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RETORTING UNGRADED OIL SHALE AS RELATED TO IN SITU PROCESSING

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INTRODUCTION

Processes to recover oil from oil shale by in situ retorting are currently of great interest. Many investigators (1, 2, 3, 4, 5) have considered the possibilities of such a process because elimination of mining, crushing, and transporting the oil shale, and of disposing of the spent shale, could result in economic advantages over conventional aboveground processing. An in situ retorting technique may also make possible recovery of oil from deposits that are too deeply buried, too lean, or in beds too thin to be suitable for mining.

In situ retorting and recovery processes based on using nuclear explosions to fracture the oil shale have been discussed in the literature for several years (1, 2, 3, 4, 5). The fracturing would be accomplished by detonating a nuclear explosive near the bottom of an oil shale section at sufficient depth to insure complete containment. Following the detonation, collapse of the shale above the point of explosion would result in a nuclear chimney full of broken shale similar to a large batch retort. The size distribution of this broken shale would be different from that of any retorting charge previously investigated.

The properties of such a mass of broken oil shale are largely unknown. Predictions based on nuclear explosions in other rock types have been made about the size of a nuclear chimney in oil shale and the extent of fracturing beyond the chimney area (1, 2, 3). Assumptions based on particle size studies (3) indicate that pressure drops through a rubble column or nuclear chimney in oil shale should be low. Complete determination of the chimney characteristics, including radius, height, properties of the rubble column, and extent of the surrounding fractured area, will require a nuclear fracturing experiment in oil shale.

Following the development of the nuclear chimney, a retorting method that will recover most of the potential shale oil contained in the rubble column must be used. This method will be a batch operation capable of processing a mass of broken oil shale that will have a high bulk permeability, that will vary in size from sand-grain-sized particles to pieces several feet across, and that will vary in richness from barren shale to shale assaying 50 or more gallons per ton.

Previous research work on large-scale batch retorting methods which was done by the Bureau of Mines near Rifle, Colo. (6), studied the effects of particle size, air rates, and recycle gas rates on product recovery. Air rates studied ranged upward from 5 standard cubic feet per minute per square foot of retort cross section with recycle gas-to-air ratios of 0:1 to about 3:1. The retorts were operated using narrow particle size ranges. All fines, material smaller than 1/2 inch, were removed by screening, and the maximum particle size used was generally about 3-1/2 inches. The yield of oil from this experimental program ranged from about 60 to 90 percent of Fischer assay depending on particle size and grade of shale. This research did not include processing of large particles at low retorting rates.

The present study was started to determine the retorting characteristics of oil shale ungraded in size and varying greatly in richness. In general the oil shale charge used in the study has been mine-run material up to pieces as large as 20 inches in two dimensions. The third dimension may be as large as 36 inches, but because mine-run oil shale tends to be slabby this dimension probably averaged from 12 to 18 inches. Grade of the charge ranged from 26.0 to 48.0 gallons per ton by Fischer assay.

Air rates that have been investigated ranged from 0.58 to 1.94 standard cubic feet per minute per square foot of retort cross section. Recycle gas-to-air ratios have ranged from 0:1 to 4.27:1. These conditions have resulted in operating temperatures up to about 1,500°F. Yields of oil as high as 80 percent of Fischer assay have been obtained.

FIGURE 1. - Experimental oil shale retort.

