ELECTRICAL AND THERMAL TRANSPORT PROPERTIES OF GREEN RIVER OIL SHALE HEATED IN NITROGEN

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Abstract

The electrical and thermal transport properties of selected grades of Green River oil shale were characterized by simultaneous parameter measurement techniques. Data were obtained on thermal conductivity, thermal diffusivity, dielectric constant, dielectric loss tangent and differential thermal analysis of Green River oil shale heated in a nitrogen environment.

Thermal conductivity varies from 0.2 to 1.0 BTU/ft-hr-0°F and tends to decrease with increasing temperature. The thermal diffusivity varies from 0.2 to 0.45 ft²/day and also tends to decrease with increasing temperature. Both thermal conductivity and thermal diffusivity decrease with increasing kerogen content.

Dielectric constant, which measures electrical energy stored in the material, decreases with increasing frequency. As temperature increases, dielectric constant initially decreases; then increases again, attaining values close to room temperature value. Loss tangent, a measure of electrical energy absorbed by the material, decreases with increasing frequency and increases with increasing temperature. At temperatures approaching the retorting temperature, a secondary peak appears in the loss tangent. This peak correlates with the onset of kerogen decomposition, as indicated by DTA. These data are indicative of potential applications as retort diagnostics and electrical heating and fracture processes.

Introduction

Although oil shale retorting is a thermal process, the thermal transport properties of oil shale are incompletely known (Cameron Engrs. 1974). Thermal conductivity is a measure of the static thermal response of the material. However, dynamic thermal response, or temperature-time distribution in the material, is determined by thermal diffusivity. Thus, both thermal conductivity and thermal diffusivity are needed to calculate heat flow through a material since they constitute the thermal transport properties of the material. Previous studies employed transient line probe techniques that do not suitably average over the structural heterogeneities created by the varve structure in oil shale (Tihen and others 1968; Prats and O'Brien 1975). Both of these parameters have not been directly measured on similar samples, but, instead, have been inferred from data published by different authors.

The electrical properties of minerals have been used in geophysical prospecting applications for many years (Keller and Frischnecht 1967). Recently, electrical techniques have been studied as possible ore bed heating and fracture tools (DuBow, ed. 19 ). The electrical transport properties consist of dielectric constant, a measure of the fraction of energy in an electric field stored inside the material, and loss tangent, a measure of the fraction of the energy in an electric field dissipated by
material (Parkhomenko 1967). Other sets of parameters may equivalently describe these properties. These electrical transport properties vary as a function of applied frequency of excitation, as a function of temperature, and also as a function of the grade of oil shale. Evaluation of potential applications of electrical properties requires these data to be available. Moreover, the electrical and thermal properties of many materials are interrelated (Smith and others 1967). The simultaneous measurement of both parameters, using techniques described below, can help elucidate the origins of variations in the electrical and thermal properties of the material.

Our approach has been to measure thermal and electrical properties simultaneously, as a function of temperature and potential oil yield. Specifically, thermal conductivity and a.c. electrical impedance were measured simultaneously, as a function of temperature and potential oil yield. A.c. electrical impedance and differential thermal analysis were measured simultaneously, as a function of temperature and potential oil yield. In addition, thermal diffusivity was measured as a function of temperature and potential oil yield.

Measuring thermal and electrical properties simultaneously tends to eliminate inter-sample artifacts and highlight interparameter relationships. In addition, these techniques yield certain derived parameters, such as dipole activation energies, structural transition temperatures and temperature coefficients of expansion and resistance (DuBow and Nottenburg 1976). In order to improve the resolution and repeatability of the experiments, experimental techniques have been automated, using an HP 2100 minicomputer and an 8080 microprocessor system. The digital control and data acquisition system allows data storage for future studies and results in a larger quantity of data being obtained in a shorter time than manual techniques allow.

Although measurements were made simultaneously, results will be presented sequentially in order to unify the thermal and electrical characteristics. Experimental technique and data reduction will be discussed in the sections describing individual properties.

Thermal Conductivity

Thermal conductivity was obtained simultaneously with a.c. electrical impedance. The electrical impedance portion of this measurement and simultaneous DTA/electrical impedance measurement are described in the electrical impedance section.

