MECHANISMS HELPING TO HEAT OIL-SHALE BLOCKS

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INTRODUCTION

Oil shale rubble piles, like those created in the vertical modified in-situ combustion process pioneered by Occidental Oil Shale, Inc., or those postulated in Project Bronco, consist of oil-shale blocks of assorted sizes. Heating these blocks through to produce their oil seemed a formidable problem until work in the Laramie Energy Research Center's large scale batch combustion retorts showed that temperatures high enough to evolve shale oil were attained completely through blocks weighing several tons (1-3)[1]. Although some anomalously high rates of temperature increase in shale blocks during combustion retorting have been reported (2,3) and explanations for these high rates attempted (5,9), the high rates appear too rapid for ready explanation. However, some mechanisms do operate to help heat oil-shale blocks and evolve their shale oil. Three separate mechanisms are identified: (1) thermal exfoliation of the shale; (2) gas evolution assisting and augmenting the exfoliation; and (3) combustion of light decomposition products from the organic matter in the oil shale. Existence of each of these is demonstrated and their combined effects are evaluated.

EXPERIMENTAL

Thermal Expansion and Exfoliation

ERDA's Laramie Energy Research Center developed apparatus to measure the thermal expansion and exfoliation effects on oil shale in relation to temperatures. The apparatus, to be described in detail elsewhere, consists of a position transducer suspended from one end of a beam and a stainless steel pad suspended from the other. The beam, supported on a knife edge at its center like a balance beam, is free to move. In operation the stainless steel pad rests on the flattened face of an oil-shale specimen prepared as a cylindrical core about 1/2-inch in diameter and 1-1/2 inches long. The pad contains a thermocouple for measuring the sample temperature. Weight on the beam is adjusted to place a small load (0.5 to 1 gm) on the core to maintain contact between the core and the pad. As the sample length changes during heating, the pad is moved which moves the position transducer to generate a corresponding electrical signal.

The sample rests on the bottom of a platinum tube equipped with a gas exit tube running up its side from the lower corner. A gas inlet is attached at the top of the sample chamber, permitting controlled flow of a selected gas around the sample. A bell jar over the beam closes the system and provides the complete atmosphere control so vitally necessary to oil-shale

1 Underlined numbers in parentheses refer to items in the list of references at the end of this report.

thermal studies (7). The sample chamber is surrounded by a furnace that provides rapid and uniform heat transfer to the sample. The heating rate of the furnace is programmable. This arrangement is very similar to the simultaneous DTA-TG-EGA apparatus developed for oil-shale study at the Laramie Energy Research Center (4).

Thermal expansion plotted with temperature is shown in Figure 1 for an oil-shale specimen cored perpendicular to the bedding planes from a 1-foot Mahogany zone sample yielding 35 gallons per ton. The sample was run in a nitrogen atmosphere and was heated at the rate of 10° C. per minute.

Several expansion events are recorded in Figure 1. The sample apparently began to increase in length as heating began. The initial lengthening probably expresses the linear expansion of the organic matter in the oil shale, undoubtedly many times (~20) larger than the mineral expansion. In 35 gallon per ton oil shale the organic matter represents about 40 volume percent of the rock (6). If the length increase between 50° and 100° C. is due to expansion of the organic matter, the organic matter's expansion coefficient is about 3.4×10^{-4} length per unit length per °C. This rather large linear expansion is on the order of but somewhat smaller than values in the same temperature range reported for asphalt and paraffin. Consequently it is not an unreasonable value. Its validity is limited, however, by possible inclusion of effects from the thermal event which occurs next.

The thermal expansion trace (Figure 1) shows that very rapid lengthening occurs through the temperature interval 190° to 225° C. By the time this sample had reached 225° C. it had increased its length by about 8 percent. This elongation is accompanied by sharp irregularities in the trace. These irregularities are real, expressing equipment response to sudden events, the development of fissures. Visual examination of a core sample heated through this temperature interval and then cooled reveals numerous fissures approximately parallel to the bedding planes.

