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THERMAL DIFFUSIVITY OF GREEN RIVER OIL SHALE BY THE LASER-FLASH TECHNIQUE

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ABSTRACT

The thermal diffusivity of Green River oil shale has been measured by the laser-flash technique. Measurements were carried out in the temperature range 25–350 °C and for various grades of shales ranging from 6 to 100 gal./ton. The thermal diffusivity (α) is seen to decrease with increasing temperature, especially for shales with low organic content. Richer shales, on the other hand, show very little sensitivity in their α values to temperature and grade. The α values measured for Green River oil shales fall in the range 0.1–0.9 $\times$ 10^{-2} cm^2/sec. Anisotropic effects were also observed for these α values; shales cored parallel to their bedding planes have diffusivities about 20–30% higher than those for the samples cored perpendicular to the stratigraphic planes. The presence of pore water in the shale is also shown to have a significant effect on α.

INTRODUCTION

Efficient utilization of technologically important materials like oil shale requires good characterization of their thermophysical behavior. Accurate knowledge of thermal transport parameters like thermal conductivity and thermal diffusivity is essential for the design of above-ground and in-situ retorting schemes currently envisioned for the extraction of oil from oil shale. Thermal diffusivity determines the temperature–time history in a material for a given set of boundary conditions; it is a critical parameter for the diffusion of heat under various thermal excitation schemes. Furthermore, a knowledge of the thermal diffusivity enables calculation of another useful thermophysical property, namely, the thermal conductivity through the equation

$$\alpha = \frac{\kappa}{\rho c} \tag{1}$$

where α is the thermal diffusivity, κ the thermal conductivity, ρ the density and c the specific heat of the material. A direct and rapid measurement of the thermal diffusivity of oil shale would therefore be useful for determining the heat flow mechanisms in a

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heated block of shale. These data, when combined with the thermal conductivity and specific heat values, will provide the information necessary for modelling heat flow mechanisms in shale beds. Accordingly, this investigation was undertaken with a view to measuring the thermal diffusivity of Green River oil shale experimentally as a function of temperature, organic content and the orientation of bedding planes. The experimental results were subjected to various statistical analyses and equations developed to illustrate the relationship of thermal diffusivity to the various parameters chosen as the experimental variables.

The thermal diffusivity was measured by application of the "laser-flash" technique[1]. This technique was chosen for the proposed study in view of its inherent advantages over other methods available for the measurement of thermal diffusivity. Firstly, the problem of thermal contact resistance is totally eliminated in this method. Secondly, the absolute accuracy of temperature sensors is not a limiting factor in the accuracy of the results, since only relative temperature changes are measured. Thirdly, no information is required on the amount of thermal energy deposited on the sample. The technique is also rapid and could be of potential use as a diagnostic tool in field applications of oil shale[2].

Literature data on the thermal diffusivity values of Green River oil shale is fragmentary[3, 4]; experimental[3] and calculated[4] values are available only for a limited range of temperatures and shale grades. Moreover, the only published report on the experimental measurement of the thermal diffusivity of Green River oil shale[3] utilizes the transient line-probe method[5] which is subject to several experimental difficulties mentioned above. The problems of thermal contact resistance are particularly severe with this technique. According to Tihen et al.[3], "Perfect contact between the shale and the heating source is not attainable; therefore the first part of the curve must be corrected for the error which imperfect contact introduces". This method also involves determination of thermal diffusivity by measurement of the slopes of heating curves; this introduces an additional error, especially when only the first part of the curve is utilized[3]. Steady-state techniques, as applied to thermally active materials like oil shale, are also often handicapped by their inability to resolve time and temperature dependent conduction phenomena. The above difficulties are overcome by the transient nature, short measurement times and remote heat sources employed in the flash method for the determination of thermal diffusivity.

EXPERIMENTAL

Apparatus

Figure 1 shows the block diagram of the experimental set-up for the diffusivity measurement.

The pulse energy source is a Coherent Radiation Model 41* CO_2 laser, capable of delivering 350 W continuous power at 10.6 μm wavelength. It is also capable of

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* The use of trade names does not imply endorsement by the authors, NSF (RANN) or the D.O.E.