Thermal conductivity data were obtained, using the comparative technique (Tye 1967). Figure 1 shows an outline of the test stack. The weight on top of the stack corresponds to an applied uniaxial load. A temperature gradient is impressed across the test stack via the upper and lower stack heaters. This temperature gradient divides among the upper and lower pyrex discs and the oil shale sample under test. Copper electrodes make electrical contact with the shale for impedance measurements and help improve thermal contact between the oil shale and the pyrex reference discs.

From the temperature drops across each of the test stack elements, thermal conductivity may be obtained from the following equation (Tye 1967)

$$K_S = \frac{\Delta T_B}{\Delta T_T} \left[ \frac{L_S}{L_T} \frac{\Delta T_T}{K_T} + \frac{L_B}{L_B} K_B \right]$$

where $S$, $T$, and $B$ refer to the oil shale, top reference and bottom reference, respectively. $L$ is the thickness, $\Delta T$ the temperature drop, and $K$ the thermal conductivity. Three zone guard heating was used to minimize lateral heat flow and to maintain one-dimensional heat flow. The gaseous environment has a significant effect upon the thermal properties of oil shale. Even small amounts of air in the test stack volume results in an exothermic decomposition that dominates thermal conductivity (Smith and others 1967). Therefore, all measurements were carried out in a rapidly-flowing, nitrogen atmosphere. Samples were two in. (5 cm) in diameter and 3/4 in. (19 mm) thick.
Figure 1. - Thermal conductivity test stack.
In figure 2, thermal conductivity for five different grades of oil shale is plotted as a function of temperature. The thermal conductivity exhibits a gradual decrease with temperature and with increasing oil yield.

The samples appear to cool down rapidly during the reaction, indicating occurrence of endothermic behavior. This agrees closely with the DTA data, discussed in subsequent sections. Measurements are difficult during endothermic decomposition of kerogen, due to inability to obtain thermal equilibrium. Samples heated at low nitrogen flow rates develop a white, ashy aureole, adjacent to their external surfaces, indicating oxidation of residual carbon from decomposition of organic matter. This behavior is even more pronounced for samples with high oil-yield (40 gpt (0.18 m³) or greater); these samples undergo such strong exothermic reactions that temperatures cannot be controlled accurately. The "richer" samples also lose structural integrity at temperatures greater than 400°C.

A marked change in thermal conductivity is also seen, in all cases, after decomposition of organic matter, except for samples with very low oil-yield. This would seem to suggest that samples with low organic content exhibit a smaller temperature variation of thermal conductivity than those with high organic content; the fall-off in thermal conductivity values is quite appreciable; final values in some cases approaching 50 percent of original value. The initial sharp decrease in thermal conductivity with temperature, observed for some samples, is correlated with loss of capillary water. This observation is corroborated by thermal behavior of these samples, as shown by DTA; a sharp change in the slope of the baseline and a gradual endothermic behavior (starting around 170°C), preceding the main decomposi-
tion endotherm due to organic matter, are interpreted as arising from the same effect. We made no attempt in our experiments to control the amount of moisture initially present in the samples.

Thermal Diffusivity

We measured thermal diffusivity with the laser-flash technique (Lindroth 1974). The experimental setup is shown in figure 3. The laser is a high power, carbon dioxide laser, chosen because 10.6 micron radiation is strongly absorbed in most rocks. The laser beam, expanded by a 3:1 beam expander, illuminates the oil shale sample which is enclosed in a cylindrical tube, oven-heated to a preset temperature. The temperature-time history of the sample's rear surface is obtained with a thermocouple whose signal is amplified by a high-gain, low-noise amplifier and recorded in a transient digitizer for subsequent transmission to a computer or an oscilloscope.

From the temperature-time history of this surface, the thermal diffusivity may be obtained according to

$$\alpha_S = \frac{1.37 L_S^2}{t_{1/2}}$$

where, $\alpha_S$ is the thermal diffusivity of the oil shale, $L_S$ is the thickness of the oil shale disc, and $t_{1/2}$ is the time it takes for the oil shale sample to attain one-half the maximum change in temperature obtained upon heating with the laser. Samples are approximately 7/8 in. (22.2 mm) in diameter; thickness is approximately 3/16 in. (4.77 mm). Temperature gradients across the sample are typically 2 to 5°C. It is worth noting that only relative, not absolute, measurements of temperature are required.

