A Method of Measuring Thermal Diffusivities of Rocks at Elevated Temperatures

W. H. SOMERTON and G. D. BOOZER
University of California, Berkeley, California

A method is presented for the measurement of thermal diffusivity of synthetic and natural rock materials at elevated temperatures. The method involves heating of cylindrical test specimens at a constant rate of rise of the edge temperature and measuring the temperature differential between a point just inside the sample edge and the center of the sample. It is shown that for a fixed geometry and a constant heating rate thermal diffusivity is inversely proportional to the temperature differential.

A record of the variation of diffusivity with temperature may be obtained through the temperature range of 150 to 1000°C. (except where thermal reactions occur) within a period of less than 2 hr.

Measurements are reproducible within ± 10% for a given material. Accuracy of the values obtained is believed to be good; however there are no data available for direct comparison with the materials tested. Use of an approximate equation for calculation of diffusivity from experimental data leads to errors of the order of only 0.5%. Fairly good agreement was obtained between steady state measurements and measurements by the present method.

Knowledge of the thermal characteristics and behavior of solid nonmetallic materials has become increasingly important with the advent of high-temperature processes including in situ combustion in petroleum reservoirs and underground nuclear explosions. Thermal data for these materials, particularly at high temperatures, are very sparse owing in part to the difficulties of measurements with existing methods and to the large amount of time needed to obtain reproducible results.

The thermal properties to be considered here include heat capacity, thermal expansion, thermal conductivity, and thermal diffusivity. Earlier work (*1*) has shown that heat capacities may be estimated with considerable reliability from a chemical or mineralogical analysis of the sample. Thermal expansion of most nonmetallic solids is relatively small, of the order of 2 to 4% in the temperature range 0° to 1000°C. In heat transfer calculations the effects of thermal expansion are negligible and may be disregarded. Thermal conductivity is a more difficult quantity to measure and is considerably more temperature dependent than the other two properties. Thermal diffusivity, defined as the thermal conductivity divided by the product of bulk density and specific heat, is likewise difficult to measure and is also temperature dependent.

Several steady state methods of measuring thermal conductivity have been presented (*1* to *5*). In general these methods suffer from one or more of several disadvantages: the large amount of time necessary to attain steady state conditions, heat losses to the surroundings, contact or surface resistance, and limited temperature range. When test materials may be molded into special shapes, the steady state methods of Adams (*6*) and Kingery (*7*) are applicable to high-temperature measurements.

A few unsteady state methods for measuring thermal diffusivity have been reported (*8* to *10*). Thermal conductivity is calculated from the measured diffusivity values and known or assumed specific-heat and bulk-density data.

The unsteady state method reported in this paper is similar in principle to the method of Thomas (*10*). The present method however is applicable to any consolidated nonmetallic material and gives a continuous record of the change of diffusivity with temperature in the range of 150° to 1000°C.

DEVELOPMENT OF METHOD

The present method of measuring thermal diffusivity involves the heating of cylindrical samples with a constant rate of temperature rise at the sample edge. The temperature difference between the sample edge and the center of the sample is recorded. Interpretation of the data depends upon whether the diffusivity of the material is constant or variable with temperature. Theoretical analyses for the two cases are presented below.

Constant Diffusivity

The basic equation governing the flow of heat in a body is given as

$$\nabla(k \nabla T) = c\gamma \frac{dT}{d\theta} \qquad (1)$$

If the material is homogeneous and isotropic and the thermal conductivity is independent of temperature, Equation (1) reduces to

$$\nabla^2 T = \frac{c\gamma}{k}\frac{dT}{d\theta} = \frac{1}{\alpha}\frac{dT}{d\theta} \qquad (2)$$

The differential equation for strictly radial heat flow is

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} = \frac{1}{\alpha}\frac{dT}{d\theta} \qquad (3)$$

The initial and boundary conditions are

$$\begin{aligned} &\text{I.C.: } T(r,0) = T_o \quad \text{for } \theta = 0 \\ &\qquad\qquad\qquad\qquad 0 \leqq r \leqq a \\ &\text{B.C.: } T(a,\theta) = T_o + h\theta \\ &\qquad\qquad\qquad\qquad \text{for } \theta > 0 \\ &\qquad T(0,\theta) \text{ is finite} \end{aligned}$$