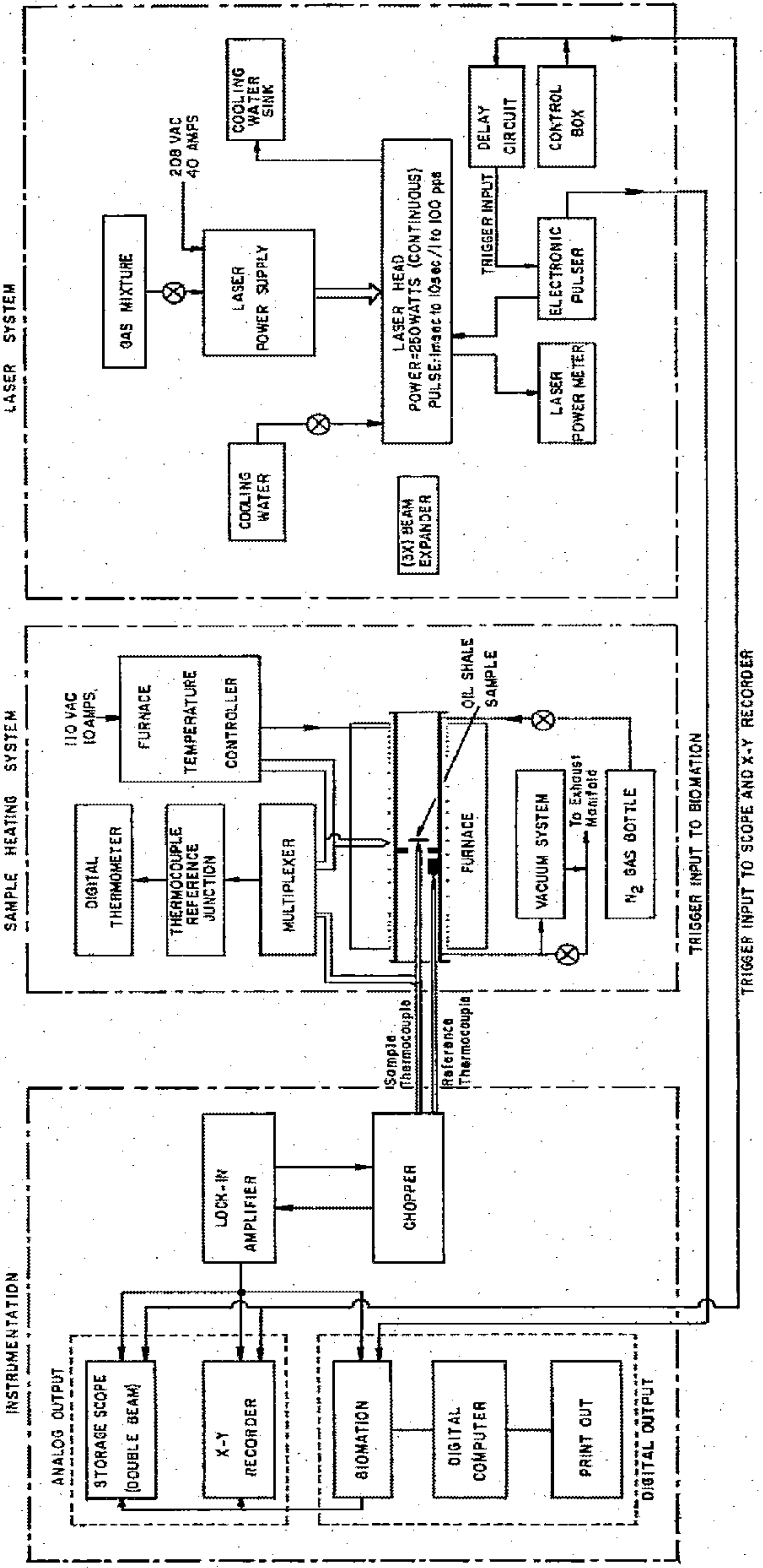

Fig. 1. Block diagram of the experimental set-up for the laser-flash diffusivity measurement.

operating in single or repetitive pulse modes with pulse rates and pulse lengths variable from 1 to 100 pps and 1 msec to 0.10 sec, respectively. Expansion of the 8 mm diameter laser output beam is achieved by use of a zinc selenide beam expander (Unique Optical Corp., New York). The beam after expansion has a diameter of 24 mm.

The stainless-steel sample holder slides inside the furnace tube so that the sample is geometrically centered inside the furnace tube. The sample is held in position by three thin sharp-edged radial legs inside the sample holder. Conduction losses are minimized by reducing contact area with the samples. A fine-wire thermocouple insulated and supported by a ceramic tube is spring-loaded against the rear surface of the sample. The furnace tube houses another matched reference thermocouple, shielded from laser heating. Both the sample and reference thermocouples are differentially connected. The furnace has provisions for sweep-gas flow and vacuum operation. Ambient temperatures are controlled to ± 1 °C by a temperature controller (Love Controls Corp., Illinois).

The sample and reference thermocouples are differentially connected to a high-gain differential amplifier (Tektronix Corp., Oregon). The amplifier output is connected to a Tektronix double-beam storage oscilloscope, an x–y recorder and to a Biomation Model 805 waveform recorder (Biomation Corp., California). The digital output from the transient digitizer is fed directly to a HP 9825 calculator (Hewlett-Packard Corp., Denver) for data processing and analysis. The analog output is fed to the scope for initial inspection of the data before transfer to the calculator.

Subsequent calculations are performed on the HP 9825 and the results displayed either on a HP Model 9872A digital plotter or on a Centronics Model 503 line-printer (Centronics Data Computer Corp., New Hampshire).

Technique

The principle of the laser-flash technique is well documented[1, 6–11] and will not be detailed here. A successful application of this technique rests in a careful evaluation of the measurement errors and boundary conditions[12]. A critical examination of the various sources of error, like finite pulse-time effects, heat losses and non-uniform heating, was made before carrying out measurements on the experimental samples. The use of digital data acquisition systems for recording the transient experimental data significantly reduces measurement errors and provides useful information for detecting and evaluating boundary condition errors[12]. The errors due to finite pulse-time effects are negligible in the present study on account of the low thermal conductivity of the oil shale samples[2], i.e. the laser pulse-time is short compared with the rise times observed for the oil shale samples. No corrections for radiative heat losses were attempted as the temperatures employed were much below the range where they become significant[13]. The absence of noticeable curvature in the temperature–time curves after attainment of the maximum temperature rise in the rear surface of the samples (Fig. 2) was also additional proof that radiative heat losses were absent. The small surface-to-volume ratio of the oil shale samples examined in

