STUDY OF THERMAL PROPERTIES OF ENDELLITE CLAY COMPOUND

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The temperature dependence of the thermal properties (specific heat, C_p, thermal diffusivity, a, and thermal conductivity, K) of endellite clay has been investigated over the temperature range $R \cdot T \leqslant T \leqslant 280$ °C using the plane temperature wave technique. The experimental results showed that in the initial stage of temperature rise both a and K diminish exponentially with increasing temperature up to ~100 °C. Above 100 °C, the thermal parameters are found to reach stable values, namely, $C_p = 0.22 \pm 0.008$ cal g^{-1} deg^{-1}, $a = (5.0 \pm 0.18) \cdot 10^{-4}$ cm^2 sec^{-1} and $K = (2.2 \pm 0.16) \cdot 10^{-4}$ cal cm^{-1} sec^{-1} deg^{-1}. The explanation of the results was supported by using DTA and TG analysis.

Clays are rigid earthy or stony rocks consisting essentially of hydrous silicates and alumina. As these clays occur in nature, they usually contain more than one mineral, and the various clay minerals differ in chemical and physical properties. In addition, a clay deposit usually contains nonclaylike minerals as impurities, although these impurities may actually be essential in determining the unique and especially favourable properties of the clay. Both crystalline and amorphous minerals and compounds may be present in a clay deposit. The predominant components of clay minerals which are hydrated silicates of aluminium and some other elements are ranging from kaolins, which are relatively uniform in chemical composition to smectites which vary widely in their base exchange properties.

The kaolin minerals include kaolinite, dickite, nacrite and halloysite (all $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) and endellite ($Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$). The structural formulae for kaolinite and endellite are $Al_4Si_4O_{10}(OH)_8$ and $Al_4Si_4O_{10}(OH)_8 \cdot 4H_2O$, respectively [1]. A diagrammatic representation of the structure of kaolinite and endellite is shown in Fig. 1 [1].

Although clays of different groups are apparently similar, they show vastly different mineralogical, thermophysical and technological properties [2]. Moreover, some clays of the same group show a drastic difference in their thermal expansion as a function of temperature [3, 4]. This behaviour was explained to be
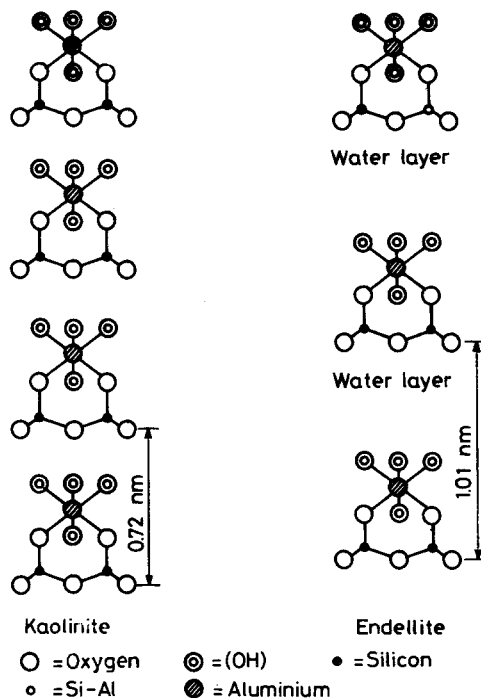
Fig. 1 Structure of kaolinite and endellite clays (from Brindley and Brown [1])

due to the different mineral impurities included in them. Therefore, the mineral composition which reveals the organization of the constituent elements is highly important.

The aim of the present work is to study the temperature dependence of the thermal properties of a member of the kaolin mineral group the "endellite", as it is used in thermal insulation fields. From the point of view of energy conservation, the study of such properties is very important and is desirable especially under conditions corresponding to industrial applications, for minimizing the energy loss during the translational processes.

As endellite is used as a thermal insulator in the Naga–Hammady sugar factory, Egypt, our study has been carried out in the range of its operating temperature (room temperature, RT, to $\approx 280°$). For this material no literature data are available and therefore the study of the thermal properties of this compound is necessary.

Experimental procedure

The clay compound (endellite) studied in the present work was supplied by the Naga–Hammady Sugar Factory, Egypt (where it is used as an outer thermal insulator). This compound has been analysed using X-ray fluorescence in the Microanalytical Centre (Cairo University, Giza, Egypt). It has been shown that several elements exist as impurities in their oxide form in the compound (Table 1).

Table 1

Impurity	Fe_2O_3	CaO	Na_2O	K_2O	CuO	ZnO
wt%	0.281	0.587	0.423	0.185	0.164	0.065

For thermal measurements, the plane temperature wave technique was used [5–8]. Proper disc-shaped specimens of thickness of 3–5 mm and diameter of 20 mm were prepared. The maximum error in the determination of both specific heat and thermal diffusivity is 3.5%, while that for thermal conductivity is about 7%. In order to minimize the errors, the results for four specimens were averaged. The details of the experimental procedure have been described in Refs [9–11].

For differential thermal analysis (DTA), a powder sample of about 0.5 g weight was prepared from the clay compound. Both the sample and the reference material (glass beads of equal weight) in the DuPont 1090 thermal analyser (Instruments Divison USA) were heated from room temperature to 280°. The temperature of both the sample and the reference material was monitored by a pair of copper-constantan thermocouples. The DTA runs were carried out at a linear heating rate of 20 deg/min. Further details of this technique have been described elsewhere [12].