Solution of this equation for the above conditions is given by Carslaw and Jaeger (*11*) as

$$T(r,\theta) = T_o + h\left(\theta - \frac{a^2 - r^2}{4\alpha}\right) + \frac{2h}{a\alpha}\sum_{n=1} \frac{J_o(rB_n)}{B_n^3 J_1(aB_n)} e^{-\alpha B_n^2 \theta} \qquad (4)$$

The right-hand term of Equation (4) represents the initial transient period of heating. This term generally becomes negligible after a few seconds, depending upon the heating rate and the diffusivity of the sample. The remaining terms of Equation (4) show a linear variation of temperature with time. When one considers only the linear part of the heating period and the temperature differential between the edge and center, Equation (4) may be solved for thermal diffusivity:

$$\alpha = \frac{a^2 h}{4\Delta T} \qquad (5)$$

Variable Diffusivity

For the variable diffusivity case Equation (1) cannot be handled in the previous manner. Thermal conductivity cannot be removed from within the differential operator, and under normal circumstances a solution would not be possible. However in the present case the edge temperature is a function of time and since the temperature differential between the edge and the center of the sample is small, diffusivity can be expressed as a function of (θ). Therefore Equation (1) may be written as

TABLE 1. PHYSICAL CHARACTERISTICS OF TEST SPECIMENS

Material	Composition	Grain density	Bulk density	Porosity
Alundum	Al_2O_3	3.97	2.94	0.26
Zirconia	ZrO_2	6.00	4.47	0.25
Sandstone	Quartz 50% Felds. & Clay 50%	2.65	2.12	0.20
Limestone	$CaCO_3$	2.71	2.21	0.186

G. D. Boozer is with California Research Corporation, La Habra, California.

$$\frac{\partial T}{\partial \theta} = \alpha\,(\theta)\,\nabla^2 T \qquad (6)$$

When one sets

$$d\delta = \alpha\,(\theta)\,d\theta \qquad (7)$$

Equation (6) reduces to

$$\frac{\partial T}{\partial \delta} = \nabla^2 T \qquad (8)$$

Upon examination of available diffusivity-temperature data, it was observed that the reciprocal of diffusivity varies nearly linearly with temperature, and thus with time in the present case:

$$\alpha\,(\theta) = \frac{\alpha_o}{1 + b\theta} \qquad (9)$$

Substituting Equation (9) into Equation (7) and integrating one obtains

$$\delta = \int_o^\theta \frac{\alpha_o\,d\theta}{1 + b\theta}$$

$$\delta = \frac{\alpha_o}{b} \ln\,(1 + b\theta) \qquad (10)$$

Solving for θ one gets

$$\theta = \frac{1}{b}\,(e^{b\delta/\alpha_o} - 1) \qquad (11)$$

By means of Duhamel's theorem the solution for variable diffusivity in the strictly radial heat flow case is given by Equation (12) for the following initial and boundary conditions:

$$\begin{aligned} I.C.:&\quad T(r,0) = T_o \qquad \text{for } \delta = 0 \\ &\qquad\qquad\qquad\qquad 0 \leq r \leq a \\ B.C.:&\quad T(a,\delta) = u(a,\delta) + v(a,\delta) \\ &\quad u(a,\delta) = T_o \\ &\qquad\qquad\qquad\qquad \text{for } \delta > 0 \\ &\quad v(a,\delta) = \frac{h}{b}\,(e^{b\delta/\alpha_o} - 1) \\ &\quad T(0,\delta) \text{ is finite} \end{aligned}$$

$$T(r,\delta) = T_o + \frac{2h}{ab} \sum_{n=1}^{\infty} \frac{B_n J_o(r\,B_n)}{J_1(a\,B_n)} \left[\frac{e^{b\delta/\alpha_o}}{B_n^2 + b/\alpha_o} + \frac{b e^{-B_n\,\delta}}{\alpha_o B_n(B_n^2 + b/\alpha_o)} - \frac{1}{B_n^2} \right] \qquad (12)$$

It can be seen that by setting $\delta = 0$ the bracketed term in the series reduces to zero for any value of n, and thus the transformed boundary condition is satisfied.

