5609, 0.7107, 1.5418, 1.6591, 1.9373, and 2.2909 Angstroms (Å). The samples tested using this model were comprised of Alabama, Indiana, and Tennessee oil shales. Within each shale group the data consisted of a uniform number of feed (head), concentrate, and tails samples. The Alabama shale was analyzed assuming kerogen to be a three-component system (carbon, hydrogen, and nitrogen), because sulfur contents were not available. The intensity values were calculated for these samples for different wavelengths. The optimum wavelength was chosen on the basis of maximum correlation obtained when scattering intensity was correlated with oil yield. Pertinent second-order regression equations involving scattering intensity and oil yield were developed. It should be noted that the organic sulfur content is used in the model. The organic sulfur content was estimated based on the total sulfur content using appropriate conversion factors.¹⁰

A statistical analysis was performed on the data. The model tested in all cases was of second order of the form:

$$Y = a + b(n) + c(n)^2$$

Where Y is the oil yield (gal/ton)
a, b and c are model coefficients, and
n is the scattering intensity

Effect of wavelength The total mass absorption coefficient of the individual component depends upon the x-ray wavelength used, and hence the first task was to assess the sensitivity of the model with respect to wavelength. Table 4-20 shows the values of R^2 for each of the shales using five wavelengths. It is clear that the model responds equally well and is independent of the wavelength. Therefore the results obtained using only an intermediate wavelength value (1.5418 Å) are plotted, tabulated and discussed.

Three components versus four components It is clear from Table 4-20 that the correlation of scattering intensity with oil yield for the Alabama shale sample is lower than that for the Tennessee and Indiana shales. One possible explanation for this might be the consideration of kerogen as a three-component system in the model, which is less descriptive than the four-component system. Also, one would expect sulfur to influence scattering more than lighter elements such as carbon, hydrogen, and nitrogen. A poorer correlation is, therefore, expected for any shale if sulfur is not included in the model. This hypothesis was tested by analyzing Indiana and Tennessee oil shale data considering the kerogen to be a three-component system. The quality of correlation was much lower for the three-component system versus a four-component system for these shales, as shown in Table 4-21.

Table 4-21. QUALITY OF CORRELATION CONSIDERING KEROGEN
TO BE A THREE OR FOUR COMPONENT SYSTEM

Shale Components	<u>Indiana</u>		<u>Tennessee</u>	
	<u>C, H, N, S</u>	<u>C, H, N</u>	<u>C, H, N, S</u>	<u>C, H, N</u>
Correlation Coefficient, R^2	0.996	0.936	0.999	0.926

Model Equations The model equations resulting from the statistical analyses of the oil yield and scattering intensity are presented in Table 4-22 and plotted in Figures 4-20 through 4-23.

Model Verification The analysis conducted using the approach of Boyce in this investigation was independently verified by the work of Dale and Matulis.¹¹ They used backscattered x-rays for coal analysis and found a strong dependence between the coherent (Rayleigh) to incoherent (Compton) intensity ratio (R/C) and mineral content. They plotted their data as $(R/C)^{-1}$ versus oil yield for three Tertiary Australian oil shales. Results are similar to the data presented here.

Table 4-20. THE VALUES OF R^2 OBTAINED BY FITTING SHALE DATA
WITH A SECOND-ORDER MODEL FOR A RANGE OF WAVELENGTHS

Shale Type (Components)	Wavelength, Å					
	<u>0.5609</u>	<u>0.7107</u>	<u>1.5418</u>	<u>1.6591</u>	<u>1.9373</u>	<u>2.209</u>
Alabama (C, H, N)	0.931	0.933	0.935	0.934	0.941	0.936
Indiana (C, H, N, S)	0.995	0.996	0.996	0.996	0.996	0.996
Tennessee (C, H, N, S)	0.999	0.999	0.999	0.999	0.999	0.999
Indiana & Tennessee (C, H, N, S)	--	--	0.978	--	--	--

Table 4-22. MODEL EQUATIONS RELATING FISCHER ASSAY OIL YIELD TO THE
SCATTERING INTENSITY OF ALABAMA, INDIANA, AND TENNESSEE SHALES

Shale	Model Equation
Alabama	Oil (GPT) = 115 - 35222 n + 26705 n ²
Indiana	Oil (GPT) = 5.36 + 817 n + 31781 n ²
Tennessee	Oil (GPT) = 1.13 - 1135 n + 238293 n ²
Indiana & Tennessee	Oil (GPT) = 4.17 + 756 n + 32356 n ²

Figure 4-20. OIL YIELD VERSUS SCATTERING INTENSITY FOR ALABAMA SHALE

Figure 4-21. OIL YIELD VERSUS SCATTERING INTENSITY FOR INDIANA SHALE

Figure 4-22. OIL YIELD VERSUS SCATTERING INTENSITY FOR TENNESSEE SHALE

Figure 4-23. OIL YIELD VERSUS SCATTERING INTENSITY FOR INDIANA AND TENNESSEE SHALES COMBINED

A comparison of this work with that of Dale and Matulis shows that the nature of variation of scattering intensity with oil yield is independent of the shale type and its chemical state. Dale and Matulis analyzed data for Australian shales by retorting the shale samples, whereas the analysis in this work was performed on Eastern shales in their physically beneficiated form. Therefore, it is to be expected that for a given shale, a single correlation could describe the variation of oil yield with scattering intensity, regardless of its physical and chemical form, whether it is physically beneficiated, thermally activated, or chemically treated. However, this hypothesis needs to be experimentally verified. Comparing these two works has given MRI a theoretical basis for making such a hypothesis.

Conclusions

An x-ray back-scatter technique initially applied for measuring the ash content of coal in tailing streams has been extended to measure the oil yield of shales, considering kerogen to be a four-component system. The technique to predict the scattering intensity, and correlating this to oil yield on the basis of carbon, hydrogen, nitrogen, and sulfur content of shale, was shown to be phenomenologically, structurally, and chemically sound.

- The scattering intensity equation modeled for oil shale in terms of carbon, hydrogen, nitrogen, and sulfur has produced high correlations of scattering intensity with oil yield for Indiana and Tennessee shales.
- The influence of sulfur on the scattering intensity was found to be significant, which resulted in a relatively poorer correlation for the Alabama shale. Since sulfur was not included in the correlation for Alabama shale, a relatively poor (0.94) correlation coefficient was found for the Alabama shale.
- It is proposed that kerogen be considered as a five-component system with the addition of a term for water, and a suitable temperature correction factor be included in the equation before it can be put into use for any one shale, irrespective of its chemical state. This is because the scattering intensity and oil yield are significantly affected by the presence of water and temperature. This extension of the work will prove very useful for making measurements of wet shale samples.

Subtask 4.4. Integrated Grinding and Flotation

Introduction and Background

Physical beneficiation of oil shale is often included as part of the above-ground processing technology for shale oil recovery. Reducing the cost and size of the high-pressure hydrogen retort for extracting shale oil via relatively low-cost, low-pressure beneficiation is an area worthy of investigation. The physical beneficiation technique in mineral technology utilizes differences in the physical-chemical properties among the mineral components of an ore. The major components in oil shale are hydrophobic organic matter (kerogen) and hydrophilic inorganic matter. Thus, separation of the organic from the inorganic components could be achieved using surface chemical-based processes such as froth flotation or oil agglomeration.

Various researchers have reported flotation and agglomeration results on Western and Eastern oil shales. Grinding of eastern shale to 80 percent passing 7 μm size for flotation using pine oil, increased the organic content of the flotation product from 8 to 21 percent. Regrinding and flotation of the concentrate improved the grade of the product; however, overall recovery decreased.

Column flotation has been shown to be effective for beneficiating ultra-fine coal and mineral particles. MRI has conducted column flotation studies on eastern shale and achieved encouraging results when the feed was introduced into the froth phase. MRI also reported that the addition of reagents to the wash water improved concentrate grade, but diminished recovery. They also found that increasing column height improved flotation performance.

In 1991-92, the University of Kentucky Center for Applied Energy Research (UK-CAER) conducted detailed flotation studies of Alabama oil shale using the Ken-Flote column technique. The results showed that to obtain a high recovery (~80 percent) of kerogen in a concentrate containing about 40 percent carbon, a retention time of about 20 minutes was required. Studies were also conducted using the SYMUSEP Separator that combines grinding and cleaning step in a single stage. The results obtained with the SYMUSEP Separator were similar to those from the Ken-Flote column.

The present research program is a continuation of previous efforts by UK-CAER in conducting beneficiation studies using the SYMUSEP Separator, column flotation studies on a pilot scale, and conducting dewatering studies of the kerogen concentrate. Due to a DOE budget cut, research efforts in pilot-scale testing and dewatering studies were curtailed. Most of the efforts focused on beneficiation studies using the SYMUSEP Separator. This report describes the work conducted by UK-CAER from June 1 through December 31, 1992.

Objectives

The objective of the present research program was to conduct pilot-scale flotation studies on Eastern oil shale using the advanced Ken-Flote column to obtain a product containing at least 114 liter/ton (30 gal/ton) oil at 90 percent recovery. Dewatering studies were also to be conducted with the concen-

trate using a novel surface modification approach (combining metal ions and surfactant) to facilitate dewatering the concentrate to low moisture contents (~20 percent) with conventional dewatering techniques. It was also the objective of the program to conduct beneficiation tests using the SYMUSEP Separator to identify optimum operating conditions.

Experimental

For flotation studies, the oil shale was ground using the Drais-Werke Mill (Figure 4-24), which is a continuous grinding attritor mill. Particle size distribution of the ground material was determined using a Granulometer that utilizes a laser beam scattering principle.

Conventional batch flotation tests were conducted using a Denver flotation machine (Model D-12). These tests were conducted to identify reagent dosages as well as to determine the grade/recovery relationship through a release analysis procedure, which can be used to define flotation limits in terms of grade and recovery.

The pilot-scale studies were conducted in a 6-inch ID x 20-foot high (0.15 m ID x 6 m) Ken-Flote column (Figure 4-25). A 5 weight percent ground oil shale slurry was prepared in an 80-gallon tank. A flotation reagent (Betz M250 frother) was added to the slurry and the conditioned slurry was fed at the 14-foot (4.2 m) height into the column. Bubbles were generated using a sintered metal sparger. The froth-pulp interface was controlled with a differential pressure cell. A gentle spray of wash water was introduced in the froth layer to remove entrained and entrapped impurities. The column flotation test conditions are listed in Table 4-23. Samples of the froth and tailings were collected after 30 minutes of starting the test. The froth generated in each test was stored in a plastic 55-gallon drum for use in dewatering studies.

Table 4-23. COLUMN FLOTATION TEST CONDITIONS

Column Dimensions	
Column Diameter, inches	6
Total Height, feet	20
Recovery Zone Height, feet	16
Froth Depth, feet	4
Froth Wash Zone, feet	2-1/2
Froth Drain Zone, feet	1-1/2
Feed Level, feet	14
Slurry Feed Rate (5% Solids), gal/min	0.5-1.6
Reagents	
Frother, pound/ton	3.5
Wash Water Rate, gal/min	0.26-0.9
Air Flow Rate, scfm	0.3-0.5

Figure 4-24. DRAIS-WERKE MILL

Figure 4-25. PILOT-SCALE KEN-FLOTE COLUMN

Laboratory-scale column flotation tests were conducted using both a 3-inch diameter x 20 foot high SYMUSEP Separator (Figure 4-26) and a 2-inch diameter x 20 foot high Ken-Flote column (Figure 4-27). Tests were conducted using the SYMUSEP Separator as a rougher flotation stage and the tailings from the separator were floated in the Ken-Flote column, i.e., the Ken-Flote column was used as a scavenger flotation stage. The feed slurry to the SYMUSEP Separator was prepared by grinding the oil shale to a d_{50} of 12 μm ($d_{90} = 66 \mu\text{m}$). A schematic diagram of the two column arrangement is shown in Figure 4-28.

The dewatering studies were conducted using laboratory vacuum and pressure filtration equipment. The pressure filtration equipment is shown in Figure 4-29. For the dewatering study, a fixed amount of column froth slurry was utilized and the amount of filtrate collected with time was recorded. At the end of the experiment, the wet filter cake was weighed, dried and weighed again to determine the cake moisture content. The surface charge (electrophoretic mobility) of kerogen particles was determined using a Zeta Meter Model 3.0.

Results and Discussion

About one ton of Alabama shale was crushed to -4 mesh size and stored in 55-gallon drums. A head sample of the shale was analyzed for oil content (by Fischer Assay) and also for chemical analysis. The results of these analyses are summarized in Table 4-24.

Table 4-24. CHEMICAL ANALYSIS OF OIL SHALE

<u>Component</u>	<u>wt %</u>
Moisture	1.20
Ash	73.20
Organic Carbon	16.39
Volatiles	15.80
Sulfur	8.39
Pyritic	6.35
Sulfate	0.31
Organic	1.73
Fischer Assay, gal/ton	11.3

Pilot-Scale Column Flotation Studies

Pilot-scale column flotation tests were conducted to determine the effects of feed rate and slurry retention time on grade and recovery of kerogen. Figure 4-30 shows that feed rate has very little impact on carbon recovery; however, about 33 percent carbon grade product at 50 percent recovery was obtained at a feed rate of 4 L/min.