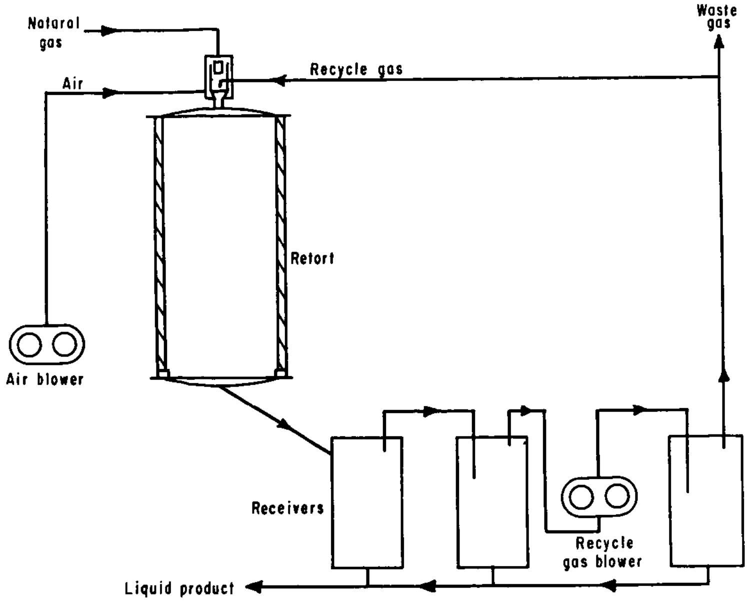

FIGURE 2.-Schematic Diagram of 10-Ton Retort.

FIGURE 3. - Block of retorted, partially burned shale.

EXPERIMENTAL PROCEDURE AND RESULTS

Apparatus

Figure 1 is a photograph of the Laramie 10-ton aboveground retort used for this investigation. The overall height of the unit is 34 feet. The retort vessel is 6 feet in diameter by 12 feet tall and has a cast refractory lining tapering from 6 inches thick at the bottom to 8 inches thick at the top. The vessel is suspended from the superstructure at three points to allow for expansion during the retorting operation. An electric hoist at the top of the superstructure, which extends 10 feet above the vessel, is used to load the oil shale charge.

A simplified schematic diagram (Fig. 2) shows the retort vessel and associated equipment. Auxiliary items are three recovery tanks, a recycle gas blower, and a primary air blower.

Located at the top of the retort vessel is a natural gas burner used to heat and ignite the shale charge. Natural gas supply for the burner is obtained from a gas line operating at about 5 psig. All of the gas supplied to the burner is measured, and samples for analysis are taken periodically.

Temperatures were measured and recorded by means of thermocouples inside thin-walled stainless steel tubes at 18-inch vertical intervals in the shale bed. Each tube or thermowell contained four thermocouples evenly spaced from the center to the outside edge of the bed. Additional thermocouples were attached to the outside shell of the retort vessel, to the gas meter, and to other points of interest. Temperatures were recorded by multipoint strip chart electronic recorders.

Rotary blowers were placed in the first two recovery tanks to agglomerate shale oil mist. The recycle gas blower was used for the same purpose, and the third tank was used for recovery of oil agglomerated by this blower.

In addition to the temperature recorders the instrumentation includes two gas flow-recorder-controllers and a process chromatograph. The flow-recorder-controllers are pneumatic instruments and were used to regulate and measure flow of recycle gas and stack gas. Gas sample inlets for the chromatograph were located at several points in the shale bed and also in the stack gas stream.

Oil Shale Charge

The oil shale charge for each experiment was prepared from mine-run shale that was obtained from the mine at Anvil Points Research Facilities near Rifle, Colo. Obtaining a representative sample of material varying widely in size and oil content is difficult, and the reliability of results based on these samples will have limits. To increase the reliability a procedure using the entire charge as a sample was developed. In this procedure the charge was segregated roughly by size into two parts, and all of the larger pieces were sampled by breaking them perpendicular to the bedding planes. The smaller pieces were sampled by a cone and quartering procedure.

Oil shale assay of the charges for these experiments ranged from 26.0 to 48.0 gallons per ton as shown in Table 1, arranged in order of increasing oil yield as a percentage of Fischer assay. Table 2 gives analyses of typical shale charges used in this study.

Since screening equipment of sufficient capacity was not available, it was necessary to determine the size distribution of each charge by separating the particles into the size catagories shown in Table 3 by actual measurement. Table 3 shows size distributions for several typical oil shale charges.

The oil shale charge was carefully loaded into the retort to avoid further breaking of the pieces. Shale particles were placed in the retort randomly in an attempt to avoid segregation by size.

Retorting

Retorting of the oil shale charge was started by heating with the natural gas burner. Length of time the burner was used ranged from a few hours to a few days. In general, external heating was not required after the top of the shale bed had been heated to about 350°F. At this temperature, stopping the flow of natural gas resulted in an immediate increase in the temperature of the shale bed because more oxygen was available for combustion of the shale.