Direct solution of Equation (12) for the constants α_o and b and use of experimentally determined temperature differentials was not attempted. However to evaluate the magnitude of error in the use of Equation (5) for calculation of variable diffusivity data Equation (12) may be expressed in the following form (*12*):

$$T(r,\delta) = T_o + h\left(\theta - \frac{a^2 - r^2}{4\alpha}\right) + \frac{2hb}{\alpha\alpha_o a} \sum_{n=1}^{\infty} \frac{J_o(rB_n)}{J_1(aB_n)B_n^3(B_n^2 + b/\alpha_o)} + \frac{2h}{a\alpha_o} \sum_{n=1}^{\infty} \frac{J_o(rB_n)e^{-B_n^2\delta}}{B_n(B_n^2 + b/\alpha_o)J_1(aB_n)} \qquad (13)$$

The second-series term in Equation (13) rapidly approaches zero as δ increases and may be dropped as was done for the similar expression in Equation (4). Setting $r = 0$ and solving Equation (13) for α one gets

$$\alpha = \frac{ha^2}{4\Delta T} - \frac{2hb}{a\alpha_o\Delta T} \sum_{n=1}^{\infty} \frac{1}{J_1(aB_n)B_n^3(B_n^2 + b/\alpha_o)} \qquad (14)$$

A comparison of this with Equation (5) shows that the series term of Equation (14) accounts for the effect of variable diffusivity. Using experimental data to evaluate the series term in Equation (14) one finds that its magnitude never exceeds 0.6% of the value of α. Thus it is concluded that Equation (5) may be used to calculate variable diffusivity data with negligible error.

EXPERIMENTAL EQUIPMENT

Test samples were 6-¾ in. long by 1-⅛ in. in diameter. The 6:1 length to diameter ratio was considered adequate to reduce end effects to a minimum. The sample was cut into three 2-¼ in. long sections to permit drilling of thermocouple holes. Five 0.070-in. diameter holes 1-⅛ in. deep were drilled into the center section to accommodate thermocouples within ceramic insulating tubes. One hole was in the exact center of the sample, and four holes were equally spaced on a circumference as close to the edge of the sample as possible. Three differential temperatures and one edge temperature were recorded.

The three core sections were stacked vertically in a 2-in. diameter insulated electric core furnace. A temperature-control thermocouple is located close to the inside wall of the furnace. Power to the furnace is supplied from a motor driven variable transformer controlled to a constant heating rate of 12°C./min. by an automatic controller. Differential thermocouple signals are amplified and recorded on a multipoint recorder. The edge temperature is recorded on a separate chart.

In addition to the above equipment a comparator type of apparatus described previously (*1*) was used to obtain thermal conductivity values at temperatures below the range of the present equipment.

TEST PROCEDURE

Four materials were used to test the method of diffusivity measurement, including two synthetic materials, aluminum oxide and zirconia, and two natural materials, a limestone and a sandstone. Physical characteristics of the test specimens are given in Table 1.

An initial heating run was made on each sample to detect the presence of temperature anomalies. The alundum and zirconia samples were free from thermal reactions, and a constant heating rate was employed throughout the test-temperature range. The sandstone showed a strong endothermic

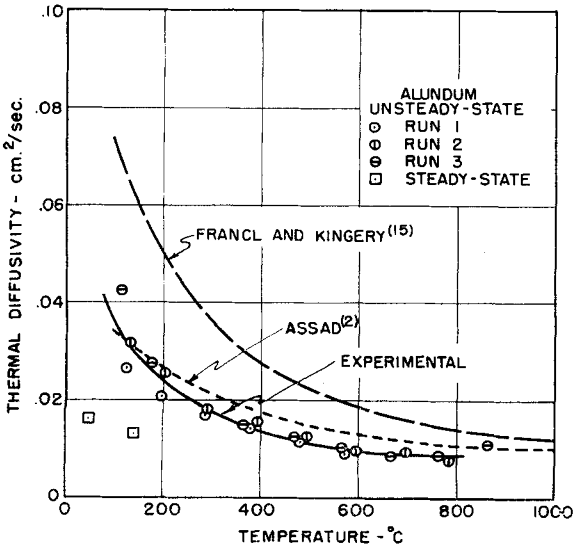

Fig. 1. Thermal diffusivity of alundum.