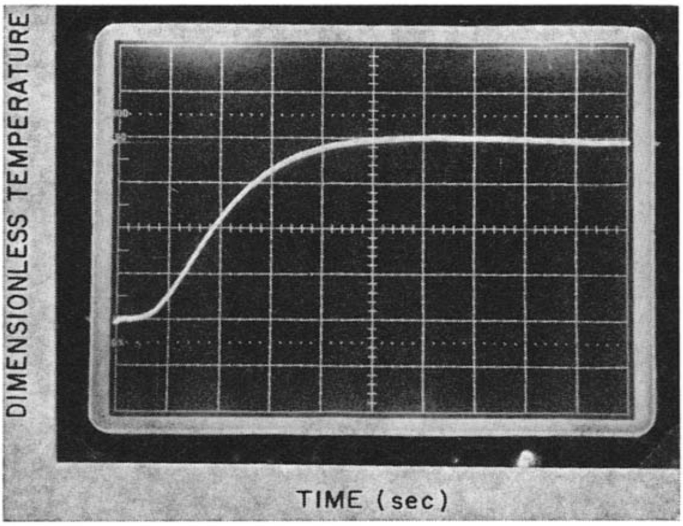

Fig. 2. A typical temperature–time profile on the rear surface of an oil shale sample.

the present study, typically in the range 5–6 cm^{-1}, also minimizes heat losses from the edges and satisfies the requirement of one-dimensional heat flow assumed in the original model used to derive the solution to the heat-flow problem[1]. The response times of the temperature sensors were also carefully checked during calibration runs; the optimum diameter of the thermocouple wires and bead characteristics were established by trial and error after several runs with various thermocouples differing in wire diameter and bead size. It must be pointed out that the required response characteristics of the temperature sensor are critically dependent on the inherent thermal characteristics of the experimental sample and, in this respect, oil shales provide the convenience of possessing relatively large thermal rise times[2]. Corrections for errors arising from non-uniform heating of the samples[12] were also not necessary in the present case, the 12.5 mm diameter samples being much smaller than the 24 mm diameter expanded laser beam. The CO_2 laser is better suited for the study of oil shale than glass lasers because 10.6 μm radiation is strongly absorbed in minerals and rocks[14].

Samples

Oil shale samples for the present study were obtained from the Paraho Mine, west of Rifle, Colorado. This mine is located in the Piceance Creek in the Mahogany Zone. Selection of samples was designed to cover a wide range of grades (6–100 gal./ton); care was also taken to select samples which were crack-free. Right circular cylindrical cores, 12.5 mm diameter, 2 mm thick, were cut both parallel and perpendicular to the shale bedding planes. All samples were carefully dried to remove free moisture and then stored in a vacuum dessicator prior to measurement. The oil yields of the shale specimens were calculated from specific gravity measurements using correlation tables[15]. Repeatability of the experimental results and any possible variations arising from compositional differences were systematically checked by coring samples with identical varve structure at 3/4 in. intervals and then selecting sets of samples of the same grade.

Calibration and data reproducibility

The experimental set-up was calibrated by running a standard stainless-steel 316 sample provided by courtesy of R. E. Taylor, CINDAS, Lafayette, Indiana. The experimental data from several runs agreed with published values to within ± 5%. Reproducibility of data for the oil shale samples, without taking into consideration sample-to-sample variations, is expected to be much better than the above value; experimental errors may be expected to be much smaller for the oil shale samples on account of their rise times being an order of magnitude larger than those for the stainless-steel specimens. When the influence of local sample variations of oil shale is taken into account, however, the data reproducibility shows a systematic trend with the "richness" of the shale. In the case of samples cored perpendicular to the bedding planes, the deviation in the experimental results are ± 5% for the lean samples (> 30 gal./ton), ± 3% for the samples of medium grade (30–60 gal./ton) and ± 1% for the rich samples (< 60 gal./ton). For the samples cored parallel to the bedding planes, the corresponding values are ± 3% for the lean grades and ± 1% for the medium and rich shales. The larger scatter of data for the lean grades is attributed to the effect of mineral occlusions and local compositional variations in the oil shale matrix.

Data analysis

Statistical and computer techniques were used to develop exponential, quadratic and second-order equations from the diffusivity values obtained experimentally. Statistical examination of these equations showed that a second-order linear regression gave the lowest standard error of estimate (R^2 between 0.99 and 0.95 and variance $\leq 10^{-3}$).

RESULTS

The temperature dependence of the thermal diffusivity, α, for several grades of Green River oil shale are shown in Figs. 3 and 5 for the samples cored perpendicular and parallel to the bedding planes, respectively. In both the cases, the α values are seen to decrease smoothly with increasing temperature, especially for the low-grade shales. Rich shales, on the other hand, show very little changes in α with temperature. The larger scatter of data for the low-grade samples is also to be noted. The above trends are clearly illustrated in Figs. 4 and 6 which show the relationship of α to the organic content for the samples cored perpendicular and parallel to the bedding planes, respectively.

A statistical analysis of the trends in the experimental results yields the following set of equations which equate the thermal diffusivity (α) to the two variable parameters, grade (G) and temperature (T), respectively.