Control of the retorting operation was based on bed temperature, on oxygen concentration in the stack gas, or on both factors. In some of the experiments a maximum bed temperature was chosen and air and recycle gas-flow rates were adjusted to maintain this temperature. In other experiments the flow rates were adjusted to maintain a minimum oxygen concentration in the stack gas and in still others to maintain a chosen oxygen concentration and a chosen temperature. In the series of experiments described here, two were made using air only with no recycle gas.

TABLE 1. - Summary of operations of the Laramie 10-ton retort

Experiment number	6	5	4	7	3	10	2	15	8	12 & 13	14	9	11
Oil yield, vol pct of Fischer assay	27.9	29.3	48.4	54.2	56.4	63.1	67.8	68.1	71.1	72.6	74.6	80.4	80.8
Fischer assay of charge, gal/ton	33.6	44.5	39.9	48.0	29.8	39.2	28.0	28.3	29.1	28.8	30.8	32.2	26.0
Air rate, scf/min/ft^2 of bed	0.84	0.71	0.84	1.00	0.58	1.06	1.33	1.94	0.85	1.04	1.11	1.23	1.36
Recycle gas-to-air ratio	3.94	4.27	0	0.92	6.90	1.34	2.67	0	0.61	0.36 1/	0.72	0.95	0.82
Total air, scf/ton	13,900	22,429	77,057	30,511	7,349	22,953	23,306	13,727	21,965	21,566	25,530	19,666	21,150
Total recycle gas, scf/ton	55,040	95,302	None	19,780	51,188	22,503	62,204	None	10,824	4,418 1/	18,428	16,984	12,575
Maximum bed temperature, °F	980	1,050	1,200	1,300	1,250	1,300	1,300	1,500	1,350	1,275	1,210	1,400	1,400
Selected oil properties													
Specific gravity, 60°/60°F	0.905	0.901	0.908	0.908	0.936	0.908	0.943	0.918	0.910	0.910	0.903	0.915	0.916
Pour point, °F	82	70	70	74	70	75	70	55	72	66	70	69	72
Viscosity, SUS @ 100°F	78	67	72	71	208	77	290	101	77	81	72	93	104
Nitrogen, wt pct	1.49	1.53	1.72	1.78	1.93	1.85	1.64	1.79	1.68	1.63	1.60	1.88	1.92
Sulfur, wt pct	0.81	0.80	0.98	0.86	0.78	0.86	0.60	0.89	0.91	0.80	0.78	0.76	0.77
Naphtha, vol pct of crude	1.5	3.5	5.0	6.6	1.2	7.9	0.8	7.0	7.7	6.5	7.1	6.7	4.8
Light distillate, vol pct of crude	23.8	27.0	26.5	20.5	13.4	20.9	11.5	20.5	24.0	23.7	25.3	18.5	21.0
Heavy distillate, vol pct of crude	26.8	42.8	44.2	41.5	42.2	47.9	40.9	38.4	45.9	40.7	42.8	38.2	40.3
Residuum, vol pct of crude	44.6	29.6	25.4	31.4	38.1	24.6	41.2	34.3	23.1	29.8	25.8	35.5	34.4
Gas composition, vol pct													
Nitrogen	77.6	75.3	76.6	74.0	74.7	72.3	80.0	68.1	74.3	74.0	75.3	72.5	74.0
Oxygen	4.3	7.9	8.9	4.9	10.3	6.1	6.1	2.1	4.9	4.5	6.5	3.8	3.5
Carbon dioxide	14.8	14.1	12.3	18.1	13.5	19.3	12.3	25.6	18.4	19.3	16.1	21.7	19.9
Carbon monoxide	2.0	2.0	1.4	1.6	1.1	1.3	1.1	2.6	1.5	1.2	1.3	1.5	1.5
Methane	0.9	0.7	0.6	0.5	0.4	0.7	0.5	1.1	0.6	0.6	0.5	0.4	0.8
Higher hydrocarbons	0.4	-	0.2	0.9	-	0.3	-	0.5	0.3	0.4	0.3	0.1	0.3

1/ Recycle gas was used during the last half of the run only.

Retorting runs were continued until the combustion zone reached the bottom of the retort. This point was determined from temperature measurements and also from sudden large increases in the oxygen concentration in the stack gas when these increases were caused by a decrease in the amount of carbonaceous material available for fuel. Retorting was assumed to be complete when the bottom thermocouples were at an average temperature of 900°F, and material balances were calculated over this period.