Figure 4-31 shows the effect of slurry retention time in the column at two different air flow rates. At an air flow rate of 0.3 scfm, recovery does not show any significant improvement over 50 percent even when the retention

Figure 4-26. LINE DIAGRAM OF THE SYMUSEP SEPARATOR

Figure 4-27. SCHEMATIC LINE DIAGRAM OF THE KEN-FLOTE COLUMN

Figure 4-28. A SCHEMATIC FLOWSHEET OF SYMUSEP AND KEN-FLOTE COLUMN SYSTEM

Figure 4-29. BENCH-SCALE PRESSURE DEWATERING APPARATUS

Figure 4-30. EFFECT OF FEED RATE TO THE PILOT COLUMN ON GRADE AND RECOVERY OF KEROGEN

Figure 4-31. EFFECT OF RETENTION TIME ON GRADE AND RECOVERY OF KEROGEN

time is more than 20 minutes. This was unexpected, because as reported previously, about 80 percent carbon recovery with >30 percent carbon grade was obtained in the 2-inch column at a 20-minute retention time. Increasing air flow to 0.5 scfm, at a lower retention time of 10 to 15 minutes provided even lower kerogen recovery. A possible explanation for this behavior is that wall effects have a significant effect on froth behavior; the 2-inch diameter column has a surface area:volume ratio three times that of the 6-inch column. If wall effects contribute to the stability of the froth, the smaller column would benefit more from this effect and provide higher recovery. It is possible that inclusion of baffles in the froth zone of the larger column would provide more surface area to increase froth stability. No additional tests were conducted with the pilot-scale column.

SYMUSEP - Ken-Flote Column Flotation

Previously it was reported that the SYMUSEP Separator performance needs to be optimized in terms of grinding speed and grinding charge. Thus, more detailed studies were conducted using the SYMUSEP Separator. It was also noted that the tailings (reject) from the SYMUSEP Separator had significant amount of kerogen present. In the present study, the SYMUSEP Separator and Ken-Flote column were run concurrently; the SYMUSEP tailings were processed in the Ken-Flote column as shown in Figure 4-31.

Figure 4-32 shows the effect of SYMUSEP grind speed on carbon recovery for SYMUSEP (rougher stage) and Ken-Flote (scavenger stage) systems. At a grind speed of 200 rpm in the SYMUSEP Separator, the first flotation stage or rougher flotation provided a concentrate with 23 percent carbon with 45 percent carbon recovery. Increasing the grind speed to 340 rpm had little effect on recovery while concentrate grade improved slightly to 26 percent carbon. Refloating or scavenging the tailings from the SYMUSEP Separator with the Ken-Flote column provided additional carbon recovery. When a grind speed of 200 rpm was used in the SYMUSEP Separator, the scavenger flotation stage provided 85 percent carbon recovery with a concentrate grade of 17.5 percent carbon. Combining the rougher and scavenger flotation products at 200 rpm grind speed provided 98 percent carbon recovery with a concentrate grade of 21.2 percent carbon. As shown in Figure 4-32, increasing the grind speed to 340 rpm and combining both rougher and scavenger products increased the concentrate grade to 25 percent carbon with an overall carbon recovery of 96 percent. These results show that in order to achieve high recovery (>80 percent) with the SYMUSEP Separator, it will be necessary to use a scavenger flotation step to recover the carbon lost in the rougher flotation stage.

Increasing the air flow rate did not improve recovery with the SYMUSEP Separator as shown in Figure 4-33. Although the overall recovery of the SYMUSEP rougher/Ken-Flote scavenger flotation scheme was quite good (90 to 95 percent recovery with 24 to 27 percent carbon in the concentrate), most of the recovery was achieved in the Ken-Flote scavenger flotation stage.

Particle size analyses (the 20th, 50th and 80th percentile) of the feed, concentrate, and tailings obtained from a combined SYMUSEP and Ken-Flote column system test are presented in Table 4-25.

Figure 4-32. EFFECT OF GRIND SPEED ON RECOVERY AND GRADE OF CARBON USING SYMUSEP AND KEN-FLOTE COLUMN SYSTEM COMBINATION

Figure 4-33. EFFECT OF AIR FLOW RATE ON GRADE AND RECOVERY OF CARBON IN SYMUSEP AND KEN-FLOTE COMBINED SYSTEM

The average particle size (d_{50}) of the three products is essentially the same; however, the coarse sized (d_{80}) particles in the feed are being significantly reduced, from 80 percent passing 66.4 μm to 80 percent passing 23.1 μm . Changing grinding charge or rpm of the SYMUSEP Separator did not provide the target particle size of 90 percent passing 10 μm .

Table 4-25. SHALE FEED, CONCENTRATE, AND TAILINGS SIZE DISTRIBUTION

Product Size, μm	$\frac{d_{20}}{\mu\text{m}}$	$\frac{d_{50}}{\mu\text{m}}$	$\frac{d_{80}}{\mu\text{m}}$
Feed	4.4	12.0	66.4
Concentrate	4.5	11.6	23.1
Tailings	4.0	11.9	25.6

To determine the cause of low kerogen recovery from oil shale, UK-CAER conducted a release analysis, which is known to define the limits of grade and recovery using the flotation technique. The release analysis also known as "tree procedure" was developed by Nicol et al.* This procedure has proven reliable for fine coal, however, its applicability to oil shale was investigated for the first time by UK-CAER for the project. Figure 4-34 shows the release analysis of oil shale ground to 90 percent passing 10 μm . According to the results, 90 percent recovery could be obtained at a product grade of about 24 percent carbon and a 30 percent carbon grade product could be obtained at 70 percent recovery. This is in contrast to the column flotation results obtained in last year's efforts where a 40 percent carbon product was obtained at about 80 percent recovery.

Figure 4-35 shows the release analysis curve (limits of flotation) for the Eastern oil shale and also the flotation data obtained using conventional and advanced column systems. These results show that the results obtained with multi-stage conventional flotation are quite close to the limiting grade-recovery curve. Also shown in Figure 4-35 is that the results obtained using the SYMUSEP Separator as a rougher flotation stage and Ken-Flote as a scavenger flotation stage were much better than the results obtained using the SYMUSEP Separator alone. The results summarized in Figure 4-35 suggest that effective beneficiation of this feed slurry would be accomplished with a multi-stage cleaning process rather than with a single-stage cleaning process since the results obtained with the rougher/scavenger circuit are quite close to the release analysis curve.

Dewatering Studies

Dewatering studies were conducted on the froth product collected from the pilot scale column. The composite froth sample contained 30 percent carbon and 10 percent solids by weight. Particle size distribution data (Figure 4-36) shows an average particle size of 7.7 μm .

* Stuart Nicol et al., 1989, "An Evaluation of the Flotation Response of Coals," Int. J. Mineral Processing, 27, pp. 243-262.

Figure 4-34. RELEASE ANALYSIS CURVE FOR THE ALABAMA OIL SHALE GROUND TO 90 PERCENT PASSING 10 MICROMETERS

Figure 4-35. GRADE AND RECOVERY DATA FOR FLOTATION TESTS TOGETHER WITH RELEASE ANALYSIS

Table 3-6. BATCH CATALYZED PFH TEST CONDITIONS AND
CARBON CONVERSIONS WITH BENEFICIATED ALABAMA SHALE
(Catalyst in Exit Line)

Test No.	<u>36-B-12</u>	<u>36-B-13</u>	<u>36-B-14</u>	<u>36-B-29</u>	<u>36-B-27</u>	<u>36-B-28</u>
Average Reactor Temperature, °F	933	934	941	929	938	935
Reactor Residence Time, min	20	21	20	31	31	30
Pressure, psig	967	965	1001	970	976	1012
Shale Particle Size, mesh	----- -20+50 -----					
Superficial Gas Velocity, ft/s	0.075	0.072	0.072	0.074	0.075	0.073
Minimum Fluidization Velocity, ft/s	----- 0.047 -----					
Mixed Catalyst	No	No	No	No	PS-85-765	PS-85-765
Pre-Sulfidation	--	--	--	--	Yes	Yes
Promoter	--	--	--	--	No	No
Catalyst/Shale, g/g	--	--	--	--	0.25	0.25
Exit Line Catalyst	PS-85-765	SPS-0674-92	MS-21008	----- SPS-0674-92 -----		
Pre-Sulfidation	No	No	No	Yes	No	Yes
Promoter	--	--	--	--	--	--
Catalyst/Shale, g/g	0.25	0.25	0.25	0.25	0.25	0.25
Product Distribution, % of Feed Carbon						
Residue Shale	29.7	26.8	39.0	30.8	27.2	26.5
Product Gas	17.6	18.1	15.1	21.3	20.1	19.4
Oil	<u>52.7</u>	<u>55.1</u>	<u>45.9</u>	<u>47.9</u>	<u>52.7</u>	<u>54.1</u>
Total	100.0	100.0	100.0	100.0	100.0	100.0

The electrophoretic mobility data of the froth (Figure 4-37) shows a zero point-of-charge at pH 3.5; this means that the particles are positively charged below pH 3.5 and are negatively charged above pH 3.5. This information is necessary in modifying the surface of kerogen for dewatering studies to be conducted using metal ions and surfactants.

Figure 4-38 shows filtration data of the froth using vacuum and pressure filtration equipment. With 11 psig (22.5-inch Hg) vacuum, after 2 minutes of filtration time a filter cake containing 45 percent moisture was obtained. Increasing the filtration time did not improve moisture reduction. Pressure filtration conducted using 40 psig pressure also gave 45 percent moisture filter cake at 2 minutes filtration time, however, after 5 minutes moisture was reduced to about 40 percent. This reduction could be due to air drying, which occurs in pressure filtration after cracks develop in the cake. At a pressure of 60 psig, a 35-percent moisture filter cake was obtained after 2 minutes of filtration time. After 5 minutes of filtration, the moisture content of the filter cake was reduced to 20 percent.

The addition of copper metal ion and an anionic surfactant to the froth prior to pressure filtration did not show any significant moisture reduction in the filter cake. This is surprising because with fine coal, metal ion-surfactant pre-treatment reduced the moisture content in filter cake from 30 to 20 percent.

Conclusions

Based on the above results it is concluded that

- The release analysis data indicates that using a 90 percent passing 10 μm grind oil shale feed in flotation, a 24 percent carbon product could be obtained at 90 percent recovery.
- Even though the oil shale was of similar characteristics to that used last year, the pilot-scale column provided only 50 percent recovery of 35 percent carbon product at up to 20 minutes of retention time. This is compared to more than 80 percent recovery obtained using the 2-inch diameter column. These differences could be due to wall effects.
- Combining the SYMUSEP Separator and Ken-Flote column as rougher and scavenger stages, a 25 to 27 percent carbon product at about 90 percent recovery could be obtained using 340 rpm grind speed and 3 lit/min air in the SYMUSEP Separator and 2 lit/min air flow in the Ken-Flote column.
- The SYMUSEP Separator alone is not effective in providing high recovery of carbon, a second stage scavenger flotation stage will be required for high recovery.
- Dewatering studies conducted on the froth obtained in the pilot-scale studies indicated that using a vacuum or pressure (40 psig) filtration approach a filter cake containing about 45 percent moisture could be obtained at 2 minutes filtration time. A lower moisture of 35 percent could be obtained in pressure filtration using 60 psig pressure.

Figure 4-37. ELECTROPHORETIC MOBILITY DATA OF THE KEROGEN CONCENTRATE

Figure 4-38. FILTRATION DATA OF KEROGEN CONCENTRATE
USING VACUUM AND PRESSURE FILTRATION

Recommendations

The following recommendations are made:

- Liberation of kerogen from oil shale should be studied in more detail. This should include the impact of utilizing various types of grinding mechanism on kerogen liberation.
- Release analyses should be performed on oil shale ground to various sizes to provide a better guideline for recovery and grade.
- Pilot-scale column flotation studies should be conducted in detail to identify optimum operating conditions.
- Dewatering studies of the oil shale concentrate should be conducted in detail using the pre-conditioning step with metal ion and various surfactants.

Subtask 4.7. Economic Analysis

Background and Objectives

In the development of any new process or technology a primary question, after technical feasibility, is whether the process is economically competitive in the marketplace. In an earlier DOE-sponsored effort (Contract No. DE-FG21-85LC11066), The University of Alabama contracted with the Roberts and Schaefer Company to perform an engineering study and cost analysis of oil shale beneficiation. The Roberts and Schaefer (R&S) report was performed in 1988 and completed in December of that year.

Since 1988, MRI has been continually involved in research and development efforts to improve the beneficiation system. These efforts have included research to assess and adapt new technology and to optimize the application of conventional technologies. It was, therefore, the objective of this task to assess the economic impact of this research and to assess the economic viability of oil shale beneficiation under current economic conditions.

Methods

The cost analysis presented here uses the R&S cost analysis as a base of comparison. The cost analysis is performed in two stages: First, the cost estimate is updated to reflect current prices and economic conditions; second, specific equipment substitutions and operating cost adjustments are made to show the impact of new technology and operating practices resulting from the research effort.

The R&S cost estimate was based on a plant designed to beneficiate 1620 ton per hour of raw shale with an average availability of 90 percent. The raw shale was assumed to contain 12.7 gal/ton of oil based on Fischer Assay. The concentrate was projected to contain 34.1 gal/ton with a kerogen recovery of 92 percent. It was further assumed that this concentrate would, in a hydro-retorting plant, yield 20,000 bbl/day of crude shale oil.

The beneficiation scheme represented by the cost estimate is shown schematically in Figure 4-39. Note that the system (and the estimate) includes all operations performed on the shale between mining and hydroretorting. The concentration area (grinding and flotation) is shown in greater detail in Figure 4-39 because that is the area in which the MRI research has focused. This figure will be referred to later when the effects of technological substitutions are discussed.

In preparing the capital cost estimate, the beneficiation plant was divided into nine process areas and five general cost areas. Materials and labor in seven categories were estimated for each process or general cost area. The capital costs were updated by multiplying each element of the cost estimate by the appropriate inflation factor from Table 4-26.

Operating costs were updated in much the same way. A major component of operating costs, electrical power, was updated on the basis of a cost schedule provided by Alabama Power Company. Similarly, natural gas costs were based on

Figure 4-39. FIRST GENERATION OIL SHALE BENEFICIATION FLOW SHEET

a quote from Alabama Gas Company. The wage roll, however, used the inflation factor shown in Table 4-26 for construction labor.