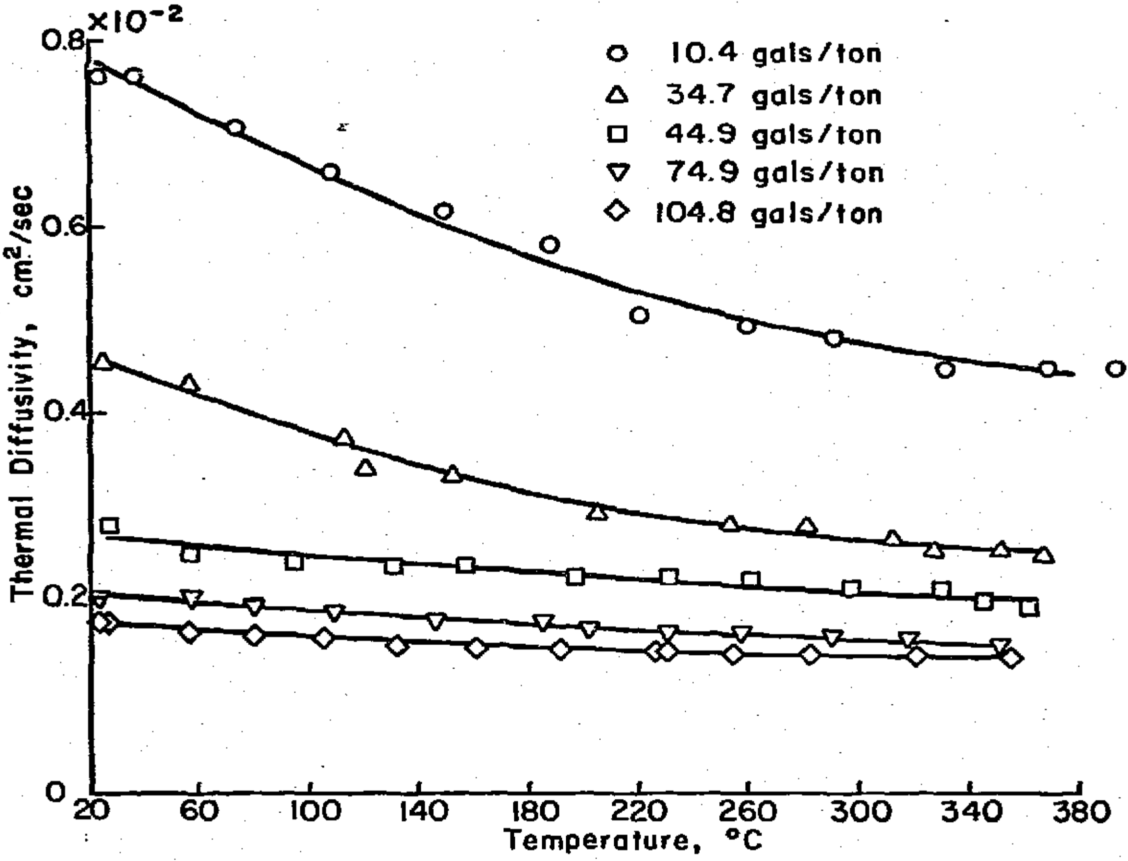

Fig. 3. Thermal diffusivity vs. temperature for oil shale samples of various grades cored perpendicular to the bedding planes.

TABLE 1

VALUES OF COEFFICIENTS IN THE EQUATION $\alpha = a + bX + cX^{2}$* FOR THE SAMPLES CORED PERPENDICULAR TO BEDDING PLANES

Temperature (°C)	a_1	b_1	c_1	*Grade (gal./ton)*	a_2	b_2	c_2
22	0.86	−0.015	9.16×10^{-5}	10.4	0.757	−0.00158	1.77×10^{-6}
100	0.76	−0.015	9.26×10^{-5}	34.7	0.4562	−0.00117	1.56×10^{-6}
200	0.64	−0.014	9.62×10^{-5}	44.9	0.2573	−0.000277	2.3×10^{-7}
330	0.52	−0.010	7.31×10^{-5}	74.9	0.1998	−0.000214	1.6×10^{-7}
				104.8	0.1729	−0.00217	3.0×10^{-7}

* $\alpha = a_1 + b_1G + c_1G^2$ for $25° < T(°C) < 300°$.
$\alpha = a_2 + b_2T + c_2T^2$ for $6 < G$(gal./ton) < 100.

$$\alpha = a_1 + b_1G + c_1G^2 \tag{2}$$

$$\alpha = a_2 + b_2T + c_2T^2 \tag{3}$$

The above equations can be used to calculate α values of Green River oil shale for