The results of measurements of thermal diffusivity of Green River oil shale are summarized in figure 4. Thermal diffusivity is seen to decrease with increasing temperature and oil yield. Trends in variation of this parameter, significantly enough, closely parallel changes observed in thermal conductivity of the material. No corrections for heat losses have been attempted in

![Figure 3. - Thermal diffusivity block diagram.](image-url)
the present data since temperatures employed are below the range where radiative heat losses become significant. The small, surface area-to-thickness ratio of oil shale test samples also serves to minimize radiative heat loss and satisfies the requirement of one-dimensional heat flow, essential for application of the "flash-technique." Thermal diffusivity values, found in the present investigation, are somewhat lower than values calculated by Prats and O'Brien (1975) from thermal conductivity data.

Dielectric Analysis/Differential Thermal Analysis (DA/DTA)

In order to estimate the effect of chemical reactions and changes of phase upon electrical and thermal impedance, we developed a technique consisting of simultaneous measurement of a.c. electrical impedance and differential thermal analysis. We modified a DTA apparatus, including electrodes for measuring electrical impedance at selected temperature intervals.
Figure 5. - Sample vessel for DA/DTA.

Figure 5 depicts the sample vessel for DA/DTA. The sample and reference discs are 7/8 in. (22.2 mm) diameter and 1/4 in. (6.4 mm) thick. The experiments were run, using intact cores of oil shale, in contrast to most previous DTA investigations in which DTA is run on powdered samples. Pulverization of the sample could alter its thermal and electrical properties. As indicated in figure 5, the sample is held, under pressure exerted by two stainless steel springs, between two silver electrodes. Nitrogen is flushed through the sample chamber in order to suppress exothermic reactions.

Figure 6 is a representative DTA curve on a 40 gpt (0.18 m³) oil shale sample. Thermal decomposition of organic matter in the shale is seen to be endothermic in nature and takes place in the range, 400-500°C. Note that decomposition temperatures are markedly dependent on source and type of oil shale. Considerable variations have been observed in temperatures corresponding to the decomposition of the organic matter - peak temperatures, in some cases, being as low as 350°C. The thermal and depositional history of any sample is therefore of extreme importance to its useful characterization by DTA. Splitting of the endothermic peak (fig. 6) could result from multi-step decomposition of the organic matter, or from decomposition of minerals, such as pyrite or magnesium siderite (Smith 1977). Using selected temperatures (typically 20° intervals), we measured a.c. electrical impedance over the frequency range, 10 Hz to 10⁶ Hz, thus obtaining dynamic a.c. impedance measurements during the course of the chemical reactions.

A.C. Electrical Impedance Measurements

A simplified block diagram of the a.c. electrical impedance set-up is given in figure 7. The measurement sequence is cyclic;
a.c. impedance is obtained over the frequency range $10 \text{ Hz to } 10^6 \text{ Hz}$. Upon a signal from the microprocessor, the frequency synthesizer applies a sine wave signal simultaneously to the oil shale and to the reference channel of the gain phase meter. The gain phase meter determines relative attenuation and phase shift of the signal as it passes through the shale. Time needed to perform this measurement depends upon frequency, being considerably shorter at higher frequencies. After an appropriate settling time, the microprocessor transmits attenuation and phase shift to the minicomputer which, in turn, stores the data on magnetic tape for subsequent processing. The computer then sends a signal to the microprocessor, indicating the data acquisition cycle is completed, and the measurement cycle repeats.

From attenuation and phase, equivalent electrical resistance and capacitance of the sample are computed. System response is automatically subtracted from the raw data during analysis. From the sample's geometry, resistance and capacitance, dielectric constant and loss tangent are calculated. These material-dependent, "constitutive" parameters are more general than the geometry-dependent, electrical impedance parameters (von Hippel 1954). Dielectric constant is a measure of the fraction of energy in the electric field energy stored in the material, while loss tangent is a measure of the fraction of energy in the electrical field.

![Electrical impedance block diagram](image)

Figure 7. - Electrical impedance block diagram.
Figure 8. - Low temperature dielectric constant of 66.7 gpt (0.302 m³) oil shale.

dissipated by the material. These two parameters commonly characterize the dielectric properties of a material, although numerous other equivalent parameter sets could also be used (von Hippel 1954).