Two factors contribute to development of these fissures in the temperature range from 190° to 225° C. The primary mechanism is failure due to thermal stress. This requires some explanation. Oil-shale cores perpendicular to the bedding planes cut many individual beds. Some contain relatively large amounts of organic matter and some contain relatively small amounts. Organic-rich layers will elongate much more rapidly than organic-poor layers. If these layers happen to be adjacent in the sample, a stress is developed. Weak planes fail suddenly, popping the shale apart. The partings are rarely completely across the specimen because the stress is relieved by partial failure. The second factor, the release of combustible gases, is treated later. However, it definitely contributes to the lengthening and to the uneven length trace.

Above 225° C. a period of little length increase appears, almost as if all the significant stress had been released. Above 300° C. a steady and gradual length increase again occurs.

At about 400° C. the organic matter begins to decompose rapidly. From 400° C. until about 485° C. the sample again shows rapid, irregular length increase. By the time it reached 485° C. this core had lengthened by almost 14 percent. Gas development is the predominant force producing this lengthening. In this temperature range the organic matter loses much of its physical competence, so evolving gases push some organic-tied layers apart.

When decomposition of the organic matter is completed at about 485° C. (Figure 1) additional heating produces little length increase. Between 485° C. and 1000° C. this sample increased in length by only 1.1 percent. Decomposition of dolomite and calcite, which occurred in this temperature range, produced no significant length change, either increase or decrease.

GAS EVOLUTION AND COMBUSTION

Oil shale is very sensitive to the presence of oxygen during heating. Smith and Johnson (7) used thermal analysis to evaluate this effect. Figures 2, 3, and 4 are extracted from that paper which gives a detailed discussion of applying thermal analysis to study of oil shale and other solid fuels. Description of the apparatus and the conditions of these runs are given there (7). Figure 2 shows the DTA (differential thermal analysis) and TG (thermogravimetry) behavior of oil shale heated in an inert atmosphere. The sample begins to lose weight at about 200° C., but its reactions are all endothermic. In Figure 3 oil shale is heated in air. Sensitivity was cut by a factor of 5 and the sample size was reduced to about 1/3 to keep the two exotherms on the chart. The two exortherms peaking at about 330° C. and 430° C. are due to combustion of the organic matter in two separate phases, the second of which is burning of carbon coke. Combustion of light ends to evolve heat definitely occurred by the time the programmed heating curve reached 200° C.

Oil shale heated in an atmosphere containing only 1 percent air (0.2 percent oxygen) shows significant heat production from oxidation of organic matter. Figure 4 shows DTA and TG traces for such a run. Sensitivity and sample size are back to those used in Figure 2. Heat from combustion of light organic fractions is being produced below the 200° C. point of the temperature program even though the oxygen supply is very small. Two exotherms are generated by oil shale heated in atmospheres containing 20 percent or 0.2 percent oxygen, although their intensities decrease with smaller oxygen concentrations. The important point is that the oil shale produces significant heat by oxidation even at very low oxygen levels.

DISCUSSION

Oil-shale specimens not only expand during heating but show two separate temperature zones of fracturing. Although the behavior of only one sample is shown (Figure 1), other oil shales exhibit similar behavior. This fracturing, occurring under no load in these experiments, will also occur in an oil-shale rubble pile. In a rubble pile the shales are subjected to

point loads. At other locations on a block the shale is free to expand and fracture into surrounding void space under essentially no load.

The two separate zones of rapid expansion with fracturing are particularly important to heating of oil shale. This is graphically demonstrated by comparing the temperature locations of the oxidation exotherms in Figures 3 and 4 with the temperature locations of the rapid expansion. Expansions (which occur in any atmosphere) coincide with combustion exotherms in an oxygen-bearing atmosphere. In addition the expansion trace in Figure 2 shows that in these zones of rapid expansion the core both expands and contracts. During expansion the surrounding atmosphere, oxygen-bearing in combustion-based processes, is sucked into the core, then expelled with the contractions. This automatically provides oxygen and expels combustion products. The combustion itself may provide some atmosphere exchange. By burning rapidly the gases may be unable to transfer heat rapidly to the surrounding oil shale. Gas pressure capable of expelling the remaining combustion products would build. The remaining gas would then cool by gradually heating the surrounding rock. This would draw in additional oxygen-bearing gas.