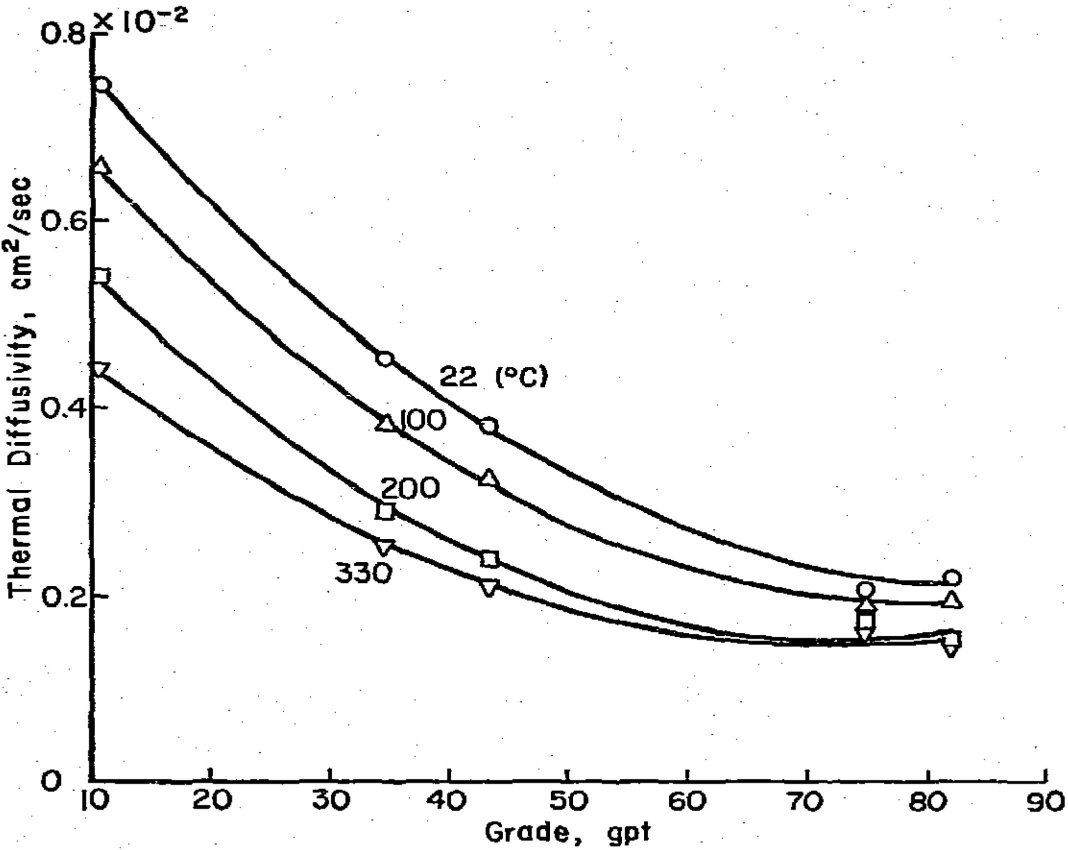

Fig. 4. Dependence of thermal diffusivity on grade at various temperatures for perpendicular cored samples.

TABLE 2

VALUES OF COEFFICIENTS IN THE EQUATION $\alpha = a + bX + cX^2$ FOR SAMPLES CORED PARALLEL TO THE BEDDING PLANE

Temperature (°C)	a_1	b_1	c_1	*Grade (gal./ton)*	a_2	b_2	c_2
22	1.00	−0.016	8.9×10^{-5}	16.8	0.803	−0.00192	0.29×10^{-5}
100	0.82	−0.014	8.0×10^{-5}	26.2	0.628	−0.00776	0.086×10^{-5}
200	0.77	−0.015	8.6×10^{-5}	36.2	0.471	−0.000744	0.10×10^{-5}
330	0.65	−0.011	6.4×10^{-5}	55.3	0.363	−0.000871	0.126×10^{-5}
				81.0	0.288	−0.000744	0.10×10^{-5}

* $\alpha = a_1 + b_1G + c_1G^2$ for $25° < T(°C) < 300°$.
$\alpha = a_2 + b_2T + c_2T^2$ for $6 < G$(gallons/ton) < 100.

temperatures in the range 25–300°C and grades varying from 6–100 gal./ton. The coefficients in the above equations are listed in Tables 1 and 2 for samples cored perpendicular and parallel to the bedding planes, respectively.

The thermal diffusivities measured in the present study were used to generate values of the thermal conductivity from eqn. (1) and reported values of the heat capacity for Green River oil shale[16]. Results are shown in Figs. 7 and 8 for varying temperature and grade, respectively.

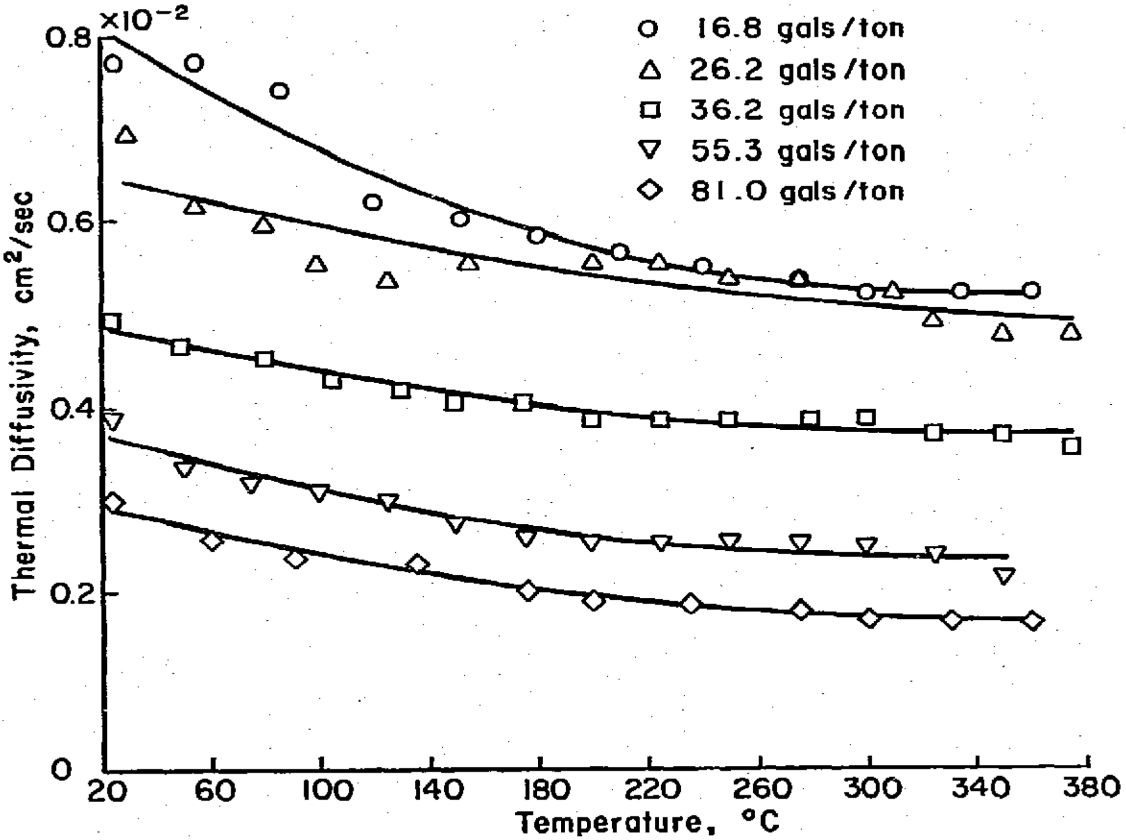

Fig. 5. Thermal diffusivity vs. temperature for oil shale samples of various grades cored parallel to the bedding planes.