Following the retorting the shale charge was cooled in the absence of air. When cool, the spent, partially burned shale was dumped from the retort and sampled. Samples were assayed' for oil content and analyzed for carbon, hydrogen, nitrogen, and sulfur. Typical analyses are shown in Table 4.

During the retorting operation liquid products were collected in three recovery tanks. Part of the liquid product drained from the bottom of the retort and was collected in the first tank. However, much of the oil left the retort as a stable mist so mechanical methods of agglomerating were required. Impellors were placed in the first two recovery tanks to agglomerate mist particles, and the recycle gas blower was used for the same purpose. Oil agglomerated from the mist was collected in the three recovery tanks. Some oil mist or vapor was vented. Although no attempt was made to recover this material, the amount was determined by adsorption of oil from a measured quantity of waste gas.

The oil and water mixture was taken from the tanks at the conclusion of each experiment, and because shale oil and water form stable emulsions both gravity and distillation were used to separate the two. After separation samples of water and of oil were analyzed. Preliminary work, which will be expanded, indicates that the water contains some soluble organic compounds as well as inorganic materials. Selected properties of the oil samples are shown in Table 1.

Gas samples taken from the retort were continuously analyzed during each experiment. These analyses were used to control the operation, and to observe the progress of the combustion zone. Average values of each constituent in the stack gas for each experiment are given in Table 1.

DISCUSSION

Oil Recovery

Oil yields from 27.9 to 80.8 percent of Fischer assay were obtained from the 13 runs shown in Table 1. The major part of these variations in yield is due to changes in the measured and controlled operating variables such as air rate, recycle gas-to-air ratio, and Fischer assay of the oil shale charge, but the remainder of the variations in yield are due to uncontrolled variables such as shale particle size distribution and location of the particles in the retort bed. The effects of these uncontrolled variables may be of major importance in the retorting of an actual nuclear chimney in oil shale.

An oil yield of 80.8 percent of Fischer assay is not as high as yields reported previously (4, 6) for other internally heated retorts using carefully sized oil shale charges. However, for ungraded charges yields would be expected to be somewhat lower.

Losses of potential oil can be attributed to several factors. One such loss is shown in the first column of Table 4, where 21.1 gallons of oil per ton remained in the discharged shale. This type of loss can be caused by channeling or by operating at gas-flow rates too high to completely retort the large pieces. Another loss is due to oil discharged with the stack gas as vapor or oil mist. The loss averages about 5 pounds per ton of oil shale charge. Improvements in the recovery system can eliminate this loss. A third type of loss may result from burning the oil as it is formed or by burning the residual organic matter before the oil has been drained away. Losses of this type may be minimized by adequate control of the process parameters including air and recycle-gas flow rates and bed temperatures.

Retorting Rate

Retorting rates covered by this study ranged between 1 and 17 pounds of shale per hour per square foot of retort cross section, depending on operating conditions. No relationship between retorting rate and oil yield was observed during this preliminary investigation.

Liquid Product Properties

In appearance, oil from the 10-ton aboveground retort is similar to oils produced by other internally heated retorts. The oil is black and viscous, has relatively high pour point, and has a distinctive odor. Selected properties of the oils are shown in Table 1. Murphy (4) has shown that oils produced in conventional retorts operating near maximum conversion have similar properties. Table 5 compares the properties of the oils discussed by Murphy and some of the oils recently

TABLE 2. - Analyses of typical oil shale charges

Sample number	6	7	14	11
Oil, Fischer assay, gal/ton	33.6	48.0	30.8	26.0
Water, Fischer assay, gal/ton	2.4	4.6	1.8	2.8
Mineral carbon, wt pct	4.81	4.55	4.96	4.51
Organic carbon, wt pct	13.28	16.79	12.43	10.27
Total carbon, wt pct	18.09	21.34	17.39	14.78
Hydrogen, wt pct	1.88	2.34	1.82	1.53
Nitrogen, wt pct	.44	.56	.39	.35
Sulfur, wt pct	.58	1.02	.79	.72
Gross heating value, Btu/lb	2642	3454	2398	2037