In addition to the heat effects inside the block, the combustible gases evolving from the shale will travel out from the block. They have been observed evolving and burning along fissures in oil-shale blocks. Such combustion at the block surface provides heat to the block and its immediate atmosphere.

After retorting is completed, the carbon residue is distributed throughout the shale block. Because the original organic volume fraction has shrunk by 90 percent (8), the spent shale is now porous. The carbon residue is available for burning if oxygen can reach it. The fissuring produced by heating the oil shale provides access routes which help oxygen diffuse into the spent shale.

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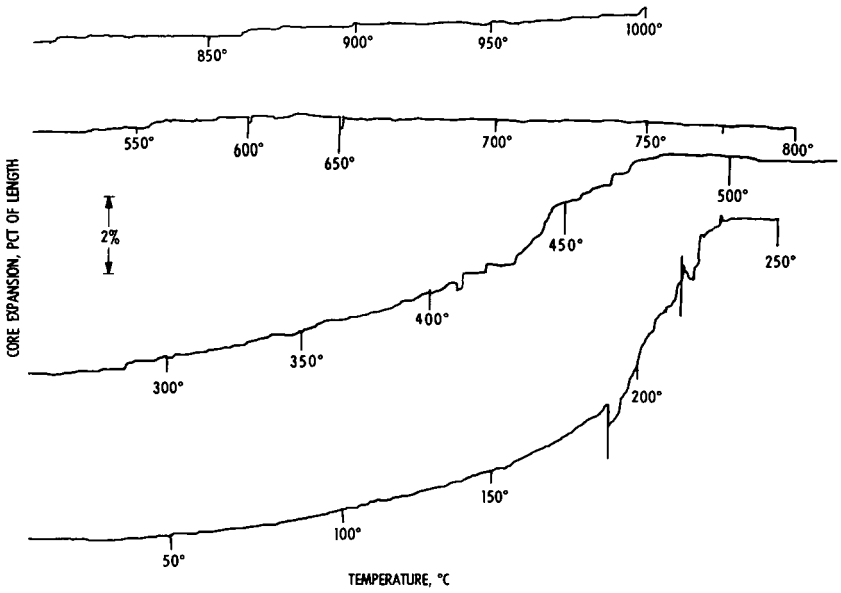

Figure 1. Thermal expansion of oil-shale core cut perpendicular to bedding planes.

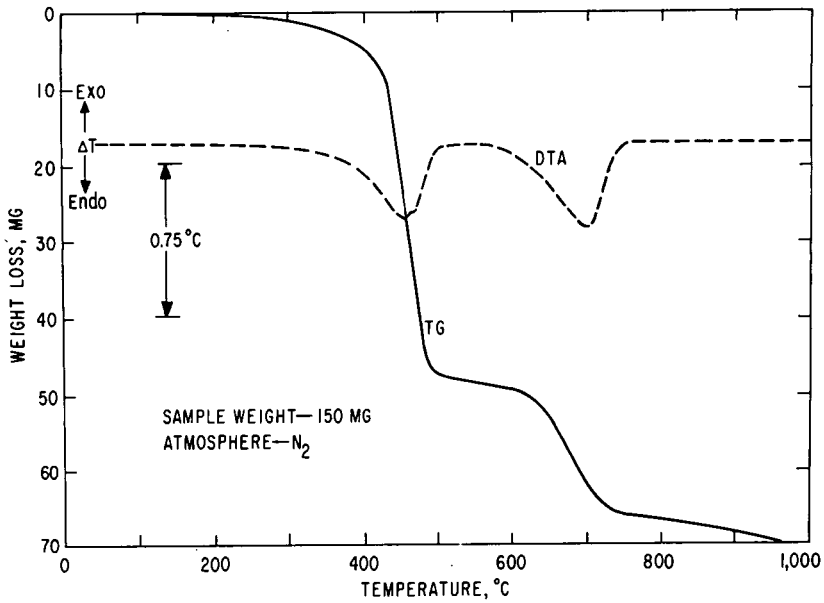

Figure 2. Thermal analysis (DTA-TG) of oil shale in an inert atmosphere.