DISCUSSION

The results of the present investigation show that the thermal diffusivity of Green River oil shale is strongly influenced by the amount of organic matter in it and by temperature, especially for the low-grade shales. The greater sensitivity of α to temperature for the leaner grades of shale is explained by the volume occupied by the organic matter, which is a controlling variable in the thermophysical properties of oil shales. The relatively small volume occupied by the organic matter in the low-grade shales ($\sim > 30$ gal./ton) effectively means that local compositional variations in the mineral matrix and the presence of mineral inclusions will have a dominant effect on the thermal diffusivity and thermal conductivity of the shale. The poorer reproducibility of data for the leaner shales can also be effectively accounted for on this basis. On the other hand, the larger volume occupied by the organic matter in the rich shales

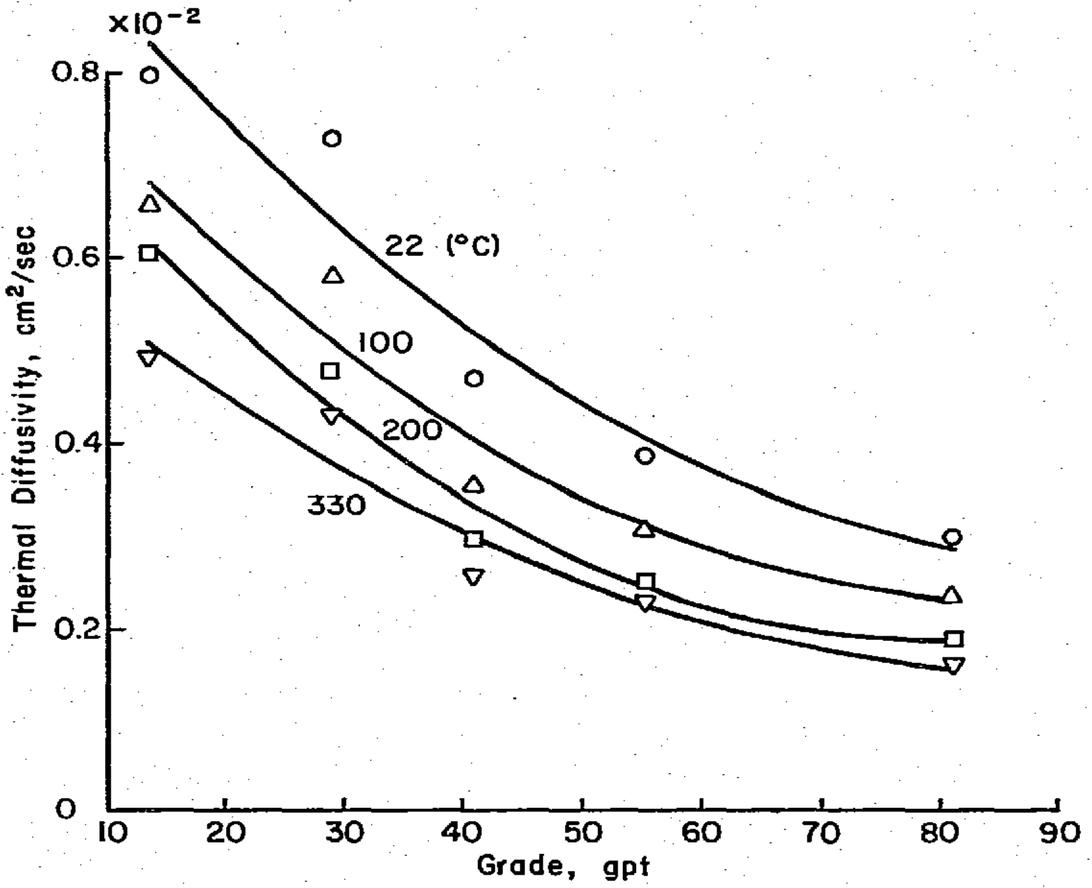

Fig. 6. Dependence of thermal diffusivity on grade at various temperatures for samples cored parallel to the stratigraphic lines.

and the relatively minor variations in the composition of the organic matrix from location to location in the same bedding plane[17] render their α values relatively insensitive to grade and temperature. These conclusions are, however, valid only at temperatures in the range where significant degradation of the organic matter does not occur. The splitting-off of the polar segments in the macromolecular chain, their subsequent fragmentation and the creation of voids in the oil shale structure as a result of thermal degradation, are likely to have a profound effect on the thermal and physical properties of the material. The temperatures chosen for the present study are well below the range where thermal degradation of the shale organic matter is known to occur[18].