Table 4-26. INFLATION FACTORS

	<u>May 88</u>	<u>May 92</u>	<u>Ratio</u>
CE Plant Cost Index	343.0	377.6	1.101
Process Machinery	373.0	329.2	0.883
Structural Supports	343.5	351.8	1.024
Engineering & Supervision	262.8	271.3	1.032
Construction Labor	318.1	335.7	1.055
Buildings	--	--	1.000
Electrical Materials	--	--	

Updated Beneficiation Costs

Table 4-27 summarizes the capital costs of an oil shale beneficiation plant at 1992 prices. The current costs are 6.3 percent higher than the costs estimated in 1988. The increase is due primarily to the increase in purchased equipment costs that constitute 85 percent of the direct capital costs.

The current estimated costs of operating a beneficiation plant are summarized in Table 4-28. These costs are shown on an annual basis as well as per unit of derived product. Note that operating costs have increased by only \$0.04/ton of concentrate over the 1988 cost. The cost of electric power, which is the largest operating cost, actually decreased during that period. The distribution of power costs among cost areas is presented in Table 4-29. An itemization of operating supply costs is presented in Table 4-30.

The total cost of delivered oil shale concentrates is summarized in Table 4-31. In preparing this table, the cost of capital was computed at interest rates of 15, 12, 10, and 8 percent to illustrate the sensitivity of costs to prevailing economic conditions. The range shown here is realistic, given a current prime rate of 6 percent.

It should also be noted that the cost of capital presented in Table 4-31 is simply the amortization cost (at the assumed interest rates for a 25-year amortization period) reverted to a cost per unit of product basis. It would perhaps have been preferred to perform a discounted cash flow analysis. Such an analysis would have calculated the return on investment resulting from various assumed oil prices. Such an analysis would incorporate the effects of depreciation and taxes and would have permitted the evaluation of financing alternatives.

The cost of mined ore is a major item in Table 4-31, representing about one third of the total delivered concentrate cost. This cost has been arbitrarily increased by 10 percent over the 1988 estimate, but may still be very optimistic.

The data in Tables 4-27 through 4-31 were developed by R&S and updated by MRI to current prices and economic conditions. In total, the data in these

Table 4-27. 1992 BENEFICIATION PLANT CAPITAL COST ESTIMATE

COST AREA	TOTAL MAT	TOTAL LABOR	TOTAL COST
GENERAL	\$8,940,215	\$3,103,502	\$12,043,717
CRUSHING	10,778,126	\$5,052,261	\$15,830,387
B M GRINDING	7,273,866	\$2,183,229	\$9,457,095
S B M GRINDING	72,048,724	\$2,393,759	\$74,442,483
FLOTATION	9,822,989	\$1,152,578	\$10,975,567
THICKENING	15,409,169	\$1,116,446	\$16,525,615
FILTERING	20,365,604	\$1,450,735	\$21,816,339
DRYING	5,784,003	\$872,836	\$6,656,839
BRIQUETTING	10,266,765	\$1,490,653	\$11,757,418
TAILING DISPOSAL	666,230	\$56,022	\$722,252
MILL BUILDINGS	4,415,676	\$6,939,763	\$11,355,439
ANC BUILDINGS	3,079,819	\$640,654	\$3,720,473
SITE PREP	\$0	\$3,830,049	\$3,830,049
MOBILE EQUIP	1,921,018	\$0	\$1,921,018
SUB TOTALS	\$170,772,204	\$30,282,487	\$201,054,691
ENGINEER LABOR			\$8,042,188
ENGINEER D COST			\$201,055
CONSULTANTS			\$200,000
CONST MGMT			\$6,825,731
STARTUP			\$2,010,547
FIELD CHANGES			\$605,650
SALES& USE TAX			\$6,830,888
INSURANCE			\$1,306,855
PROFIT			\$10,052,735
CONST SERVICES			\$1,543,289
SUBTOTAL			\$37,618,937
TOTAL EST COST			\$238,673,628
CONTINGENCY			16,690,447
TOTAL CAPITAL REQUIRED			\$255,364,075
ROBERTS & SCHAEFER ESTIMATE			\$240,204,925

Table 4-28. 1992 BENEFICIATION OPERATING COSTS

ITEM	ANNUAL COST	COST/TON	COST/BBL-FA	COST/BBL-PFH
ELECTRICAL POWER	\$27,345,072.71	\$6.24	\$7.69	\$3.74
OPERATING SUPPLIES	\$21,894,313.00	\$5.00	\$6.16	\$2.99
NATURAL GAS	\$5,661,343.00	\$1.29	\$1.59	\$0.77
LABOR (WAGE ROLL)	\$4,228,857.00	\$0.97	\$1.19	\$0.58
SUPERVISION	\$1,291,014.00	\$0.29	\$0.36	\$0.18
MAINTAINING TAILING POND	\$1,600,667.00	\$0.37	\$0.45	\$0.22
MAINTENANCE SUPPLIES	\$1,707,635.00	\$0.39	\$0.48	\$0.23
GENERAL EXPENSE	\$1,300,000.00	\$0.30	\$0.37	\$0.18
TOTAL OPERATING COST	\$65,028,901.71	\$14.85	\$18.29	\$8.89
ROBERTS & SCHAEFER ESTIMATE	\$64,875,856.00	\$14.81	\$18.24	\$8.87

Table 4-29. ELECTRICAL POWER CONSUMPTION COST SUMMARY

AREA	CONNECTED LOAD	DIVERSITY FACTOR	COST PER YEAR
GENERAL	2,413	70%	\$537,471
CRUSHING	4,415	70%	983,395
BALL MILL GRINDING	14,065	70%	3,132,833
STIRRED B.M.GRINDING	69,916	70%	15,573,062
FLOTATION	10,848	70%	2,416,279
THICKENING	3,927	70%	874,698
FILTRATION	3,191	70%	710,762
DRYING	2,929	70%	652,404
BRIQUETTING	7,110	70%	1,583,679
TAILINGS DISPOSAL	3,486	70%	776,470
MILL BUILDINGS	337	100%	75,063
ANCILLARY BUILDINGS	130	100%	28,956
TOTAL	122,768		\$27,345,073

Table 4-30. COST OF OPERATING SUPPLIES

Item	Usage	Units	Tonnage Basis		Item Usage			Item Unit Cost	Annual Cost
			Quantity	Units	Lbs/Hr	Lbs/Day	Lbs/330 Days		
Grinding Balls Primary Mills	2	Lb/Ton	1620	TPH	3240	77,760	25,660,800	\$0.25	\$6,415,200
Primary Stirred Ball Mills	30	Gm/Ton	1620	TPH	107	2569	847,824	1.00	847,824
Regrind Stirred Ball Mills	30	Gm/Ton	1037	TPH	69	1645	542,712	1.00	542,712
Subtotal Grinding Balls									\$7,805,736
Flotation Reagent Rougher Flotation	0.1	Lb/Ton	1620	TPH	162	3888	1,283,040	0.50	641,520
Cleaner Flotation	0.1	Lb/Ton	1037	TPH	104	2489	821,304	0.50	410,652
Flocculant (Nalco 8872)									
Primary Thickener	20	ppm	3844	TPH (pulp)	154	3690	1,217,779	0.772	940,126
Concentrate Thickener	20	ppm	2637	TPH (pulp)	105	2532	835,402	0.772	644,930
Coagulant (Nalco 8852)									
Primary Thickener	10	ppm	3844	TPH (pulp)	77	1845	608,890	0.487	296,529
Concentrate Thickener	10	ppm	2637	TPH (pulp)	53	1266	417,701	0.487	203,420
Subtotal Reagents									\$3,137,177
Binder for Briquetting	0.025	Ton/Ton	543	TPH	27,150	651,600	215,028,000	0.05	10,751,400
Small Items & Miscellaneous									200,000
Total Operating Supplies									\$21,894,313

Table 4-31. DELIVERED CONCENTRATE COST

COST OF CAPITAL		CAPITAL INVESTMENT	Cost/\$/Year	COST/YEAR	COST/TON	COST/BBL-FA	COST/BBL-PFH
15%Interest		\$255,364,075	-0.1547	(\$39,504,670)	(\$9.02)	(\$11.11)	(\$5.40)
12%Interest		\$255,364,075	-0.1275	(\$32,558,912)	(\$7.43)	(\$9.16)	(\$4.45)
10%Interest		\$255,364,075	-0.1102	(\$28,132,968)	(\$6.42)	(\$7.91)	(\$3.84)
8%Interest		\$255,364,075	-0.0937	(\$23,922,195)	(\$5.46)	(\$6.73)	(\$3.27)
DEFERRED CAPITAL COST		DEFERRED CAPITAL					
15%Interest		\$474,846	-0.1547	(\$73,458)	(\$0.02)	(\$0.02)	(\$0.01)
12%Interest		\$618,516	-0.1275	(\$78,861)	(\$0.02)	(\$0.02)	(\$0.01)
10%Interest		\$740,636	-0.1102	(\$81,594)	(\$0.02)	(\$0.02)	(\$0.01)
8%Interest		\$889,803	-0.0937	(\$63,356)	(\$0.02)	(\$0.02)	(\$0.01)
OPERATING COST				(\$65,028,902)	(\$14.85)	(\$18.29)	(\$8.89)
COST OF MINED ORE					(\$12.79)	(\$15.75)	(\$7.65)
TOTAL COST OF CONCENTRATES							
15%Interest					(\$36.67)	(\$45.16)	(\$21.95)
12%Interest					(\$35.08)	(\$43.21)	(\$21.00)
10%Interest					(\$34.07)	(\$41.97)	(\$20.40)
8%Interest					(\$33.11)	(\$40.79)	(\$19.82)

tables are the base line against which MRI has assessed the impact of their present research.

Impact of Research on Beneficiation Costs Technology Changes

A beneficiation scheme that represents MRI's current concept of an efficient oil shale beneficiation plant is presented in Figure 4-40. The technological changes in the flow sheet (compared to Figure 4-39) have all been demonstrated by MRI research, or, in the judgment of MRI, are achievable.

In Figure 4-40, the primary ball mills would be used to grind to a finer size (i.e., 150 mesh) than assumed in the R&S analysis. This requires that the primary ball mill be operated in closed circuit. Data presented in Subtask 4.1.6 show that the primary mill product contains a substantial portion of material of flotation size (i.e., $\sim 20 \mu\text{m}$).

Capture of the finished product requires a two-stage cyclone circuit. By this approach however, half, or more, of the total feed stream by-passes the primary stirred ball mill.

The conventional (mechanical) flotation cells selected in the R&S estimate are replaced with column cells. The performance superiority of column cells has been proven over the period of this contract.

Figure 4-40 further shows that the rougher flotation concentrate goes directly to cleaner flotation. This obviates the need for the primary thickener and reduces the load to the regrind stirred ball mill. The possibility of producing a final concentrate in this fashion depends largely on the size of the feed to the rougher flotation stage. In MRI's previous report (May 1992), it was shown that a clean concentrate could be produced from a feed having a d_{90} of $19 \mu\text{m}$. In the current work, however, MRI was less successful in producing a clean concentrate at a $d_{90} = 24 \mu\text{m}$ (Subtask 4.6.1). Scavenger flotation tests also showed that the cleaner flotation tailing was a true middling that would require regrinding.

Table 4-32 summarizes the estimated energy consumption for the current beneficiation flow sheet shown in Figure 4-44.

Capital Cost Changes

The specific changes to be made in the capital cost estimate which result from MRI research are:

1. Increase the capacity of the primary (conventional) ball mill grinding circuit.
2. Decrease the capacity of the primary and regrind stirred ball mill circuits.
3. Substitute column flotation cells for conventional cells.
4. Eliminate the primary thickener.

Figure 4-40. CURRENT OIL SHALE BENEFICIATION FLOW SHEET

Table 4-32. ESTIMATED BENEFICIATION ENERGY CONSUMPTION

<u>Unit</u>	<u>Feed, %</u>	<u>kWh/ton</u>	<u>Net kWh/ton</u>	<u>Total Net kWh/ton</u>
Ball Mill	100.0	16.48	16.48	42.87
Primary				
Stirred Mill	50.0	40.00	20.00	
Secondary				
Stirred Mill	12.5	49.52	6.39	

To calculate the increased ball mill capacity needed, MRI assumed an installed power capacity requirement of 16.48 kWh/t (from Table 4-32)

$$(16.48 \text{ kWh/ton}) \times (1620 \text{ ton/h}) = 26,698 \text{ kW}$$

$$26,698 \text{ kW} \times (1.34) = 35,775 \text{ HP}$$

assuming an efficiency of 85 percent, the installed capacity is

$$35,775 \text{ HP}/0.85 = 42,088 \text{ HP}$$

The R&S engineering study recommended three 18-foot x 24-foot ball mills with 5000 HP each, for a total of 15,000 HP. The capital cost of the primary grinding area is, therefore, increased by a factor of 2.81 (i.e., 42,088/15,000).

The primary stirred ball requirements in the new flow sheet are considerably less than in the original (R&S) estimate. The specific energy consumption is 40 kWh/ton. It was shown that a volume of 1800 mL/min of a 50 percent solids slurry was ground in the Netzsch mill having a capacity of 2 liters (in the John Option Configuration). This corresponds to a capacity of 1244 g/min for a 2-liter volume, or

$$1244/2 = 622 \text{ g/liter/min}$$

$$622/453.6 = 1.371 \text{ lb/liter/min}$$

$$1.371 \times 60 = 82.275 \text{ lb/liter/h}$$

Thus, a 2500-liter stirred ball mill (as specified in the R&S report) has a throughput capacity of

$$82.275 \times (2500)/2000 = 102.8 \text{ ton/h}$$

For a feed rate of 810 ton/h, eight 2500-liter stirred ball mills would be required rather than eighteen as originally specified.

Similarly, six 1500-liter stirred ball mills would be required rather than the originally estimated fifteen. The revised estimate of total stirred ball milling capacity is 29,000 liters or 43 percent of the original. Capital costs are assumed to be proportionately lower.