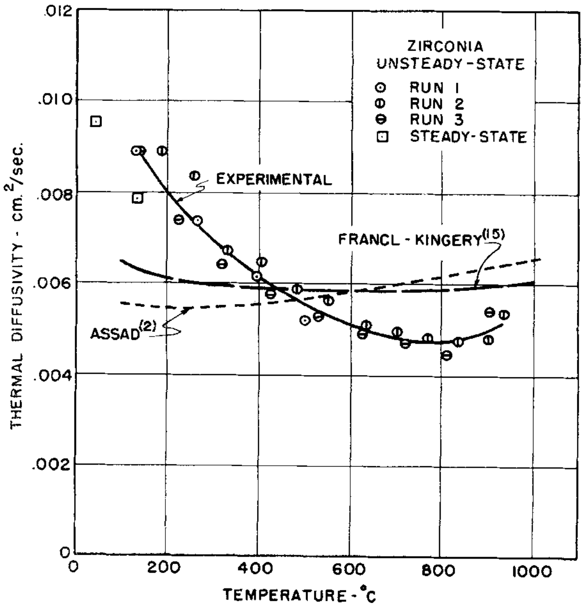

Fig. 2. Thermal diffusivity of zirconia.

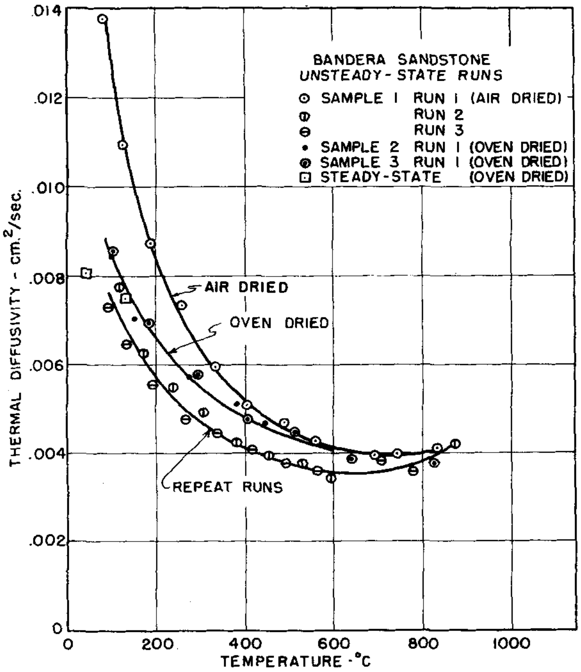

Fig. 3. Thermal diffusivity of bandera sandstone.

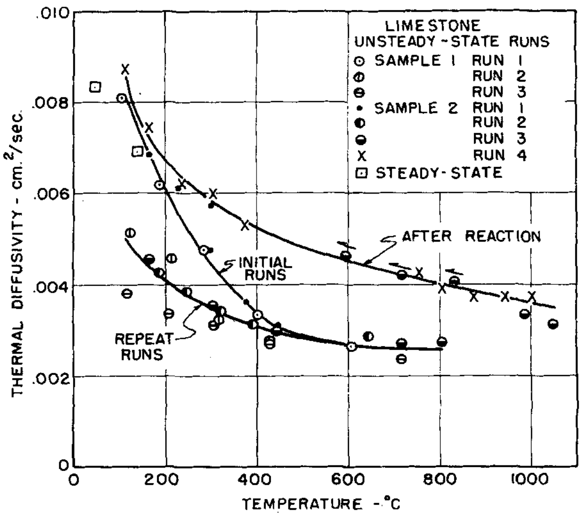

Fig. 4. Thermal diffusivity of limestone.

reaction at 550° to 600°C., this being α-β quartz inversion. The sample was heated at a constant rate to 550°C. and was then allowed to soak until the reaction was complete ($\Delta T = 0$). Heating was then continued at the constant rate to the maximum temperature. The limestone showed no important anomalous behavior until the release of carbon dioxide and conversion to calcium oxide at approximately 830°C.