The thermal diffusivity of Green River oil shale also exhibits considerable anisotropy (Figs. 3–6); the values for the samples cored parallel to the varves are seen to be about 20–30% higher than those for shales cored perpendicular to the bedding planes. The presence of sedimentary varves in the material therefore probably represents regions of high thermal resistance for heat flowing perpendicular to the varve structure. For example, we can visualize a simple model in which an oil shale system containing N different constituents (representing the various minerals and the

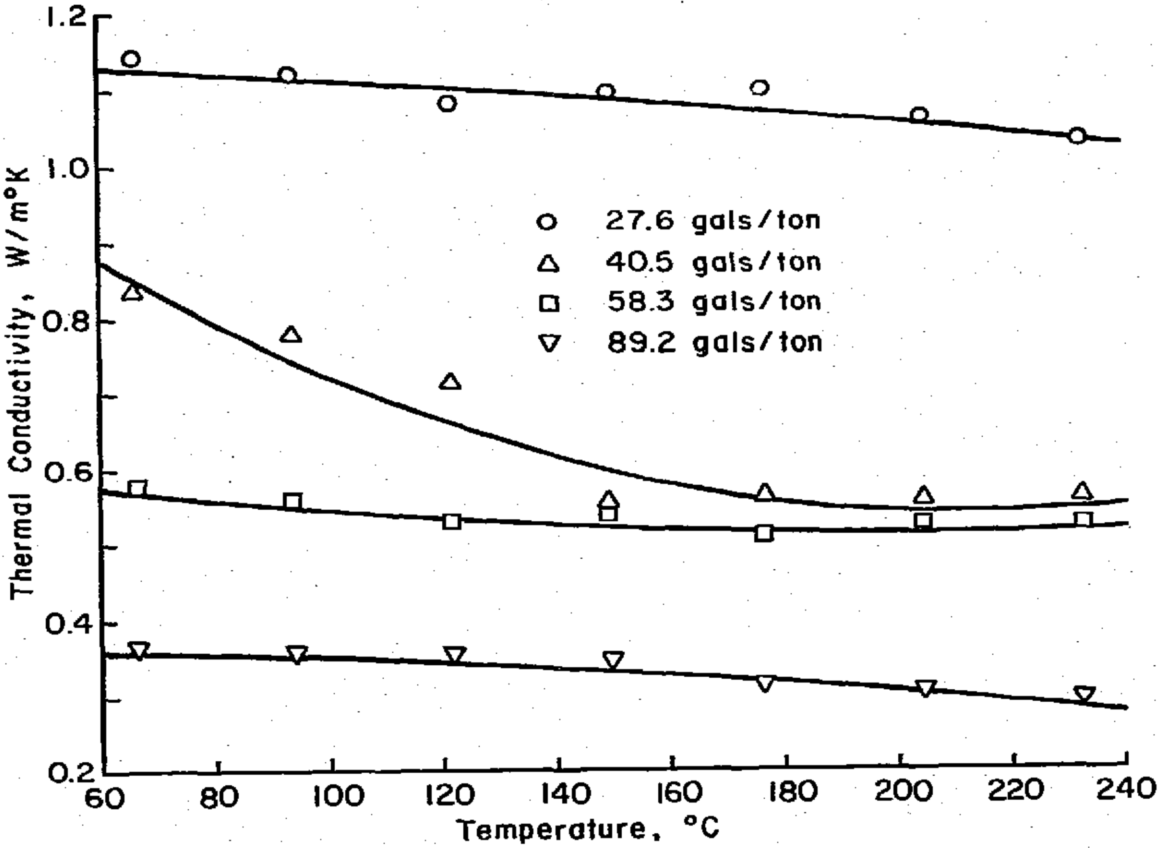

Fig. 7. Variation of thermal conductivity with temperature for Green River oil shales of different grades.

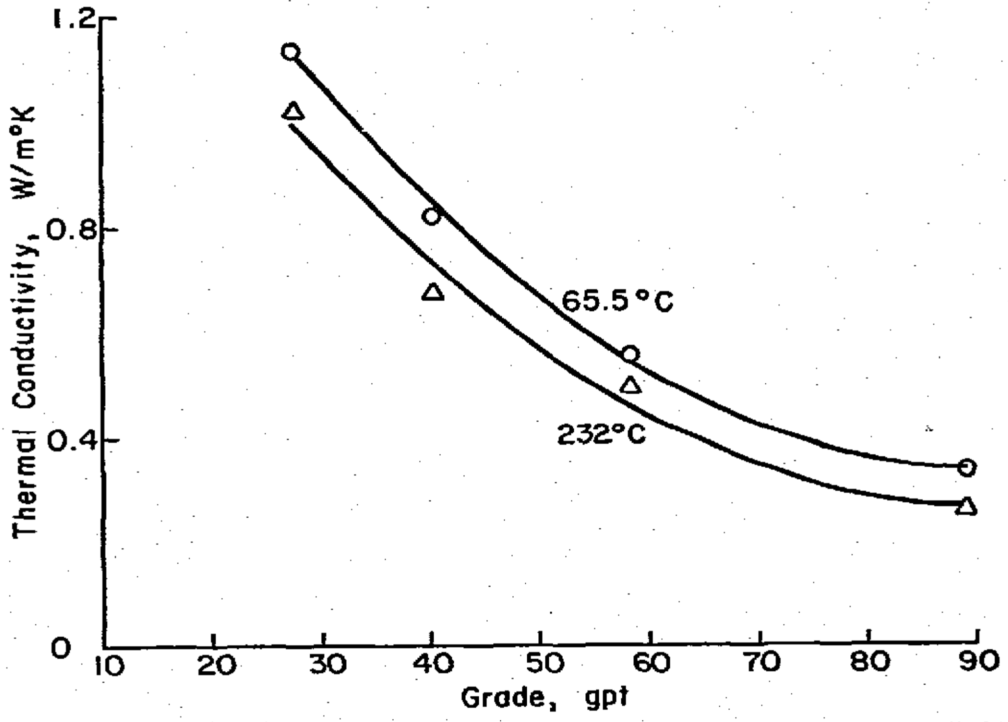

Fig. 8. Thermal conductivity vs. grade at two temperatures for Green River oil shale.