Substitution of column flotation cells for mechanical cells was done on a cell for cell basis. It was assumed that an 8-foot x 32-inch column cell could replace a 1500 ft³ Outokumpu cell specified by R&S. The capital cost adjustment was made by taking the difference in the cost of the flotation cells and adding it to the current cost. It was assumed that all peripheral equipment and labor costs would remain the same. Note that the cost of the flotation section is increased by the substitution.

Elimination of the primary thickener is the final change in the capital cost estimate. All material and labor costs were reduced in the ratio of the cost of the primary thickener to the cost of the primary plus the concentrate thickener.

Table 4-33 presents the revised capital cost estimate containing all the changes discussed here. This table shows quite clearly that the research conducted over the past five years has had a significant impact on the capital cost of an oil shale beneficiation facility.

Operating Cost Changes

Changes in the operating costs that accompany the flow sheet changes represented in Figure 4-44 include changes in power consumption and in the cost of operating supplies. Estimated power consumption by cost area is presented in Table 4-34. The specific changes from the R&S estimate are adjustments in the primary and stirred ball milling power to match the estimated grinding power presented in Table 4-32. Note also that the connected load in the flotation section is reduced to reflect the use of column rather than mechanical cells.

The cost of power is presented in Table 4-35. This calculation is based on the estimates from Table 4-34. The annual power cost is substantially higher than that in the original R&S estimate. MRI feels that the original estimate was based on faulty data and could not be achieved in practice. The current estimate, while still not optimal, is, readily achievable.

Several critical changes in the cost of operating supplies can be justified. First, the research has shown that sand can be substituted for steel grinding media in the stirred ball mills. This eliminates a \$1.4 million per year cost. Similarly, the primary thickener reagents can be eliminated as a result of the flow sheet change. Finally, bulk samples of concentrate were briquetted successfully during the program without using a binder. Thus, the binder, which is a major cost item, can be eliminated.

The revised supply cost estimate, containing the foregoing changes, is presented in Table 4-36. These data, together with the revised electrical power cost is included in Table 4-37 to form a revised operating cost estimate.

Summary

The cost of delivered shale concentrates, which includes the revisions in capital and operating cost estimates, is presented in Table 4-38. This

Table 4-33. REVISED CAPITAL COST ESTIMATE

COST AREA	TOTAL MATERIAL	TOTAL LABOR	TOTAL COST
GENERAL	\$8,940,215.17	\$3,103,501.56	\$12,043,716.73
CRUSHING	\$10,778,126.10	\$5,052,260.98	\$15,830,387.09
B M GRINDING	\$20,366,824.45	\$6,113,040.69	\$26,479,865.14
S B M GRINDING	\$30,952,131.97	\$1,028,358.94	\$31,980,490.92
FLOTATION	\$11,986,988.75	\$1,152,578.43	\$13,139,567.18
THICKENING	\$6,980,353.71	\$505,749.98	\$7,486,103.69
FILTERING	\$20,365,604.18	\$1,450,734.55	\$21,816,338.72
DRYING	\$5,784,003.25	\$872,836.49	\$6,656,839.74
BRIQUETTING	\$10,266,765.40	\$1,490,652.56	\$11,757,417.95
TAILING DISPOSAL	\$666,230.29	\$56,021.89	\$722,252.18
MILL BUILDINGS	\$4,415,676.04	\$6,939,762.69	\$11,355,438.73
ANC BUILDINGS	\$3,079,819.18	\$640,653.64	\$3,720,472.82
SITE PREP	\$0.00	\$3,830,048.75	\$3,830,048.75
MOBILE EQUIP	\$1,921,018.15	\$0.00	\$1,921,018.15
SUB TOTALS	\$136,503,757	\$32,236,201	\$168,739,957.79
ENGINEER LABOR			\$6,749,598.31
ENGINEER D COST			\$168,739.96
CONSULTANTS			\$200,000.00
CONST MGMT			\$6,825,731.00
STARTUP			\$1,687,399.58
FIELD CHANGES			\$644,724.02
SALES& USE TAX			\$5,460,150.27
INSURANCE			\$1,096,809.73
PROFIT			\$8,436,997.89
CONST SERVICES			\$1,543,289.00
SUB TOTAL			\$201,553,397.54
CONTINGENCY			\$14,108,737.83
TOTAL			\$215,662,135.36

Table 4-34. POWER CONSUMPTION BY COST AREA

COST AREA	CONNECTED LOAD	DIVERSITY FACTOR	EST. CONSUMPTION kWh
GENERAL	2,413	70%	1,689
CRUSHING	4,415	70%	3,090
BALL MILL GRINDING	39,382	70%	33,475
STIRRED B.M.GRINDING	50,000	70%	42,752
FLOTATION	8,150	70%	5,705
THICKENING	3,927	70%	2,749
FILTRATION	3,191	70%	2,233
DRYING	2,929	70%	2,050
BRIQUETTING	7,110	70%	4,977
TAILINGS DISPOSAL	3,486	70%	2,440
MILL BUILDINGS	337	100%	337
ANCILLARY BUILDINGS	130	100%	130
TOTAL	125,470		101,672

Table 4-35. ELECTRICAL POWER COST

ASSUMPTIONS

Single Metering Point	
Power Factor	95%
Operating Hours/Month	657

LOAD INFORMATION

	125,470	125,470	
Diversity Factor, %			1.00

TOTAL KVA DEMAND 101,622.00

ENERGY COSTS

Demand Charges @ \$5.01/KVA	\$5.01
ENERGY CHARGES	
1st 250 KWH, Cents	0.023855
All other KWH, Cents	0.010855
Fuel charges, Cents	0.0165

CALCULATIONS:

Total KWH per month	66,765,654.00
Demand Charge	\$509,126
1st 250 KWH	606,048.20
All other KWH	448,964.47
Fuel Cost	1,101,633.29

Sub Total \$2,665,772.19

DEDUCT (Federal Tax) 2.66%	\$70,909.54
Sub Total	\$2,594,862.65
State Utility Tax @ 1.8%	\$46,707.53
Sub Total	\$2,641,570.17
Gross Receipt Tax	\$52,897.25
TOTAL POWER COST /MONTH	\$2,694,467.43

ANNUAL POWER COST \$32,333,609.11

Table 4-36. REVISED COST OF OPERATING SUPPLIES

Item	Usage	Units	Tonnage Basis		Item Usage		Item Unit Cost	Annual Cost
			Quantity	Units	Lbs/Hr	Lbs/Day	Lbs/330 Days	
Grinding Balls Primary Mills	2	Lb/Ton	1,620	TPH	3240	77,760	25,660,800	\$6,415,200
Subtotal Grinding Balls								
Flotation Reagent Rougher Flotation	0.1	Lb/Ton	1,620	TPH	162	3,888	1,283,040	641,520
Cleaner Flotation	0.1	Lb/Ton	1,037	TPH	104	2,489	821,304	410,652
Flocculant (Nalco 8872)								
Concentrate Thickener	20	ppm	2,637	TPH (pulp)	105	2,532	835,402	644,930
Coagulant (Nalco 8852)								
Concentrate Thickener	10	ppm	2,637	TPH (pulp)	53	1,266	417,701	203,420
Subtotal Reagents								
Small Items & Miscellaneous								\$1,900,522
Total Operating Supplies								
								200,000
								\$8,515,722

Table 4-37. REVISED OPERATING COST SUMMARY

ITEM	ANNUAL COST	CONCENTRATE COST /TON	KEROGEN COST /BBL	RETORTED OIL COST /BBL
ELECTRICAL POWER	\$32,333,609.00	\$7.38	\$9.09	\$4.42
OPERATING SUPPLIES	\$8,515,722.00	\$1.94	\$2.39	\$1.16
NATURAL GAS	\$5,661,343.00	\$1.29	\$1.59	\$0.77
LABOR (WAGE ROLL)	\$4,228,857.00	\$0.97	\$1.19	\$0.58
SUPERVISION	\$1,291,014.00	\$0.29	\$0.36	\$0.18
MAINTAINING TAILING POND	\$1,600,667.00	\$0.37	\$0.45	\$0.22
MAINTENANCE SUPPLIES	\$1,365,038.00	\$0.31	\$0.38	\$0.19
GENERAL EXPENSE	\$1,300,000.00	\$0.30	\$0.37	\$0.18
TOTAL OPERATING COST	\$56,296,250.00	\$12.85	\$15.83	\$7.69

Table 4-38. REVISED ESTIMATE OF DELIVERED CONCENTRATE COST

COST OF CAPITAL		CAPITAL INVESTMENT	Cost/\$/Year	COST/YEAR	COST/TON	COST/BBL-FA	COST/BBL-PFH
15%Interest		\$215,662,135	-0.1547	(\$32,362,803)	(\$7.62)	(\$9.38)	(\$4.56)
12%Interest		\$215,662,135	-0.1275	(\$27,496,916)	(\$6.28)	(\$7.73)	(\$3.76)
10%Interest		\$215,662,135	-0.1102	(\$23,759,082)	(\$5.42)	(\$6.68)	(\$3.25)
8%Interest		\$215,662,135	-0.0937	(\$20,202,965)	(\$4.61)	(\$5.68)	(\$2.76)
DEFERRED CAPITAL COST		DEFERRED CAPITAL					
15%Interest		\$474,846	-0.1547	(\$73,458)	(\$0.02)	(\$0.02)	(\$0.01)
12%Interest		\$618,516	-0.1275	(\$78,861)	(\$0.02)	(\$0.02)	(\$0.01)
10%Interest		\$740,636	-0.1102	(\$81,594)	(\$0.02)	(\$0.02)	(\$0.01)
8%Interest		\$889,803	-0.0937	(\$83,356)	(\$0.02)	(\$0.02)	(\$0.01)
OPERATING COST				(\$56,296,250)	(\$12.85)	(\$15.83)	(\$7.69)
COST OF MINED ORE					(\$12.79)	(\$15.75)	(\$7.65)
TOTAL COST OF CONCENTRATES							
15%Interest					(\$33.27)	(\$40.98)	(\$19.92)
12%Interest					(\$31.94)	(\$39.33)	(\$19.12)
10%Interest					(\$31.08)	(\$38.28)	(\$18.61)
8%Interest					(\$30.27)	(\$37.28)	(\$18.12)

represents MRI's best estimate of the cost of concentrates (or oil) produced by the beneficiation system illustrated in Figure 4-44.

The data show that substantial cost reduction has been achieved through MRI research efforts. The cost of a barrel of oil contained in the concentrates has been reduced by almost \$2.00.

Further analysis, however, may show that specialty products might be economically produced. Analyses should be performed to determine the effect of higher mining grades, higher recovery, and higher product prices. MRI also believe that further cost reduction in beneficiation can be achieved. The greatest opportunity for cost reduction is still in reduction of grinding costs. This might be achieved through increased primary grinding and, hence, decreased stirred ball mill grinding, or by substitution of vibratory milling for stirred ball mill grinding. MRI recommends that research in the beneficiation of Eastern oil shales be continued.

References (Task 4)

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Task 6. Environmental Data and Mitigation Analysis

Subtask 6.2.2.1 Acclimation to PFH Liquid Waste

Introduction

The liquid waste produced during the production of oil from oil shales by the PFH process is expected to be about 19 gallons per barrel of oil produced. The composition of this liquid waste is also expected to vary based on the shale source and the operational parameters of the process. Table 6-1 gives a partial listing of those components making up the composition of the liquid waste from a mini-bench scale hydroretorting unit while processing Tennessee Chattanooga shale.¹

Table 6-1. COMPOSITION OF SOUR WATER GENERATED BY
HYDRORETORTING TENNESSEE CHATTANOOGA SHALE

<u>Compound</u>	<u>Concentration, ppm</u>
Thiocyanate	7,350
Sulfides	58,500
Sulfates	7,150
Acetone	200
Methyl ethyl ketone	50
Pentanone	15
Phenol	40
Methyl phenol	30
NH ₃	42,700
Acetonitrile	360
Propionitrile	40
Aniline	500
Methyl anilines	180
Pyrrole	130
Methyl pyrrole	70
C ₂ -pyrrole	15
C ₂ -pyridines	5
Cyanide	45
Methyl pyridines	30

Prior to either the reuse or disposal of this liquid waste, it will certainly require treatment to remove some of these compounds. In previous studies it was shown that a synthetic waste containing acetone, pyrrole, propionitrile, and thiocyanate was treatable biologically both in batch and in continuous flow reactors.² It has also been shown that aniline, phenol, and methyl ethyl ketone (MEK) are treatable in combination batch biological reactors.³

As a continuation of these studies, two samples of raw liquid wastes were supplied by IGT for biological acclimation studies. The wastes differed in that one was from hydroretorted beneficiated Alabama shale and the other was from hydroretorted raw (not beneficiated) Indiana shale. Both samples had been in storage for some time prior to being delivered to TTU for this study.

Objective

The overall objective of this subtask was to acclimate microorganisms to liquid wastes obtained from the processing of Eastern oil shales by the PFH process. This overall objective was to be achieved by:

1. Removing the hydrogen sulfide (H_2S) and ammonia (NH_3) to below toxic levels
2. Determining the concentrations of the compounds of interest before and after the removal of H_2S and NH_3
3. Determining the desired concentrations of essential nutrients and pH needed in the liquid waste to sustain microbial growth, and
4. Attempting biological acclimation to full-strength and diluted liquid waste using a biological seed from previous treatability studies and/or other sources.

Experimental Methods

Removal of H_2S and NH_3 . Since the liquid waste from the Alabama shale was believed to better represent the liquid waste expected from an industrial application of the PFH process, it was decided to use this sample for the acclimation studies. Before acclimation studies could begin, the H_2S and NH_3 concentrations had to be reduced to below toxic levels. Even though the Alabama shale liquid waste was going to be used in the acclimation studies, there was interest in seeing how the Indiana shale liquid waste responded under the conditions of the stripping experiment. Therefore, both liquid waste samples were subjected to air stripping to reduce the biologically harmful concentrations of NH_3 and H_2S .