Approximately 15 min. were required at the start of each run to establish the desired heating rate at the edge thermocouple. Therefore no thermal diffusivities were calculated below about 150°C. Steady state thermal conductivity runs were made at two temperatures (45° and 135°C), and thermal diffusivities were calculated to provide data at these lower temperatures. Re-establishment of the edge heating rate after soaking periods required very little time, and no significant gaps in the data resulted from this effect.

EXPERIMENTAL RESULTS

Synthetic Materials

Results of thermal-diffusivity measurements for the two synthetic materials are shown in Figures 1 and 2. The circles indicate experimental values calculated from Equation (5) for the unsteady state runs and the squares are experimental values of steady state thermal conductivities divided by the products of the heat capacity and bulk density at the indicated temperatures.

To test the validity of experimental results diffusivity values were calculated from literature data. Thermal-conductivity data for the solid materials were taken from Kingery, et al. (*13*) and heat capacity data from Kelley (*14*). The data were corrected to the porosities of the test samples by two different relations:

Francl and Kingery (*15*)

$$k_\phi = k_s\,(1 - \phi) \tag{15}$$

Assad (2)

$$k_\phi = k_s\,(k_a/k_s)^\phi \tag{16}$$

The resultant literature values are shown on Figures 1 and 2 as broken and dashed lines.

The maximum spread of experimental data for the three alundum runs is ± 10% the deviation being less at the higher temperatures. Part of the deviation at lower temperatures is probably due to slight differences in initial adsorbed moisture contents of the test sample. (For the importance of this effect see Figure 3).

The experimental diffusivity values for alundum agreed favorably with literature values corrected for porosity by the method of Assad. Good agreement with the trend but poor agreement with the magnitude of literature values corrected by the method of Francl and Kingery are apparent from Figure 1. There is considerable question that porosity alone is an adequate basis for adjusting thermal-conductivity values. Differences in particle size distribution, particle shape, and degree of sintering or cementation probably are important in determining the thermal conductivity of porous, granular materials.

The steady state values for alundum showed poor agreement with unsteady state data. The principal cause of this discrepancy was the lack of a steady state thermal conductivity standard in the appropriate range of conductivity. The guard ring comparator method is known to yield satisfactory data only when the conductivity of the standard is reasonably close to the conductivity of the test specimen. The ratio of the conductivity of alundum to the bakelite standard is approximately 8, considerably higher than is permissible in a comparator apparatus.

The spread of the experimental data for the three zirconia runs was somewhat less than for alundum, being approximately ± 8%. The magnitude of the experimental values agreed well with the literature values, but the trend was considerably different. X-ray analysis disclosed the presence of only traces of impurities, probably insufficient to influence the diffusivity values appreciably. The close agreement between diffusivity values calculated from steady state thermal conductivity measurements and the trend of unsteady state diffusivity values tends to confirm the correctness of the latter values.

Natural Materials

Results of diffusivity measurements on two natural materials, a sandstone and a limestone, are shown in Figures 3 and 4 respectively. These results are presented to demonstrate some of the problems encountered in the measurements.

In Figure 3 the upper curve shows the important effect of adsorbed moisture on the magnitude of diffusivity values. Sample one was originally oven dried but was permitted to stand under atmospheric conditions for several days prior to the test. Samples two and three were oven dried and stored in a desiccator until tested to prevent adsorption of moisture.

Runs on samples two and three show good agreement considering probable variations of physical properties of different samples of the same natural material. The lower set of experimental points shows the effects of repeated heating of the same sample. The difference in behavior of reheated samples is due to the completion of irreversible reactions during the initial run. Reversible reactions such as $\alpha - \beta$ quartz inversion recur for all runs on both heating and cooling curves.

Results of the limestone diffusivity measurements are shown in Figure 4. The first and second runs on each sample were stopped at a maximum temperature of approximately 700°C. to prevent the possible loss of carbon dioxide. A mild endothermic reaction occurred however at between 500° to 580°C., indicating the probable presence of calcium hydroxide in the original samples. Initial runs on the two samples showed close agreement. Repeat runs gave lower diffusivity values at the lower temperatures, but there is an indication of convergence of all runs at temperatures in excess of 580°C. The large spread of repeat-run data is probably due to variation in the degree of completion of calcium hydroxide reaction and the amount of moisture adsorbed by the samples between runs.