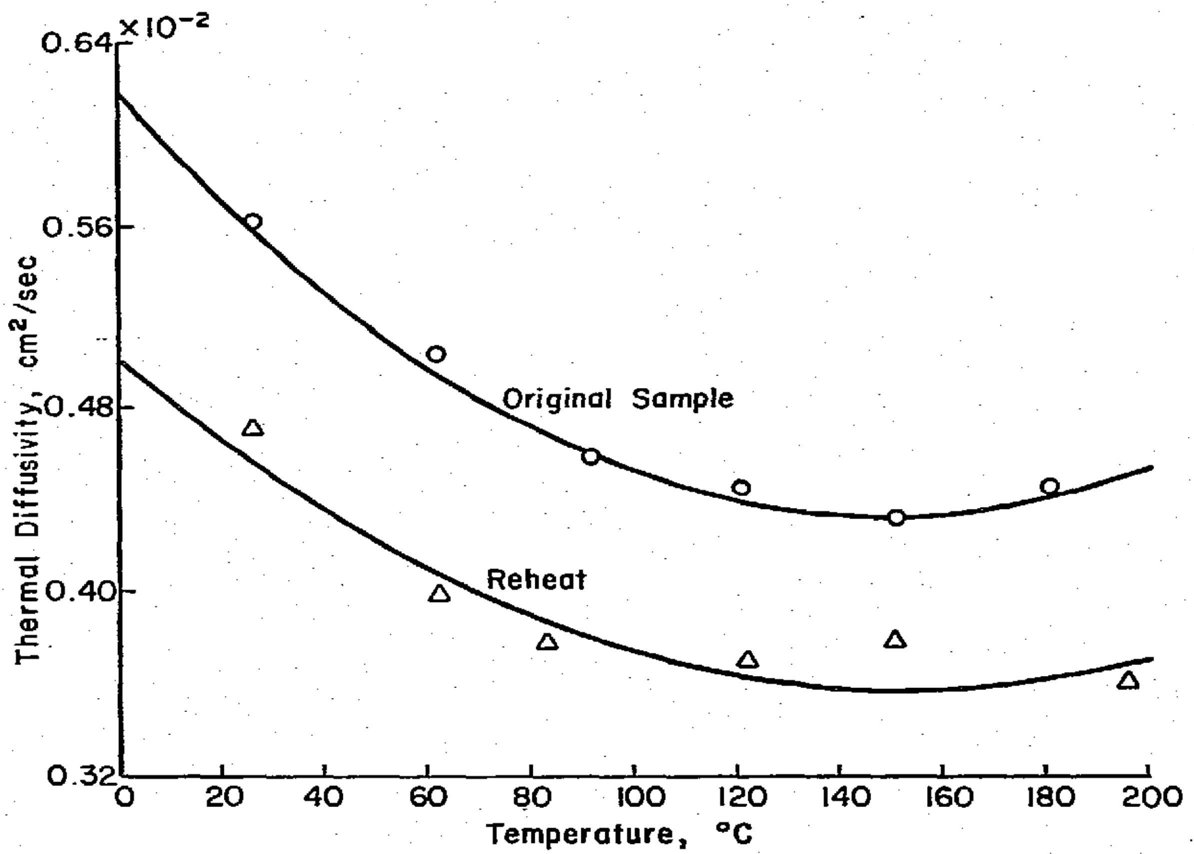

Fig. 9. Effect of reheating on the thermal diffusivity of a 25.5 gal./ton oil shale sample.

organic components), each with a characteristic thermophysical parameter λ_i and relative volume fraction v_i, will have an overall value λ represented by

$$\frac{1}{\lambda_\perp} = \sum_{i=1}^{N} \frac{v_i}{\lambda_i} \tag{4}$$

for heat flowing through each constituent in series and

$$\lambda_\parallel = \sum_{i=1}^{N} \lambda_i v_i \tag{5}$$

for heat flowing through each constituent in parallel. Equation (4) represents the case when heat flows through an oil shale sample in a direction perpendicular to the bedding planes and eqn. (5) holds for the sample cored parallel to the stratigraphic lines. On the basis of the above model, a significant degree of anisotropy may be expected for a highly stratified material like oil shale.

The presence of water molecules in the shale matrix can have an appreciable effect on its thermal diffusivity; the α values for the material reheated after an initial heating to 300°C are found to be significantly lower than the corresponding values for the original material. Figure 9 shows the results for a 25.5 gal./ton shale; the α values at the various temperatures for the reheated material are about 15% lower than the corresponding values for the starting material. Similar trends have been observed for other shales of varying degrees of richness. Heating to 300 °C is known to release the water molecules chemically bonded to the clays present in Green River oil shale[19].

Finally, the thermal diffusivity values experimentally measured in the present study are somewhat lower (~ 10%) than the results published by Tihen et al.[3]. The limited range of grades and temperatures available in the Tihen's work[3], however, restricts comparisons of the present data to a few points. Differences in the experimental techniques (see above) could account for the observed discrepancies; variations arising from compositional differences among the shale samples used in the two studies may also be a contributing factor, although on the basis of the results in the present investigation, such differences are likely to be of negligible importance except for shales with low organic content.

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