Stripping was achieved by raising the temperature of the liquid wastes to about $80^\circ C$, adjusting the pH to a favorable value, and bubbling diffused air through it. To get the nitrogen in the strippable gaseous form, NH_3 , the pH was raised to about 10.5. The free NH_3 was then stripped by bubbling diffused air through the heated liquid waste. To prevent the loss of water and organics by evaporation and volatilization, the gases emitted from the waste were passed through a condenser and the condensate returned to the flask holding the liquid waste.

The concentration of the NH_3 in the liquid waste was monitored using a Fisher specific ion electrode. When the concentration decreased to below 500 mg/L, which is reported to be the threshold inhibitory concentration for the activated sludge process, the pH was reduced slowly to 6.5.⁴ At this pH the sulfides present tend to be converted into gaseous H_2S that can likewise be stripped out via the diffused air. If the pH was dropped too rapidly, solids formed in the liquid phase. This was attributed to the formation of large quantities of H_2S at a rate faster than it could be stripped, possibly forcing the formation of sulfur, insoluble metal sulfides and/or other sulfur compounds. To avoid this, the pH was reduced slowly, thus allowing the H_2S to be liberated at a slower rate. To determine if the H_2S was reduced to acceptable

levels, a presence/absence qualitative evaluation was made by placing lead acetate strips in the gases exiting the condenser. Once the strips showed the absence of H_2S in the off gas, the procedure was stopped.

To evaluate the potential loss of volatile organics during air stripping in an industrial application, a 300-mL portion of the Alabama shale liquid waste was brought to a boil and the condensate collected. Figure 6-1 illustrates how the apparatus was configured to incorporate a trap for volatiles. The pH of the liquid was adjusted to 9.5. Boiling was observed at 88°C . The temperature in the liquid stabilized at about 90°C , which resulted in a temperature of about 80°C at the base of the condenser. Within a period of about one hour and twenty minutes, about 50 mL of distillate were collected for analysis.

Chemical Analysis

Raw waste - The chemical characteristics of the raw PFH liquid waste were determined as follows. The chemical oxygen demand (COD), free NH_3 and kjeldahl nitrogen, were determined using procedures outlined in Standard Methods.⁵ The pH was determined using a Fisher pH electrode. The buffering capacity was determined by preparing pH titration curves using 6N NaOH and 6N HCl.

Stripped waste - Prior to attempting acclimation of microorganisms to the stripped Alabama liquid waste, certain chemical characteristics, as determined on the raw liquid waste, were needed to evaluate the compatibility of the waste to microorganisms. In addition the concentration of certain metals was determined using atomic absorption spectrophotometry. A titration curve was developed for the stripped Alabama liquid waste using 1N NaOH and 1N H_2SO_4 .

Acclimation Process

A number of dilutions were prepared for the initial acclimation attempts with Alabama liquid waste. The dilutions are presented in Table 6-2 along with the calculated COD and the thiocyanate concentrations. The concentration of thiocyanate was a concern, since it has been shown to inhibit microbial growth at a concentration of 600 mg/L.² The dilutions, including the nutrient and buffer additions, were placed in 250-mL Erlenmeyer shaker flasks. Each shaker flask was inoculated with a biological seed previously acclimated to synthetic waste that included some of the major organic constituents of the PFH liquid waste. Once the results were obtained from these initial dilutions, three concentrations (5, 10, and 25 percent) were selected for continued acclimation studies.

Results and Discussion

Chemical Analysis

Raw waste - The chemical characteristics of the raw PFH liquid wastes are presented in Table 6-3. The buffering capacities of the raw wastes, as determined by titration, are shown in Figure 6-2. The titration curves show

Figure 6-1. APPARATUS USED FOR THE COLLECTION OF VOLATILES AND THE REMOVAL OF AMMONIA AND SULFIDE

Figure 6-2. TITRATION CURVES FOR A 100-mL SAMPLE OF LIQUID WASTE DERIVED FROM PFH SHALE PROCESSING

that both wastes were strongly buffered in the pH range of 7 to 11. The buffering capacity of the Indiana shale liquid waste was higher than that of the Alabama shale. The quantity of NaOH solution (100 percent) required to raise the pH of the Alabama shale liquid waste to 10.5 was 33.4 g/L; for the Indiana shale liquid waste, the quantity was 39.1 g/L.

Table 6-2. LIQUID WASTE DILUTIONS AND CALCULATED CONCENTRATIONS

<u>Dilution, %</u>	<u>COD</u>	<u>SCN⁻</u>
	----- mg/L -----	
100	31,300	1,130
50	15,650	565
25	7,725	280
10	3,130	110
5	1,560	57
3.33	1,040	38
2.5	780	28
2	630	23
1.67	520	19
1.4	450	16
1.25	390	14
1.11	350	13
1	310	11

Table 6-3. CHARACTERISTICS OF RAW PFH WASTEWATER

<u>Characteristic</u>	<u>Alabama</u>	<u>Indiana</u>
	----- mg/L -----	
COD	70,400	67,000
NH ₃ -N, Total	19,000	30,700
NH ₃ -N, Free	15,200	22,800
NH ₃ -N Bound	3,770	7,840
pH	8.7	9.3

Stripped waste - The chemical characteristics of the stripped PFH liquid wastes are presented in Table 6-4. The COD of the stripped Alabama liquid waste was 31,300 mg/L. This was used as a general indication of the availability of a carbon source for the microorganisms. The low concentration of metals confirmed the suspicion that these metals would need to be added as essential nutrients for biological growth. The high concentration of sodium resulted from the use of NaOH to adjust the pH during the stripping process.

A titration curve was developed for the stripped Alabama liquid waste. As indicated in Figure 6-3, the stripped liquid waste had a low buffering capacity in the pH range of about 6 to 11. Since most bacteria have pH optima near neutral and minimum and maximum pH values for growth near 5 and 9, respectively, this titration curve indicated that a buffer may be necessary to support biological growth on the Alabama shale liquid waste.⁶

Figure 6-3. TITRATION CURVE FOR A 50-mL SAMPLE OF LIQUID WASTE FROM ALABAMA SHALE AFTER AIR STRIPPING

Table 6-4. CHARACTERISTICS OF STRIPPED PFH WASTEWATER

<u>Characteristic</u>	<u>Alabama</u>	<u>Indiana</u>
	----- mg/L -----	-----
COD	31,300	32,200
Ca	0.16	0.28
Fe	0.45	0.70
Mn	0.93	0.33
Mg	0.090	0.080
Na	19,200	34,000
SCN ⁻	1130	1320
Buffer Capacity	Low	Low
NH ₃ -N, Total	550	1060
NH ₃ -N, Bound	410	950
NH ₃ -N, Free	130	110
pH	8.3	7.1

Determination of Nutrient Additions Because the stripped Alabama liquid waste had a total nitrogen concentration of 550 mg/L, it was decided to attempt acclimation without adding nitrogen. A phosphate buffer was used both as a phosphorous source and to buffer the waste at a pH of about 7. The concentrations of other required elements needed for the acclimation studies are presented in Table 6-5.

Acclimation Process. Except for the 100 percent dilution, a visible microbial growth was established within 24 hours for each of the dilutions given in Table 6-2 for the Alabama shale liquid waste. This growth was confirmed by preparing nutrient agar spread plates of the dilutions. After about 10 days this growth became inactive.

Table 6-5. CONCENTRATION OF NUTRIENTS
AND BUFFER ADDED TO LIQUID WASTE

<u>Nutrients & Buffer</u>	<u>Concentration, mg/L</u>
CaCl ₂	7.5
FeCl ₃ ·6H ₂ O	0.5
MnSO ₄ ·H ₂ O	10.0
MgSO ₄	50.0
KH ₂ PO ₄	530
K ₂ HPO ₄	1070
Nitrogen	None

Three dilutions (5, 10, and 25 volume percent) were used for the continuation of the acclimation studies. A new biological seed was acquired from a mixture of activated sludge, cow and horse manure, and soil. Each time, however, the growth achieved would become inactive within about 10 days, as determined by nutrient agar spread plates. During this same time period, the COD decreased for the 5, 10, and 25 percent dilutions by about 51, 34, and 20 percent,

respectively. Thus, acclimation of a viable microbial growth, supported by a substantial drop in the COD, was not achieved during these tests.

Analyses performed on both the Alabama and Indiana shale liquid wastes by an outside laboratory are presented in Tables 6-6 and 6-7. The data in Table 6-6 suggest a high concentration of sulfides and a low concentration of organics in the stripped waste. The data presented previously in Table 6-4 indicated a COD for the stripped waste that is considerably higher than can be accounted for by the oxidation of the sulfide. These data would seem to be contradictory. During the acclimation experiments, there was no odor present that would generally accompany sulfides present in the gaseous form of H_2S . The data in Table 6-7 indicate that there are numerous compounds that will volatilize from the liquid waste under certain stripping conditions. Further investigation is needed to substantiate these analyses and to determine the next steps for the acclimation process.

Conclusions

1. The data indicated a COD of about 30,000 mg/L in the stripped liquid wastes. There was no odor typically indicative of H_2S .
2. If this raw liquid waste is representative of untreated PFH liquid waste, the results indicate that it will take large amounts of chemicals to adjust the pH to ranges where the NH_3 and H_2S can be stripped.
3. The stripped waste may require additions of essential nutrients to support biological growth and also a buffer to maintain the pH in a range compatible to biological growth.
4. There was evidence that a toxic substance remained in the waste even after being air stripped. More research is needed to substantiate and identify this effect.

Table 6-6. LIQUID WASTE COMPOSITION

Waste Compound	Alabama		Indiana	
	Raw	Stripped	Raw	Stripped
NH ₃ -N	15,000	220	22,000	230
Sulfide	121,000	7,600	64,200	7,800
Methanol	400	20	400	--
Ethanol	40	--	80	--
1-Propanol	80	--	50	--
Acetone	460	--	660	--
MEK	270	--	120	--
2-Pentanone	10	--	--	--
Acetic Acid	900	110	600	20
Propionic	160	80	180	20
Butanoic	--	--	--	--
Phenol	120	120	210	150
Methyl Phenols	60	50	100	30
Butonitrile	400	--	70	--
Propionitrile	50	--	--	--
Ethyl Amine	--	--	--	--
Aniline	250	40	270	10
Methyl Aniline	150	10	90	--
Pyrrole	270	--	560	--
Methyl Pyrroles	80	--	120	--
C ₂ -Pyrroles	50	--	140	--
Pyridine	20	--	70	--
Methyl Pyridine	50	--	80	--
C ₂ -Pyridines	25	--	20	--
Acetamide	50	--	260	--
Propamide	--	--	--	--
Unidentified	790	340	420	70

Table 6-7. CONCENTRATION OF VOLATILES IN ALABAMA LIQUID WASTE

Compound	Volatiles, mg/L	Compound	Volatiles, mg/L
Methanol	900	Ethyl Amine	450
Ethanol	40	Aniline	1000
1-Propanol	30	Methyl Aniline	850
Acetone	130	Pyrrole	500
MEK	30	Methyl Pyrroles	300
2-Pentanone	--	C ₂ -Pyrroles	200
Acetic Acid	--	Pyridine	30
Propionic	--	Methyl Pyridine	80
Butanoic	--	C ₂ -Pyridines	60
Phenol	200	Acetamide	--
Methyl Phenols	250	Propamide	--
Acetonitrile	110	Unidentified	1800
Propionitrile	50		

Subtask 6.2.2.2 Compatibility Studies

Introduction

The liquid waste generated from the production of oil from Eastern oil shales by the PFH process is expected to have numerous organic constituents, including but not limited to those listed in Table 6-8. Since there are no commercial PFH processes, the U.S. Environmental Protection Agency has not established the discharge limits for this liquid waste. Of those listed below, phenol, aniline, and MEK have been classified under the Resource Conservation and Recovery Act (RCRA) as hazardous chemicals.⁷ Other selected organic compounds expected to be present in this waste, acetone, pyrrole, propionitrile, and thiocyanate, have been shown to be efficiently removed from a synthetic waste by biological treatment in both batch and continuous flow reactors.²

Table 6-8. PARTIAL LIST OF ORGANICS IN SOUR WATER
FROM HYDRORETORTING TENNESSEE CHATTANOOGA SHALE

<u>Component</u>	<u>Concentration, mg/L</u>
MEK	50
Phenol	40
Aniline	500
Methyl pyridine	30

Other researchers have shown that phenol is biodegradable under aerobic conditions at concentrations up to 1000 mg/L by microorganisms that have been previously acclimated to the compound.⁸⁻¹² Aniline has also been shown to be readily biodegradable in an aerobic environment.¹³⁻¹⁵ Researchers have found that 4-methyl pyridine can be biologically degraded under both aerobic and anaerobic conditions.¹⁶⁻¹⁹ MEK, even though it has been shown to be air strippable, has been found to be primarily removed by biodegradation in an activated sludge unit.²⁰

In earlier studies, microorganisms were acclimated to, and were shown to degrade a synthetic waste containing aniline, MEK, and phenol in a batch reactor.³ In this same study, there was no success in acclimating microorganisms to 4-methyl pyridine at concentrations from 50 to 250 mg/L. The results presently being reported were derived from a continuation of this research.

Objective

The overall objective of this subtask was to demonstrate the biological compatibility of phenol, aniline, MEK, and 4-methyl pyridine in various mixtures of 2, 3, and 4 compounds. The overall objective was to be achieved by evaluating the use of 4-methyl pyridine as a nitrogen source, and evaluating the compatibility of compounds, or extent to which the presence of one compound interfered with the simultaneous degradation of another.

Experimental Methods

Waste Characteristics The concentrations selected for the compatibility studies were 250 mg/L for phenol and MEK and 300 mg/L for aniline and 4-methyl pyridine. To evaluate the compatibility of these compounds in combination, a method of determining the concentrations simultaneously was needed. A capillary column was used on the gas chromatograph, and definable peaks were established for each compound in a combination solution. The parameters of the test are given in Table 6-9.