The temperature for the third run on sample two was increased to approximately 850°C., and the sample was soaked at this temperature until complete conversion to calcium oxide had occurred. Completion of the reaction was very positive as indicated by a sudden drop in the temperature differential. After the reaction was completed, the temperature was again increased and diffusivity values for the reacted material were calculated. Three additional points, designated with reverse arrows, were calculated from the cooling curve. After cooling, a fourth run was made on sample two. The resulting data gave diffusivity values for the nearly pure calcium oxide produced by the reaction.

ANALYSIS OF METHOD

The method presented is believed to give reliable thermal-diffusivity data for synthetic and natural rock materials within the temperature range of 150° to 1000°C. There are certain limitations in the method, and these are discussed in detail.

The theoretical analysis requires that the test specimen be heated at a constant rate of temperature rise. Physically this is difficult to accomplish with the present control equipment. Considerable time is required to achieve a linear heating rate initially, and in most cases the edge temperature is as high as 150° to 200°C. before reliable data may be obtained. Some points have been calculated below this temperature range by means of the instantaneous heating rate at the temperature of analysis. Although reasonable diffusivity values are obtained, as seen from comparison with steady state values, the reliability of these values is unknown.

After a linear heating rate has been achieved, it may be held constant to within ± 7%. Thermal reactions may change the rate appreciably unless the sample is soaked at the reaction temperature. Natural materials show minor thermal reactions which do not affect the heating range significantly, and soaking is not considered necessary. However minor reactions show clearly on the differential curves, and data within the temperature range of these reactions are not used for calculations.

Other difficulties with the method are mechanical in nature and subject to correction. Frequent standardizing and adjustment of recorders will reduce instrument errors to the minimum. Since three differential thermocouples are used, errors due to faulty thermocouples may be detected. Although only a single edge temperature thermocouple was used, a reasonable check was obtained by comparing the edge-thermocouple reading with the control-thermocouple reading at the conclusion of soaking periods. Reasonable care must be exercised in properly locating and aligning the thermocouple holes. Significant errors from the cause can be detected from the differential temperature records.

This method has several distinct advantages over earlier methods. The method is rapid, calculations are relatively simple, and a complete record of diffusivities may be obtained for most materials over a wide temperature range. Sample preparation is comparatively easy with the use of diamond tools. Since the important temperature measurements are made with differential thermocouples located completely within the sample, errors due to surface resistance are essentially eliminated.

SUMMARY AND CONCLUSIONS

A rapid unsteady state method has been developed for measuring thermal diffusivities of synthetic and natural nonmetallic solids in the temperature range of 150° to 1000°C. Less than 2 hr. is required for a complete run. Measurements are reproducible within ± 10% for a given material. A simplified method of interpretation of experimental data leads to errors of the order of 0.5%.

Gaps in the diffusivity data occur in the temperature range of minor thermal reactions for natural materials. Samples are soaked at the temperature of major reactions such as the $\alpha - \beta$ quartz inversion, and no serious disturbance of the curves results.

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NOTATION

a = radius, center to edge, cm.
b, α_o = constants relating diffusivity to time, sec.$^{-1}$ and sq. cm./sec., respectively
c = specific heat, cal./g. °C.
h = heating rate, °C./sec.
k = thermal conductivity, cal./sec. sq. cm. °C./cm.
k_ϕ = thermal conductivity of porous material
k_s = thermal conductivity of solid material
k_a = thermal conductivity of saturating fluid
r = any radius $o \leqq r \leqq a$, cm.
T = center-line temperature, °C.
T_o = initial temperature, °C.
ΔT = differential temperature, edge to center, °C.
J_o = Bessel function first kind, zero order
J_1 = Bessel function first hand, first order
B_n = roots of Bessel equation: $J_o(aB_n) = 0$
α = diffusivity, sq. cm./sec.
δ = transformed time
ϕ = fractional porosity
θ = heating time, sec.

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