Figures 8 and 9 depict the behavior of dielectric constant of 66.7 gpt (0.302 m³) shale as a function of temperature and frequency. Similar behavior was observed for other grades. Dielectric constant is seen to decrease from a relatively high value at low frequencies (412 Hz) to a lower value at high frequencies. In addition, dielectric constant is seen to decrease initially with increasing temperature. However, at about 250°C, dielectric constant is seen to begin increasing again, especially at lower frequencies. At temperatures where significant amounts of organic decomposition occur, dielectric constant attains values approaching low temperature values. However, falloff with frequency is more rapid. The origins of this effect are as yet not well understood. Pore pressure effects and capillary water in the shale could possibly play a role in this effect. This possibility is indicated by the shift in baseline slope on the DTA at about 250°C.

Typical data, showing variation of dielectric parameters with frequency, are shown in table 1 for a 37 gpt (0.17 m³) oil shale sample. The dielectric constant, ε', shows the frequency dependence, characteristic of water-bearing sedimentary rocks and minerals (Parkhomenko 1967): a sharp decrease in dielectric constant at low frequencies, and relative insensitivity to frequency at higher values, typical for all samples studied. The high values of dielectric constant found for the oil shale samples may be explained in terms of the Maxwell-Wagner theory for interfacial polarization (Cole 1961). The presence of semi-conducting clay particles, giving rise to a membrane effect, might also account for the large values of dielectric constant (Keller and Licastro 1959). The data, shown in table 1, also reveal a sharp increase in a.c. conductivity with increasing frequency. This behavior is consistent with Parkhomenko's published work on the electrical properties of limestone, marl and dolomite (1967). This shows that the less the water-content, and/or the higher the resistivity of the material, the greater the decrease in resistivity with increasing frequency. Water content of oil shale is variable; it seldom exceeds 6-10 percent, however, a figure well within the limits observed for sedimentary rocks exhibiting similar dielectric behavior.
The nature of dispersion observed in oil shale for the loss tangent, \( \tan \delta \), is shown by a typical curve (Fig. 10) for a 26 gpt (0.12 m\(^3\)) sample. Presence of a broad peak, at low frequencies (<1000 Hz), is interpreted in terms of interfacial polarization effects. Occurrence of secondary maxima in \( \tan \delta \), at higher frequencies, observed only at higher temperatures, is also significant. The peak maxima show a pronounced dependence on temperature, shifting to higher frequencies with increasing temperature. It is possible to extract activation energies for dipole relaxation processes from such temperature dependent behavior. In materials as heterogeneous and complex as oil shale, the wide range of relaxation times significantly complicates the interpretation of these data. Dependence of the magnitude of \( \tan \delta \) on temperature also indicates that at high temperatures, where \( \tan \delta \) shows values of less than 1, conduction is primarily ohmic; thereas, at low temperatures (\( \tan \delta < 1 \)), conduction is by displacement mechanisms. This behavior is consistent with observed changes in resistivity of oil shale with temperatures; changes in resistivity, of over five orders of magnitude, are commonly observed for oil shale samples.

Figure 11 shows loss tangent versus frequency for a 29.8 gpt (0.14 m\(^3\)) shale. The same major features are observed as for the 26 gpt (0.12 m\(^3\)) sample. A secondary peak in the loss tangent appears at temperatures where organic decomposition begins to occur, as indicated by the DTA curve. However, temperatures at which this secondary peak begins to occur are lower for higher grade shale.

Figure 12 shows the temperature dependence of dielectric constant of oil shale for different grades, ranging from 7.5 to 60 gpt (0.034-0.302 m\(^3\)). Sharp changes in \( \varepsilon' \) values, at temperatures in the range 100-150\(^\circ\)C, are possibly correlated with loss of capillary water and change in pore structure of samples. The pronounced increase in dielectric constant, at temperatures above 270\(^\circ\)C, probably arises from the onset of decomposition of organic matter. Thermal behavior of samples, as shown by their DTA carried out simultaneously under the same conditions, exhibits remarkably similar trends and points towards a common origin for observed effects.