Table 6-9. GAS CHROMATOGRAPHY OPERATING PROCEDURES

<u>Instrument</u>	<u>HP 5890A</u>
Detector	Flame Ionization
Column	SGE BP x 70
Carrier Gas	Hydrogen @ 8 mL/min
Detector Gases	Hydrogen @ 17 mL/min Air @ 400 mL/min
Injection Port Temperature	240°C
Detection Port Temperature	280°C
Initial Temperature	35°C
Initial Time	1 min
Temperature Rate	10°C/min
Final Temperature	140°C
Final Time	1 min

The approximate retention times of the compounds MEK, 4-methyl pyridine, aniline, and phenol, are 1.48, 6.8, 11.48, and 13.08 minutes, respectively. Standard curves were established for each compound in a combination solution.

Microbiological Acclimation Prior to proceeding with the treatability studies of the combined compounds, a microbial growth acclimated to the specific synthetic waste mixture was needed. Microorganisms were acclimated to waste with the compounds combined in combinations of 1) phenol and aniline, 2) phenol and MEK, 3) MEK and aniline, and 4) phenol, aniline, MEK and 4-methyl pyridine. Cylindrical 1.5-liter reactors were prepared with the essential nutrients and the organics comprising mixtures of two, three and four compounds. The concentration of nutrients and buffer are listed in Table 6-10.

Table 6-10. CONCENTRATION OF NUTRIENTS
AND BUFFER FOR SYNTHETIC WASTE

<u>Nutrients or Buffer</u>	<u>Concentration, mg/L</u>
(NH ₄) ₂ SO ₄	500
MnSO ₄ (Hydrated)	10
CaCl ₂	7.5
MgSO ₄	1
FeCl ₃	0.5
KH ₂ PO ₄	526
K ₂ HPO ₄	1070

Microbiological seed from reactors that had been previously acclimated to the individual compounds was added to each reactor that had the compound present in combination. Air was supplied through a diffuser stone. The biological culture was maintained by operating the system in batch mode. At intervals of 3 to 4 days the solids in the reactor were allowed to settle and approximately two-thirds of the volume removed from the supernatant. The reactor was then brought back to volume with distilled water; also adding the organic compounds present as the substrate mixture, and nutrients in quantities such that they were recharged to the required concentrations.

In pursuit of a seed that would acclimate to 4-methyl pyridine, a sample of industrial sludge known to contain polyaromatic hydrocarbons was collected from Chattanooga Creek in Chattanooga, Tennessee. Since this creek has been known to be polluted with both industrial and municipal waste for many years, this sludge was a possible source of microorganisms acclimated to organics similar in structure to 4-methyl pyridine. A seed was taken from the sludge and placed in a shaker flask with 250 mg/L of 4-methyl pyridine, and the essential nutrients and buffer required for biological growth. Periodically, a spread plate, with a nutrient agar media, was prepared from the shaker flask solution to check for the presence of a viable microbial seed.

Tests were conducted to determine if microorganisms would use 4-methyl pyridine as a nitrogen source. A shaker flask was prepared with 250 mg/L of phenol and 50 mg/L of 4-methyl pyridine, along with other essential nutrients. Two biological seeds were used. The first was from a reactor that had microorganisms acclimated to phenol at 250 mg/L; the second was from a combination of municipal activated sludge, cow and horse manure, and soil. To check for the presence of a viable microbial seed, nutrient agar spread plates were prepared on the solution periodically.

Compatibility Studies Compatibility studies were initiated once a dense biomass was achieved in the acclimation vessels. A 1.5-liter cylindrical reactor was prepared for each of the mixtures of compounds to which microorganisms were acclimated: 1) phenol and aniline, 2) phenol and MEK, 3) aniline and MEK, and 4) phenol, aniline, MEK, and 4-methyl pyridine. Prior to inoculating the reactors from the acclimation vessels, a time-zero sample was taken. Then a 25-mL seed was taken from the associated acclimation vessels and placed in the compatibility reactor. At appropriate intervals, samples were taken to determine the extent of substrate degradation. The samples were immediately filtered through a 0.45 μ m nylon membrane filter. Vials for COD determinations were prepared; the remaining sample was refrigerated.

The results of earlier experiments showed that MEK was slowly stripped from solution during aeration.³ Therefore, the change in concentration observed during the compatibility experiments was a result of both biological removal and air stripping. To account for that portion removed as a result of air stripping, a sterilized reactor identical to the reactors used in the compatibility studies was prepared. The results from this experiment were used to determine the removal by air stripping. Combining the data gave the desired results of biological removal without air stripping. This correction was used in all cases where MEK was included in the organic mixture.

Samples were analyzed for COD to determine the change in the concentration of total organics. The method used was the closed reflux, ampule variation of colorimetric analysis, as specified by Standard Methods.⁵ To determine the concentration of the specific compound, a Hewlett-Packard 5890A was used for gas chromatography analyses.

To evaluate if 4-methyl pyridine could be air stripped, a sterile reactor was prepared and operated over the same time frame as the compatibility studies. The air flow rate was approximately equal to that used in the compatibility studies (257 mL/min/L). The reactor was sampled periodically and analyzed for 4-methyl pyridine.

The results of the compatibility experiments included in this subtask are based on non-duplicated experiments. These experiments should be repeated for confirmation.

Results and Discussion

Microbiological Acclimation No viable biological growth was attained on the 4-methyl pyridine with the seed from industrial sludges out of the Chatanooga Creek. When 4-methyl pyridine was the nitrogen source and phenol was the sole carbon source, neither of the two seeds became acclimated. This would suggest that 4-methyl pyridine does not provide readily available nitrogen for microorganisms.

Compatibility Studies A compatibility study was performed on a combination synthetic waste with phenol and MEK at an initial concentration of about 250 mg/L, and aniline and 4-methyl pyridine at about 300 mg/L. The COD decreased from an initial value of 1937 to 63 mg/L in about 94 hours. This change in COD was associated with a simultaneous reduction in the concentration of the organic compounds. The concentration of the 4-methyl pyridine was greater than the residual concentration of COD after 94 hours. This was expected since this compound is less than 20 percent oxidized during the COD test. Figure 6-4 shows the change in COD and the concentration of the organic compounds with respect to time during the experiment.

The MEK concentration decreased to less than 1 mg/L after about 43 hours. Once the MEK was removed, the rate of removal of phenol and aniline increased. Their concentrations declined to less than 1 mg/L after about 94 hours. The changes in the concentration of these compounds with respect to time are presented in Figure 6-5. The data presented in both Figures 6-4 and 6-5 were corrected for the air stripping of MEK.

As indicated in Figures 6-4 and 6-5, the concentration of 4-methyl pyridine decreased by about 46 percent after 109 hours. This reduction could have been the result of biodegradation, or bioadsorption. Figure 6-6 shows that it was not the result of air stripping. Further tests will be required to determine the mechanism responsible for this reduction.

The compatibility study with phenol and MEK had initial concentrations of both compounds at about 250 mg/L each. The results of this experiment are presented in Figure 6-7. The COD was reduced from an initial concentration of

Figure t-4. CHANGE IN COD, PHENOL, MEK, ANILINE, AND 4-METHYL PYRIDINE WITH TIME

Figure 6-5. CHANGE IN PHENOL, ANILINE, MEK, AND 4-METHYL PYRIDINE WITH TIME

Figure 6-6. CHANGE IN 4-METHYL PYRIDINE WITH TIME DUE TO AIR STRIPPING
AT AN AIR FLOW RATE OF APPROXIMATELY 257 mL/min/L

Figure 6-7. CHANGE IN COD, PHENOL AND MEK WITH TIME
(Data Corrected for Air Stripping of MEK)

1043 to 19 mg/L in about 37 hours. During this same period of time, the concentrations of MEK and phenol were reduced from an initial 222 and 254 mg/L, respectively, to less than 1 mg/L.

The compatibility study with phenol and aniline had initial concentrations of about 250 and 300 mg/L, respectively. The COD was reduced from an initial concentration of 1269 to about 80 mg/L in 89 hours. Phenol decreased from an initial concentration of 248 to less than 1 mg/L in about 42 hours. Aniline was reduced from an initial concentration of 297 to less than 1 mg/L in about 89 hours. Figure 6-8 gives the changes in COD and the concentrations of the organic compounds with respect to time during the experiment.

The data in Figures 6-7 and 6-8 suggest that under the conditions of the experiment MEK will be preferentially biodegraded before phenol and aniline, and that phenol will be biodegraded before aniline. Since these results were not duplicated, more research is needed to confirm them.

The compatibility study with MEK and aniline had initial concentrations of about 250 and 300 mg/L, respectively. The results for this experiment are presented in Figure 6-9. The COD was reduced from an initial value of 1269 to a low of 49 mg/L in about 88 hours. The concentration of MEK changed from an initial value of 217 to less than 1 mg/L in 31 hours, and the aniline concentration decreased from an initial 288 to less than 1 mg/L in 42 hours. As in the other combination experiments, MEK was degraded first.

Conclusions

1. 4-methyl pyridine (300 mg/L) was not inhibitory to the simultaneous biodegradation of MEK (250 mg/L), phenol (250 mg/L), and aniline (300 mg/L) to concentrations of less than 1 mg/L each.
2. A seed taken from an industrial sludge containing large concentrations of polyaromatic hydrocarbons was not able to acclimate to 4-methyl pyridine at 250 mg/L under the conditions of this experiment.
3. Microorganisms were not able to utilize 4-methyl pyridine as a nitrogen source in an environment with phenol as the only other carbon source. Both phenol acclimated and unacclimated seeds were attempted.
4. A mixture of phenol and aniline at initial concentrations of about 250 and 300 mg/L, respectively, was indicated to be biodegradable to concentrations less than 1 mg/L.
5. MEK and aniline, at initial concentrations of about 250 and 300 mg/L, respectively, were not inhibitory to the biodegradation of each other.
6. MEK and phenol at initial concentrations of about 250 mg/L were each biodegraded to concentrations less than 1 mg/L.
7. At an air flow rate of ≈ 257 mL/min/L, 4-methyl pyridine was not air stripped.

Figure 6-8. CHANGE IN COD, PHENOL AND ANILINE WITH TIME

Figure 6-9. CHANGE IN COD, ANILINE, AND MEK WITH TIME
(Data Corrected for Air Stripping of MEK)

8. MEK was indicated to be biodegraded preferentially over phenol and aniline in a batch reactor.

Subtask 6.2.3 Waste Management Facility Conceptual Design

Introduction

The liquid waste produced during the production of oil from Eastern oil shales by the PFH process is expected to range from about 14.8 to 19 gallons per barrel of oil produced. Chemical analyses show that the liquid waste contains numerous organic and inorganic components ranging in concentration from a trace to several thousand milligrams per liter. Its chemical composition indicates that it may be classified as a hazardous waste due to toxicity characteristics.

The objective of liquid waste treatment is to produce a water having qualities acceptable for reuse within a combined PFH plant and steam power plant. If reuse is not feasible, the objective of treatment is to produce a water having qualities suitable for discharge subject to section 402 of the Clean Water Act. Although a single technology would be desirable, the complexity of the chemical composition dictates that more than one operation or process may be needed. The major treatment technology being investigated at the present time is that of biological treatment. Pre- or posttreatment technologies used in conjunction with biological treatment are likely to be needed in order to produce an acceptable effluent.

The water quantity demands of a combined PFH plant and steam power plant are significantly greater than that which will be provided by the liquid waste stream from the PFH plant. Therefore, liquid waste management facilities must account for the treatment of import water to satisfy water demands.

Objective

The overall objective of this subtask was to initiate preliminary investigations into a conceptual design for the liquid waste management facility. This overall objective was achieved by: 1) Estimating water quantity requirements for a combined PFH-power plant, 2) Determining the sources of raw water necessary to meet water quantity requirements, 3) Evaluating the chemical characteristics of raw water, 4) Determining the quality of water needed for reuse with the combined PFH-power plant, 5) Identifying treatment requirements for the sour water generated from the PFH process, 6) Evaluating data from previous research performed at TTU on biological treatment of synthetic wastes containing suspected sour water contaminants, 7) Making preliminary estimates of the need for and extent of post biological treatment, and 8) Enumerating deficiencies of data needed to complete a conceptual design.

Water Quantity Requirements

Water quantity requirements for the liquid waste management facility are based on the estimated demands that the combined PFH plant and steam power plant will place on the treatment facility during daily plant operation. Three major water needs have been identified, including boiler feedwater,

quench water, and cooling water. The demand of each and the assumptions whereby the demands were estimated are described below.

The water quantity requirement for boiler feedwater is estimated to be 2.02 million gallons per day (MGD), and the requirement for quench water within the hydrogen plant is estimated to be 0.53 MGD. These quantities are based on mass flow rate data for the "Combined PFH Plant and Steam Power Plant Original Design."²¹

The water quantity requirement for cooling purposes is based on the following assumptions. Primary cooling will be accomplished by a closed recirculating system. A closed recirculating system is one in which water is circulated through desired heat exchange locations in the PFH plant in a closed loop with negligible evaporation or exposure to the atmosphere. Closed systems generally require little or no makeup water except for leaks, expansion tank overflows, and surface evaporation from system vents.²² For this study, water losses for the closed cooling water loop are considered negligible. Heat will be removed from the closed system loop by a secondary cooling water cycle. The secondary cooling water cycle will be an open recirculating system utilizing one or more cooling towers. Makeup water will be provided for this system to balance the water lost by evaporation, blow down, tower drift, and other miscellaneous losses. Based on a cooling system as described above, the required daily makeup water is estimated to be 7.55 MGD.²³ This value depends to a large extent on plant location and on cooling tower design. The value chosen is closer to the high end of quantity demands.