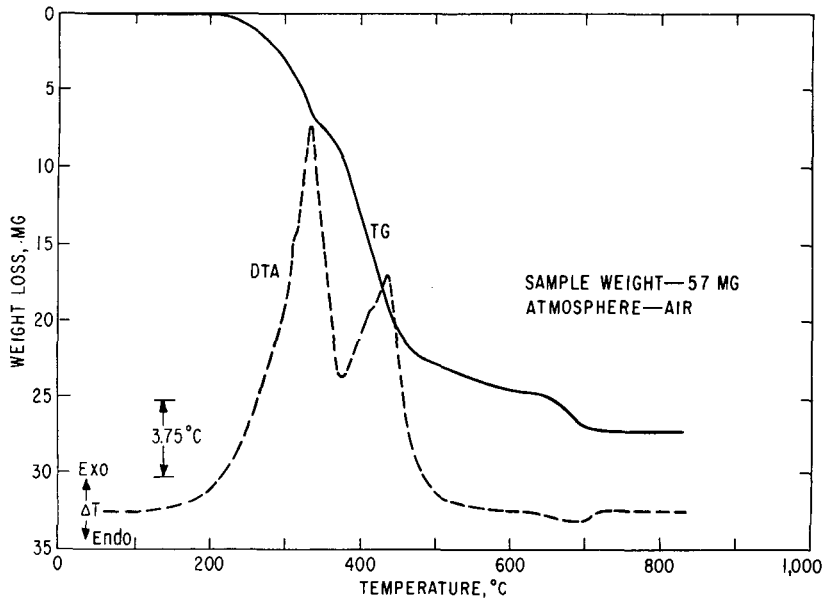

Figure 3. Thermal analysis (DTA-TG) of oil shale in air.

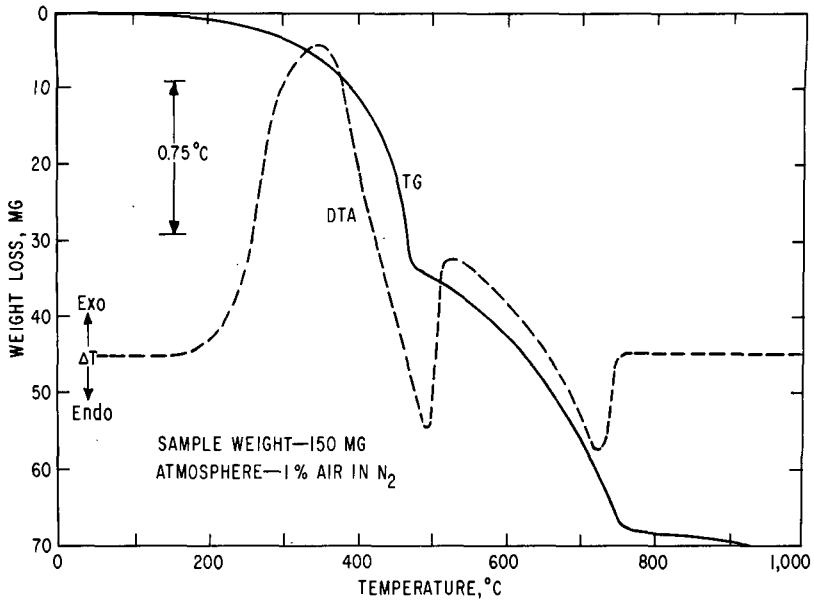

Figure 4. Thermal analysis (DTA-TG) of oil shale in 1 percent air in inert atmosphere.