TABLE 3. - Particle size distribution of shale charges, weight percent

Particle size, inches	Sample number 6	7	14	11
-2	36.9	13.0	30.1	72.0 (-2 and +2 -6 combined)
+2 -6	4.8	38.9	6.5	
+6 -12	13.9	10.3	15.9	9.2
+12 -20	14.8	20.7	18.4	6.3
+20	29.6	17.1	29.0	12.5

TABLE 4. - Analyses of discharged oil shale charges

Sample number	6	7	14	11
Oil, Fischer assay, gal/ton	21.1	0	1.0	0
Water, Fischer assay, gal/ton	1.7	0.8	0.5	0.8
Mineral carbon, wt pct	4.42	3.34	3.48	2.19
Organic carbon, wt pct	8.26	1.65	3.71	1.43
Total carbon, wt pct	12.68	4.99	7.19	3.62
Hydrogen, wt pct	1.05	0.14	0.23	0.14
Nitrogen, wt pct	0.36	0.12	0.21	0.09
Sulfur, wt pct	0.70	0.93	0.82	0.74
Gross heating value, Btu/lb	1528	153	504	137

TABLE 5. - Properties of shale oils

Properties	Conventional retorts[1] Gas-flow	Gas combustion	N-T-U	Aboveground retort[2] Experiment No. 14	11
Gravity, °API	17.3	20.0	22.0	25.2	23.0
Pour point, °F	80	85	90	70	72
Viscosity, SUS 210°F	58.0	50.4	45.8	36	38
Sulfur, wt pct	.70	.63	.80	.78	.77
Nitrogen, wt pct	2.20	2.09	1.90	1.60	1.92
ASTM distillation, °F					
Initial boiling point	225	290	196	122	122
5 percent distilled	463	446	436	348	392
50 percent distilled	641	-	662	690	735
Cut point	660	694	680	810	810
Recovery, percent	77	49	71	75	66

1/ Described by Murphy (4).
2/ Equivalent ASTM distillation was calculated from crude oil analysis distillation.

produced in the aboveground retort. The oil from the aboveground retort has a higher API gravity, lower pour point, and lower viscosity than the oils obtained from the other retorts. Sulfur and nitrogen contents are essentially the same.

Gas Composition

An average gas analysis for each experiment is given in Table 1. These gases have little fuel value and consist mainly of nitrogen and carbon dioxide. Small quantities of oxygen, carbon monoxide, methane, and higher hydrocarbons are present. The higher hydrocarbons are ethane and ethylene. Only trace quantities of propane have been observed.

Energy Considerations

An efficient batch retorting process should be able to derive most, or all, of its energy needs from combustion of the carbonaceous residue remaining on the spent shale. This residue amounts to about 25 weight percent of the organic matter that was present in the raw shale, and has a theoretical heating value of from 200 to 300 Btu per pound of raw shale. Since approximately 260 Btu are required to raise a pound of 28-gallon-per-ton raw shale to 900°F and retort it at that temperature (7), little or no heat other than that supplied by combustion of the organic residue is needed.

When retorting large particles of oil shale not all of the carbonaceous material remaining on the spent shale can be used as fuel. Figure 3 shows that a part of this material in the central portion of the larger particles may not be oxidized. Furthermore the rate of combustion may be too low to produce a useful amount or level of energy as the fuel is progressively burned from the outside portions of the particle. Therefore, in certain instances some additional fuel may be required.

The total volume of air used for these experiments varied up to 77,000 scf/ton of oil shale charge. Previous batch retorting (6) required 10,000 to 13,000 scf of air per ton. Both air and fuel requirements are related to the efficiency of the retorting system, with heat losses from the retort vessel accounting for a major part of the energy needs.

SUMMARY

Retorting oil shale ungraded as to size and oil content such as might be expected in a nuclear chimney is technically feasible. Yields as high as 80 percent of Fischer assay have been obtained by retorting ungraded shales with a maximum particle size of 20 inches in two dimensions.

The oils produced from these ungraded oil shale charges are similar to oils produced by other internally heated retorts but they tend to have more desirable properties. Their API gravities are higher, and their pour points and viscosities are lower. These more desirable properties are advantageous for transporting the oils or for further processing.

Sufficient carbonaceous material remains on the spent shale to furnish the energy requirements of the retorting process; however, in the larger particles this material may not be readily available for fuel. Air requirements for the experimental work varied widely.

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