Additional water demands may be encountered as pilot-plant studies progress. These additional water demands may include items such as dust control and shale moisturizing. It is assumed that potable and fire protection demands will be supplied by local municipal water services. Preliminary water quantity demands are summarized in Table 6-11.

Table 6-11. WATER REQUIREMENTS

	MGD
Boiler Feedwater	2.02
Quench Water	0.53
Cooling Water	<u>7.55</u>
Total	10.10

Water Sources

Water quantity requirements will be satisfied from two primary sources, liquid waste from the PFH facility and import water. The quantity of water supplied by each and the assumptions whereby the quantities were determined are described below.

The quantity of water to be generated by the PFH facility is estimated to be about 0.74 MGD. This quantity is based on mass flow rate data for the "Combined PFH Plant and Steam Power Plant Original Design."²¹

The remaining water requirement of 9.36 MGD will be import water. Import water consists of water imported from sources such as free flowing streams and impoundments. The import requirement is less than the lowest import quantity (11.3 MGD for a 50,000 bbl/day plant) used in the "Water Availability Study" conducted by TTU to evaluate water availability for potential Eastern oil shale processing facilities in six eastern states.²⁴ Therefore, all sites recommended in the study will adequately satisfy the current import requirement.

Water Quality Criteria

Before schematic design of the liquid waste management facility can proceed, various water qualities are required. Needed water qualities can be grouped into two categories: 1) initial quality of water requiring treatment and 2) water quality criteria for recycle within the plant. Based on the knowledge that two water sources have been identified, initial water qualities are needed for the liquid waste generated from the PFH plant and for import water. Based on water quantity demands, water quality criteria for boiler feedwater, quench water and cooling water are needed.

Water Quality of Liquid Waste from PFH Process The chemical characteristics of the liquid waste resulting from the production of oil from oil shales by the PFH process are expected to vary depending on the characteristics of the raw shale and the shale processing conditions. Table 6-12 shows the characteristics of a sour water produced from a mini-bench-scale PFH unit operated using Tennessee Chattanooga Shale.¹ Treatment recommendations are based on these characteristics and the assumption that the liquid waste will be pretreated by state-of-the art processes to recover oil, sulfur, and NH₃.

Import Water Quality Import water for the combined PFH-power plant consists of water imported from sources such as free flowing streams and impoundments. Since the import requirement is less than the lowest import quantity (11.3 MGD for a 50,000 bbl/day plant) used in the "Water Availability Study"²⁴ investigations were directed at determining water quality characteristics at the sites selected in the study which can serve a 50,000 bbl/day processing facility. Import water quality was investigated for each state to ensure an adequate representation of water quality. The states investigated include: Alabama, Indiana, Kentucky, Michigan, Ohio, and Tennessee.

Primary rivers will be the main sources of water for 50,000 bbl/day processing facilities. Therefore rivers were the focus of this investigation. Rivers which were evaluated are listed in Table 6-13 along with the states in which they serve as potential water sources.

A summary of the import water quality data that were located during the investigation is shown in Table 6-14.²⁵⁻²⁸ Upon evaluation of the water quality data, the Scioto River in Ohio clearly has the most undesirable water quality characteristics. Therefore, the use of these water quality characteristics as design parameters for treatment recommendations of import water will provide the most conservative approach.

Table 6-12. CHEMICAL COMPOSITION OF LIQUID WASTE
GENERATED BY HYDRORETORTING TENNESSEE SHALE

<u>Trace Metals</u>	<u>mg/L</u>	<u>Trace Metals</u>	<u>mg/L</u>
Ag	0.6	K	4
Al	6	Li	<1
As	1.1	Mg	1.5
Ba	2	Mn	0.5
Ca	7	Na	13
Cd	0.3	Ni	2
Cl	<10	Pb	<2
Cr	0.7	Sb	0.3
Cu	3.7	Se	4
Fe	2.9	V	<2
Hg	3.1	Zn	9.4
<u>Sulfur Compounds</u>	<u>mg/L</u>	<u>Nitrogen Compounds</u>	<u>mg/L</u>
Thiocyanate	7350	NH ₃	42,700
Sulfide Sulfur	58,500	Acetonitrile	360
Miscellaneous	7150	Propionitrile	40
<u>Oxygenated Compounds</u>		Aniline	500
Acetone	200	Methyl Anilines	180
MEK	50	Pyrrole	130
Pentanone	15	Methyl Pyrrole	70
Phenol	40	C ₂ -Pyrrole	15
Methyl Phenol	30	Methyl Pyridines	30
<u>Miscellaneous Compounds</u>		C ₂ -Pyridines	5
Fluoride	19	Cyanide	45
		Unidentified	180

Table 6-13. IMPORT WATER FROM PRIMARY RIVERS

<u>State</u>	<u>River</u>	<u>State</u>	<u>River</u>
Alabama	Tennessee	Michigan	Thunder Bay
Indiana	Ohio	Ohio	Scioto
Kentucky	Ohio	Tennessee	Cumberland

Boiler Feedwater Quality Criteria. Boiler feedwater should be of such quality as to avoid the three major water-related boiler system problems - deposits, corrosion, and carryover.²² A brief description of each is given below.

Deposits, particularly scale, are a serious problem at the high temperatures found in boilers. Scale is primarily due to the precipitation of compounds that become insoluble at higher temperatures. Silica and aluminum are two contaminants which have a strong tendency toward this type of scale formation.²⁹ In addition to scale, damaging deposits may be in the form of sludge.

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Table 6-14. CHARACTERISTICS OF IMPORT WATER SOURCES

Water Source River	<u>Tenn.</u>	<u>Ohio</u>	<u>Thunder Bay</u>	<u>Scioto</u>	<u>Cumber- land</u>
Analysis, mg/L or otherwise indicated					
Spec. Cond., $\mu\text{mho/cm}$	126	320	355	560	200
pH	7.4	7.38	8.13	8.1	8
Turbidity, NTU	13	80	2.5	85	4.2
Dissolved Oxygen	11.2	8.7	12.4	10.9	10.4
Fecal Coliforms (0.7 μm Millipore filter) per 100 mL	70	145	--	>6000	--
Hardness, as CaCO_3					
Total	59	140	190	230	88
Non-carbonate	12	70	14	--	25
Calcium	18	40	54	59	25
Magnesium	3.3	9.5	14	21	6.2
Sodium	3.7	12	5.5	18	4.6
Potassium	1.4	2.5	0.9	2.6	1.4
Bicarbonate	--	84	218	196	--
Alkalinity, as CaCO_3	46	69	179	161	63
Sulfate	8.8	51	8.3	57	28
Chloride	3.8	16	9.7	36	4.5
Fluoride	<0.1	0.2	0.1	0.2	<0.1
Silica	5.4	5	9.6	5.7	3.7
Solids, Dissolved	90	184	230	--	113
Sediment, Suspended	18	195	6	153	11
Nitrogen, as N					
$\text{NO}_2 + \text{NO}_3$	0.6	1.04	<0.1	3.2	0.3
NH_3 Total	0.04	0.07	0.01	0.18	<0.01
NH_3 , Dissolved	0.04	0.05	0.02	0.11	<0.01
$\text{NH}_3 + \text{Org}$, Total	0.2	1.2	0.5	1.3	0.4
Phosphorus, Total	0.1	0.47	<0.01	0.17	0.02
Dissolved	0.06	0.34	<0.01	0.07	<0.01
Metals, $\mu\text{g/L}$					
Aluminum	90	30	<10	60	30
Arsenic	<1	1	<1	<1	<1
Barium	24	38	20	47	21
Beryllium	<0.5	0.7	<0.5	<0.5	<0.5
Cadmium	1	<1	<1	<1	<1
Chromium	<5	<1	<1	<1	<5
Cobalt	<3	<3	<3	<3	<3
Copper	<10	6	1	26	<10
Iron	74	33	28	57	27
Lead	<10	<5	<1	1	<10
Lithium	<4	6	6	5	<4
Manganese	5	9	10	7	17
Mercury	0.1	--	<0.1	<0.1	<0.1
Nickel	<10	2	1	4	<10
Selenium	<1	<1	<1	<1	<1
Silver	<1	<1	<1	<1	<1
Strontium	49	160	110	890	96
Vanadium	<6	<6	<6	<6	<6
Zinc	3	5	<3	46	20

These deposits are carried by water to low-velocity areas where they then drop out, compacting to form a dense agglomerate similar to scale. The most common components of boiler deposits are calcium phosphate, calcium carbonate (in low pressure boilers), magnesium hydroxide, magnesium silicate, various forms of iron oxide, silica absorbed on the previously mentioned precipitates, and alumina.²² Deposits insulate boiler tubes, reducing the heat transfer rate, which leads to overheating and eventual boiler tube failure.

The second major water-related boiler problem is corrosion. The most common form of corrosion is the attack of steel by oxygen. This form of corrosion occurs in any portion of the steam cycle where oxygen is present. It is accelerated by high temperature and low pH. Galvanic corrosion can occur at localized areas of high concentrations of settled solids resulting from scale formation or sludge deposits. Corrosion may also occur due to alkali attack, improper application of feedwater treatment chemicals, and other less common forms.

The third major water-related boiler problem is carryover, defined as entrainment of boiler water into the steam system. A major cause of carryover is the volatilization of boiler water salts, such as silica and sodium compounds. Volatilized salts are carried as a mist into the steam system and may subsequently form turbine blade deposits or deposits in the superheater, causing tube failures. Foaming is an additional problem that results in carryover. Excessive concentrations of sodium or potassium can result in foaming.²⁹

Quality criteria for boiler feedwater becomes increasingly more stringent as boiler pressure increases. Therefore, a boiler pressure must be determined to insure adequate quality criteria. Based on the "Combined PFH Plant and Steam Power Plant Original Design," the maximum boiler pressure is estimated to be 2860 psi.²¹

The Electric Power Research Institute (EPRI) has established definitive guidelines for fossil plant makeup water purity. These guidelines are as close to an industry standard on boiler feedwater criteria as is available. The guidelines values for treated makeup are specific to the type of boiler used, whether or not a reheater is present, and the form of chemical treatment used within the boiler. Due to the lack of information as to the specifics of the boiler which will be used in the combined PFH-power plant, the most conservative approach will be to utilize the most stringent requirements of a high-pressure drum type boiler which contains a reheater and utilizes all volatile treatment. A summary of the guidelines for a boiler under these conditions is presented in Table 6-15. The guidelines values listed in Table 6-15 are the same as those for steam within the boiler unit.³⁰ This was done to provide maximum flexibility within the boiler unit.

Quench Water Quality Criteria. Water quality criteria for the quench water used in the hydrogen plant will vary with the type of system used. The system manufacturer will likely provide recommended water quality standards. However, high quality water is generally required for these types of systems. Since the quality of water that is likely to be needed is more stringent than

that needed for cooling water, the same criteria as that for boiler feedwater will be used.

Table 6-15. BOILER FEEDWATER QUALITY GUIDELINES

<u>Parameter</u>	<u>Max. Conc., mg/L</u>
Sodium	0.003
Chloride	0.003
Sulfate	0.003
Silica	0.010
Total Organic Carbon	0.300
Specific Conductivity (@ 25°C), μ mhos/cm	0.1

Cooling Water Quality Criteria Makeup water for the open recirculating cooling system should be of such quality as to avoid the three major water-related cooling water system problems - corrosion, scale, and fouling.²² A brief description of each is given below.

For an open recirculating system that requires substantial makeup water, corrosion presents a serious problem. Oxygen presents the most serious threat. At elevated temperatures and at points of high heat transfer, oxygen can cause severe pitting corrosion. In addition to pitting corrosion, galvanic corrosion can occur due to high concentrations of total dissolved solids. Corrosion may also occur due to alkali attack.

In addition to corrosion, scale presents a significant problem for cooling water systems with high makeup flow rates. Scale is primarily due to the precipitation of compounds that become insoluble at higher temperatures, such as calcium carbonate. Additional problems of scale are associated with the presence of hardness ions such as calcium and magnesium, which can combine with available phosphate, silica, sulphate, and carbonate to form a hard heat-transfer-limiting scale. In general, for open recirculating systems, the calcium and magnesium hardness should be low enough so that a cooling tower can operate with the circulating water equal to at least several concentrations of makeup before scale forms at a significant rate. Table 6-16 lists some important variables that must be controlled to prevent significant scale formation.

Table 6-16. PARAMETERS THAT INFLUENCE SCALE FORMATION²²

<u>Variable</u>	<u>Effects</u>
Ca, Mg	Define scaling tendency of water.
M, pH, T	Define concentrations of carbonate and bicarbonate, and solubility of calcium carbonate.
SO ₄ , SiO ₂	Must be controlled to prevent sulfate and silicate scales.

Calcium and magnesium hardness define the scaling tendency of the water. Total alkalinity (M), pH, and temperature (T) define the concentrations of carbonate and bicarbonate ions in the water, and also the solubility of calcium carbonate. All of these must be controlled within acceptable ranges to

ensure scale-free operation. Concentrations of sulfate and silica must also be controlled to prevent formation of gypsum and silica scale.

Fouling has the same effect on cooling water systems as scaling, but fouling also promotes severe corrosion under the deposits. Fouling results from the settling out of suspended solids, build up of corrosion products, and growth of microbial masses. Table 6-17 shows some sources of foulants in a typical recirculating system.

Table 6-17. SOURCES OF FOULING DEPOSITS²⁶

<u>Raw Water</u>	<u>Airborne</u>	<u>Recirculating Water</u>
Colloidal organics	Dirt	Scale: CaCO_3 , CaSO_4 , MgSiO_3
Silt, dirt	Reactive gases - H_2S , SO_2 , NH_3	Corrosion products: Fe_2O_3
Soluble iron		Process leaks - hydrocarbons, sulfides
Microbial contamination	Microbial contamination	Microbial deposits

Fouling problems are complicated by microbial activity. Slime deposits on tubes not only interfere with efficient heat transfer, but act as a trap to enmesh suspended solids, further impeding heat transfer. In addition, by-products of bacterial metabolism influence water chemistry, including the tendency for scale to form or metal to corrode.