### Table 1. - Dielectric analysis of Green River oil shale, 37 gpt (0.17 m\(^3\)).

<table>
<thead>
<tr>
<th>Frequency (c/s)</th>
<th>Resistivity (ohms-cm)</th>
<th>Capacitance farads</th>
<th>( \varepsilon' )</th>
<th>( \varepsilon'' )</th>
<th>( \tan \delta )</th>
<th>A.C. Conductivity (mho-cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.100 x 10(^{11})</td>
<td>0.161 x 10(^{-10})</td>
<td>18.54</td>
<td>1.831</td>
<td>0.098</td>
<td>0.102 x 10(^{-10})</td>
</tr>
<tr>
<td>50</td>
<td>0.442 x 10(^{10})</td>
<td>0.164 x 10(^{-10})</td>
<td>18.90</td>
<td>0.829</td>
<td>0.043</td>
<td>0.231 x 10(^{-10})</td>
</tr>
<tr>
<td>100</td>
<td>0.236 x 10(^{10})</td>
<td>0.164 x 10(^{-10})</td>
<td>18.91</td>
<td>0.776</td>
<td>0.041</td>
<td>0.432 x 10(^{-10})</td>
</tr>
<tr>
<td>1000</td>
<td>0.480 x 10(^{9})</td>
<td>0.150 x 10(^{-10})</td>
<td>17.21</td>
<td>0.382</td>
<td>0.022</td>
<td>0.212 x 10(^{-9})</td>
</tr>
<tr>
<td>4000</td>
<td>0.369 x 10(^{8})</td>
<td>0.142 x 10(^{-10})</td>
<td>16.28</td>
<td>1.240</td>
<td>0.076</td>
<td>0.276 x 10(^{-8})</td>
</tr>
<tr>
<td>10,000</td>
<td>0.963 x 10(^{7})</td>
<td>0.134 x 10(^{-10})</td>
<td>15.35</td>
<td>1.901</td>
<td>0.124</td>
<td>0.106 x 10(^{-7})</td>
</tr>
<tr>
<td>52,000</td>
<td>0.113 x 10(^{7})</td>
<td>0.108 x 10(^{-10})</td>
<td>12.39</td>
<td>3.113</td>
<td>0.251</td>
<td>0.102 x 10(^{-6})</td>
</tr>
<tr>
<td>94,000</td>
<td>0.808 x 10(^{5})</td>
<td>0.552 x 10(^{-11})</td>
<td>6.35</td>
<td>2.410</td>
<td>0.380</td>
<td>0.126 x 10(^{-6})</td>
</tr>
</tbody>
</table>

Conclusion

In these experiments, we observed a significant, close similarity, with temperature variation, in trends of different thermal and dielectric parameters of oil shale. Results indicate that interpretations, based on a combined use of thermal and dielectric
Figure 10. - Temperature dependent loss tangent versus frequency for 26.0 gpt (0.12 m³) oil shale.

measurements, yield valuable information required for a complete characterization of thermophysical behavior, especially for complex, heterogeneous materials like oil shale. Further work, aimed at accounting for observed trends in terms of a unified model, is in progress. Application of electrical prospecting methods to oil shale, particularly induction and radio wave methods, requires knowledge of frequency dependence of its electrical resistivity and dielectric constant. A detailed investigation of the relationships observed in the present work should be useful in explaining mechanisms of polarization and providing a basis for a theory on the behavior of oil shale in a.c. fields.

Results of this investigation show that when oil shale is heated in nitrogen:

1) Thermal conductivity decreases with increasing temperature and increasing grade and attains values ranging from 0.2 to 1.0 BTU/ft-hr °F;
2) Thermal diffusivity decreases with increasing temperature and increasing grade and attains values from 0.2 to 0.6 ft²/day;
3) Dielectric constant decreases with increasing frequency and attains relatively high low frequency values of over 400;
4) Dielectric constant initially decreases with increasing temperature and then increases. At temperatures where significant organic mat
Figure 11. - Temperature dependent loss tangent for 29.8 gpt (0.14 m³) oil shale.

...ter decomposition occurs, the low frequency dielectric constant attains its low temperature values;
(5) Loss tangent decreases with increasing frequency and increases with increasing temperature;
(6) At temperatures where significant organic matter decomposition occurs, the loss tangent begins to exhibit secondary peaks at frequencies around 10⁵ Hz;
(7) DTA data and changes in dielectric property data correlate well.

The thermal and electrical data developed can be used to develop sensors for retort diagnostics and to investigate the feasibility of novel electrical processing and prospecting options for oil shale.

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Figure 12. - Low frequency dielectric constant versus temperature for various grades of oil shale.

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