Rarely do corrosion, scale, and fouling occur independently of one another. Usually two or three develop together to cause loss of heat transfer and premature metal loss. Therefore, special care must be taken to avoid corrosion, scale, and fouling contaminants.

Makeup water control programs for cooling systems vary considerably because each installation presents different environmental factors and operating problems. A common method used within industry for the determination of the scaling tendency and corrosiveness of a water is the use of two calculable indexes - the Langelier and Ryznar. Both indexes make use of chemical equilibrium principles.

The Langelier Index makes use of the fact that each natural water supply is completely stable with respect to CaCO_3 solubility at a certain pH (pH_s). The pH_s can be calculated from water quality data, including calcium content, total alkalinity, temperature and total dissolved solids. Once the pH_s of the water is determined, it can be compared with the actual pH of the water. The Langelier Index is calculated from $(\text{pH} - \text{pH}_s)$. If the result is positive, the water is a scaling water - it is over saturated with respect to CaCO_3 . If the result is negative, the water is under saturated with respect to CaCO_3 and will attack the metal of the system in the presence of oxygen in an attempt to

obtain equilibrium. Therefore, the water in this condition is corrosive and the more negative the number the more corrosive the water.³¹

The Ryznar Index is a modification of the Langelier Index. Its intent is to reliably predict the likelihood of scale formation and corrosion in flowing systems. The Ryznar Index is calculated from $(2pH_s - pH)$. Ryznar Index numbers of about 7 indicate that the water is quite stable, neither corrosive nor scaling. The water becomes progressively more scale forming as the index drops below 6 and becomes progressively more corrosive as the index increases above 7.³²

Due to the extreme temperature changes that occur within cooling systems, scale and corrosion control by the Langelier and Ryznar Indexes alone rarely offer a satisfactory solution. This is because the pH_s is temperature dependent. The next step taken is chemical treatment of the water,^{21,32} which involves the addition of antifoulants, corrosion inhibitors, and microbicides to the makeup water. Chemical treatment of cooling water is beyond the scope of the current project.

Since the exact nature of the cooling system for a commercial PFH plant has not yet been defined, water treatment will involve providing water that is neither scale forming nor corrosive as indicated by the Langelier and Ryznar Indices. In addition, the water should be low in total solids and free from microbial contamination. Water of this quality is required for any open recirculating cooling system. As the cooling system is defined, an appropriate chemical treatment program can be developed.

Treatment Requirements

The liquid waste from the PFH process may be classified as a hazardous waste due to its toxicity characteristics.³³ The analysis of the liquid waste generated by hydrotreating a Tennessee shale (Table 6-11) shows three contaminants in concentrations that exceed current federal regulatory levels³⁴ (mercury, lead, and pyridine) and three contaminants with concentrations that exceed proposed federal regulatory levels³⁵ (acetonitrile, aniline, and cyanide). The concentrations for each contaminant are summarized in Table 6-18. Since an oil shale processing industry does not presently exist, the liquid waste is not a federally listed specific source hazardous waste.³⁶ However, as an oil shale processing industry develops, the possibility exists for the waste to be listed.

Table 6-18. REGULATORY LEVEL AND CONCENTRATION IN LIQUID WASTE

<u>Contaminant</u>	<u>Regulatory Level</u>	<u>Liquid Waste</u>
	----- mg/L -----	-----
Acetonitrile	20	360
Aniline	6	500
Cyanide	20	45
Pyridine	5	35
Mercury	0.2	3.1
Lead	1.5	2

Were the liquid waste regulated as a characteristic hazardous waste, treatment technology must be applied to render it non-hazardous before it can be discharged to a receiving stream or recycled in the combined PFH-power plant. The waste can be rendered non-hazardous by reducing the concentrations of contaminants to below standards developed by the regulatory agencies, possibly through an NPDES permit. Additional treatment will then be required to produce a water having acceptable qualities for reuse within the plant. All discharges will be subject to regulation under section 402 of the Clean Water Act, as amended.³⁷

If the waste becomes a federally listed hazardous waste, it must be treated and discharged subject to regulation under section 402 of the Clean Water Act, as amended.³⁶ Treatment cannot remove the classification from a listed hazardous waste. Further, federal regulations state that if any mixture contains a listed hazardous waste, the entire mixture becomes hazardous.³⁶ Therefore, if import water is mixed with the treated waste, the entire mixture is defined as hazardous. This would eliminate the possibility for waste liquid recycle. However, if the treated waste was delisted,³⁶ the waste may then be reused within the plant.

Biological Treatment of PFH Liquid Waste

Research on the biological treatment of liquid waste arising from the PFH process has been conducted at TTU since 1987. The use of biological treatment as the primary treatment method for the liquid waste was chosen because it is often a successful method of removing organic as well as some inorganic contaminants from a waste. The extended aeration modification of activated sludge was chosen because it is a relatively low-cost, reliable treatment alternative that responds well to both hydraulic and organic shocks that are often typical of industrial wastewater flows. Because the PFH process was still being developed at the time of the wastewater research, actual sour water was not available for testing. Therefore, biological studies were conducted using synthetic wastes. Nutrients and trace elements were added to synthetic wastes to assure that growth was not limited by nutritional deficiencies.

Initially, four compounds expected to be present in liquid wastes from the PFH process were selected for treatability studies: acetone, propionitrile, pyrrole, and thiocyanate. These compounds were selected because of their structural similarities to many of the other compounds expected to be present in the liquid waste. Following a period of acclimation, batch tests were conducted to evaluate the degradability of the four compounds, both individually and in combination. Extended aeration activated sludge test were subsequently conducted to determine the effectiveness of the biological population in degrading the contaminants in continuous flow regimes.

The results of the batch experiments using individual compounds were positive. The organic strength of solutions of three concentrations for each of the four compounds was greatly reduced using aerated, biologically seeded batch reactors. Biodegradation in double substrate experiments were similar to the pattern exhibited in respective individual substrate experiments. The final experiments of batch microbiological degradation included 150 mg/L of

each of the four compounds in a single reactor. All compounds were successfully reduced to less than 1 mg/L. When the four compounds were treated in a biological reactor under continuous flow conditions, all four compounds were degraded to concentrations less than 1 mg/L with a detention time less than 2 days. As a result of these tests, it was determined that all four of the compounds were biodegradable, at various concentrations, in a modified continuous flow extended aeration activated sludge process.²

Due to the success of biological degradation of the four compounds, research on the biological degradation of PFH sour water continued. Four additional compounds expected to be present in liquid wastes from the PFH process were selected for similar treatability studies. These compounds are aniline, phenol, MEK, and 4-methyl pyridine. As for the previous four compounds, synthetic wastes were used in the study. Following a period of acclimation, batch experiments were conducted to evaluate the biodegradability of the four compounds, both individually and in combinations.

Microorganisms were successfully acclimated to phenol, aniline, and MEK. However, acclimation of microorganisms to 4-methyl pyridine was unsuccessful despite numerous attempts. The results of individual batch experiments of phenol, aniline, and MEK were positive. The organic strength of solutions of three concentrations for each of the three compounds was greatly reduced using aerated, biologically seeded batch reactors. Degradation in double substrate experiments were also positive. Instances of preferential biodegradation were displayed but none of the compounds appeared to inhibit the biodegradation of the other compounds.

The final experiments of batch biological degradation included a combination synthetic waste with phenol and MEK at an initial concentration of 250 mg/L, and aniline and 4-methyl pyridine at 300 mg/L. The concentrations of phenol, MEK, and aniline were reduced to less than 1 mg/L. Preferential biodegradation occurred but inhibitive effects were not displayed. The concentration of 4-methyl pyridine decreased by about 46 percent during the test. The exact mechanism of removal for the 4-methyl pyridine is not known but possibilities include biodegradation or bioadsorption. It was experimentally determined that air stripping was not the mechanism of removal.

To date, continuous flow microbiological degradation tests have not been conducted on aniline, phenol, MEK, and 4-methyl pyridine. However, it is anticipated that successful biodegradation will occur under continuous flow conditions. Biodegradation will likely improve due to increased cell mass and better acclimated microorganisms.

As a result of the success of the biodegradation studies on synthetic wastes containing contaminants expected to be present in liquid waste arising from the PFH process, biological treatment of the PFH liquid waste remains a viable option for primary treatment of the waste. However, biological treatment cannot be considered the only treatment method that will be necessary to adequately treat the liquid waste.

Batch biodegradation tests on 4-methyl pyridine was unsuccessful. This is not to say that degradation of 4-methyl pyridine will not occur under

continuous flow conditions. This simply demonstrates the possibility that some organics present in the liquid waste may not be removed during biological treatment. This necessitates the need for consideration of post biological treatment steps to provide complete waste treatment.

In addition to the treatment of refractory organics, post biological treatment steps may be required by residual COD concentrations that may remain following metabolism of original carbon sources. The batch biodegradation studies on the synthetic wastes yielded effluent COD concentrations of about 20 to 40 mg/L. Similarly, continuous flow biodegradation experiments yielded average effluent COD concentrations of about 90 mg/L. In both cases, effluent concentrations of original substrates were below 1 mg/L.² Post-biological treatment will likely be required to reduce effluent COD concentrations.

Post-biological treatment considerations are also necessitated by water quality criteria for water reuse within the plant or discharge to a receiving stream. Post-biological treatment may be needed to polish the effluent from biological treatment to attain the stringent water quality criteria required.

Post-Biological Treatment

Although the chemical and physical characteristics of the effluent from a biological treatment unit treating actual PFH liquid waste and operating under actual continuous flow conditions will dictate the post-treatment methods to be used, preliminary estimates of post biological treatment may be made from available information.

Due to the stringent water quality required for high purity - high pressure boiler feedwater, treatment of the sour water for use as cooling water appears to be the most feasible alternative for reuse within the combined PFH-power plant. The complexity of the chemical composition of the sour water dictates that more than one post-biological treatment process may be needed to obtain a water suitable for reuse as cooling water. As a minimum it is assumed that biological treatment is followed by sedimentation and filtration. Following filtration a granular activated carbon (GAC) adsorption unit may be needed to remove refractory organics and residual COD concentrations. If organics persist past the GAC, a membrane process such as reverse osmosis may be needed. Reverse osmosis may also be required for the removal of inorganic dissolved solids. In addition, the use of the water for cooling water will require chemical treatment for bacterial control.

GAC has been demonstrated to be an effective method used in removing residual organic material remaining in the effluent of biological treatment processes. Many GACs are available and selection may depend upon adsorption characteristics as well as ease of regeneration. The GAC adsorption process is relatively inexpensive, and reactivation of the spent GAC may be cost-effective due to the capacity of the facility.³⁸ Filtration prior to the GAC unit should prevent premature plugging of the carbon bed by suspended solids.

The concentration of both organics and inorganics may be reduced by reverse osmosis. The rejection of inorganics by this process is well documented with removal rates ranging from 60 and 99 percent depending on the con

taminant being removed and the membrane used.³⁸ The development of membranes with low molecular weight cutoffs (MWC) have increased the organic removal efficiencies of membrane processes. Membranes with MWC values of 100 are available today. However, a MWC of 100 does not ensure that complete rejection will occur on organics possessing a molecular weight larger than 100.³⁸ Due to the extent of the pretreatment prior to the reverse osmosis unit, the chance of membrane fouling by excessive concentrations of organics should have been significantly reduced.

Cooling systems are sensitive to microbial contamination. Therefore, a final disinfection step is required for bacterial control. Chlorine is often used due to its ability to maintain a disinfectant residual.³⁸

If discharge is chosen in lieu of reuse, a treatment scheme similar to that described above may be necessary. Extensive treatment may be required for the sour water prior to discharge due to the increasingly stringent regulatory discharge policies.

Deficiencies of Data Needed To Complete a Conceptual Design

Prior to the completion of a conceptual design for the liquid waste management facility, various data must be obtained and various assumptions must be made. These current deficiencies can be grouped into two categories: 1) those that inhibit the completion of a treatment scheme for the sour water resulting from the PFH process and 2) those that inhibit the completion of an integrated waste treatment facility that not only treats the sour water but treats the necessary quantity of import water to satisfy total water quantity demands for a combined PFH-power plant. A listing of these deficiencies are summarized below. As research progresses, additional deficiencies will likely be encountered.

1. Various metals are present in the sour water. Some may pose a toxic threat to microorganisms in the biological unit. If this occurs, toxic metals must be removed prior to biological degradation. More data needs to be obtained on the metals present in the sour water and on their potential threat to the biological unit.
2. Some organics in the sour water may also pose a toxic threat to the biological unit. Additional information needs to be obtained on the organics present in the sour water and on their potential threat to the biological unit. If toxic organics are present, they must be removed prior to biological treatment.
3. Detailed calculations need to be performed on treatment units to determine each unit's potential for contaminant removal.
4. Detailed calculations need to be performed to size individual treatment units and to determine appropriate retention times.
5. Treatment schemes need to be developed that will provide for the treatment of import water to satisfy total water quantity requirements of a combined PFH-power plant.

6. Treatment schemes to handle the wastes generated during the treatment process (i.e., sludges, blow down, etc.) must be developed.
7. The treatment schemes for sour water, import water, and waste need to be integrated to complete a waste treatment facility that not only treats the sour water but treats the necessary quantity of import water to satisfy total water quantity demands while also providing for the treatment and disposal of waste generated during the process.

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Task 9. Information for the National Environmental Policy Act

The requirements of the National Environmental Policy Act (NEPA) are defined by statute. The objective of this task is to provide information to DOE relevant to the potential environmental impacts of the program tasks so that DOE can determine if an environmental assessment or environmental impact statement is required.

Discussion

IGT and the subcontractors working on the program prepared and submitted information to the DOE on the anticipated environmental, social, and historical impacts of the project on the local area. The NEPA document was reviewed and approved by DOE.

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