Thermogravimetry (TG) was performed to follow the change of the specimen's weight with temperature. A powder specimen of one g weight was prepared for this purpose. The DuPont TGA analyser (equipped with a copper-constantan thermocouple) was allowed to heat the specimen at a heating rate of 10 deg/min over a temperature range from room temperature to 280°.

Results

The temperature dependence of the specific heat of the endellite material under investigation is illustrated in Fig. 2. Initially C_p decreases with increasing temperature from room temperature up to about 100°. Finally, C_p seems to reach a constant value of about 0.22 ± 0.008 cal/g·deg·above 100°.

The variation of thermal diffusivity with temperature of this compound is shown in Fig. 3. Each experimental point represents the average of four diffusivity values measured at the same temperature. It is interesting to notice that the temperature dependence of the thermal diffusivity exhibits a steep decrease with increasing temperature up to about $100°$. Above this temperature, the thermal diffusivity attains a stable value of about 5×10^{-4} cm^2 s^{-1}. This behaviour seems to be similar to that of the specific heat (Fig. 2).
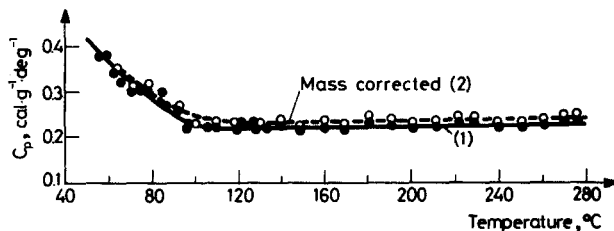

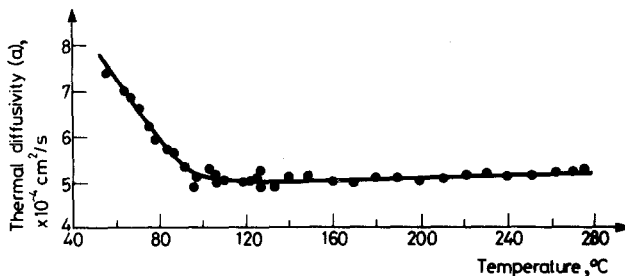Fig. 2 Variation of the specific heat, C_p, of the endellite clay compound with temperatur

Fig. 3 Thermal diffusivity, a, as a function of temperature
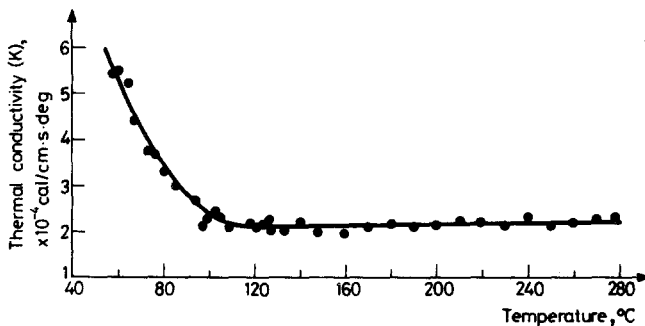

Fig. 4 Variation of the endellite thermal conductivity, K, as a function of temperature

Figure 4 shows the effect of heating on the thermal conductivity of the sample. The plot shows a sharp decrease in the thermal conductivity as the temperature rises up to about 100°. Further increase in temperature does not affect the conductivity, i.e. the thermal conductivity remains constant at a value of 2.2×10^{-4} cal/cm sec deg. This behaviour is also similar to those of the specific heat (Fig. 2) and thermal diffusivity (Fig. 3). This should be so because the thermal conductivity is proportional to both the thermal diffusivity and the specific heat according to the relation $K = \varrho a C_p$, where ϱ is the material density.

Discussion

The study of the thermophysical properties of endellite clay compound as a function of temperature is a matter of interest as it is used as thermal insulator in industry. Since no data are available for this material in order to compare with, data of nearly similar materials may be used. Referring to our results, it has been shown in Fig. 2 that the specific heat of the endellite clay compound shows a steep decrease with temperature in the initial stage ($R.T. - 100°$). This behaviour is, undoubtedly, due to the expulsion of water which has a very large specific heat compared with the value of the solid compound, as evidenced by the endothermic peak in the DTA curve, Fig. 5. The lag of the DTA endothermic peak after 100° is actually attributed to the relatively rapid heating (20 deg/min). The disappearance of the endothermic peak in the case of the second heating run, Fig. 5, gives further evidence that the above effect is due to some percentage of water in the material. As the temperature is increased, the DTA curves show, nearly, no further endo- or exothermic processes up to 280°. This is consistent with the results of C_p measurements above 100°.

An additional finding coming from the TG results, Fig. 6, is that a weight loss of about 4% of the sample has been recorded. In fact, the loss of the material's weight should result in an increase of its specific heat according to the relation [8]:

$$C_p = \frac{Q}{m\omega\theta}\, f(\varphi, \beta)$$

where Q is the absorbed heat power, m is the mass of the sample, ω is the angular frequency of the heat source, θ is the measured amplitude of the temperature oscillations and $f(\varphi, \beta)$ is a correction function which is nearly equal to unity. But after doing the corrections of the specific heat due to the weight loss we did not achieve the original value, as shown by the dashed curve in Fig. 2. This is due to the fact that the lost material has a specific heat greater than the remaining part in the compound. This explains the initial decrease of the specific heat of the compound.

Generally, it is believed that the absorbed water in clay compounds is not in a
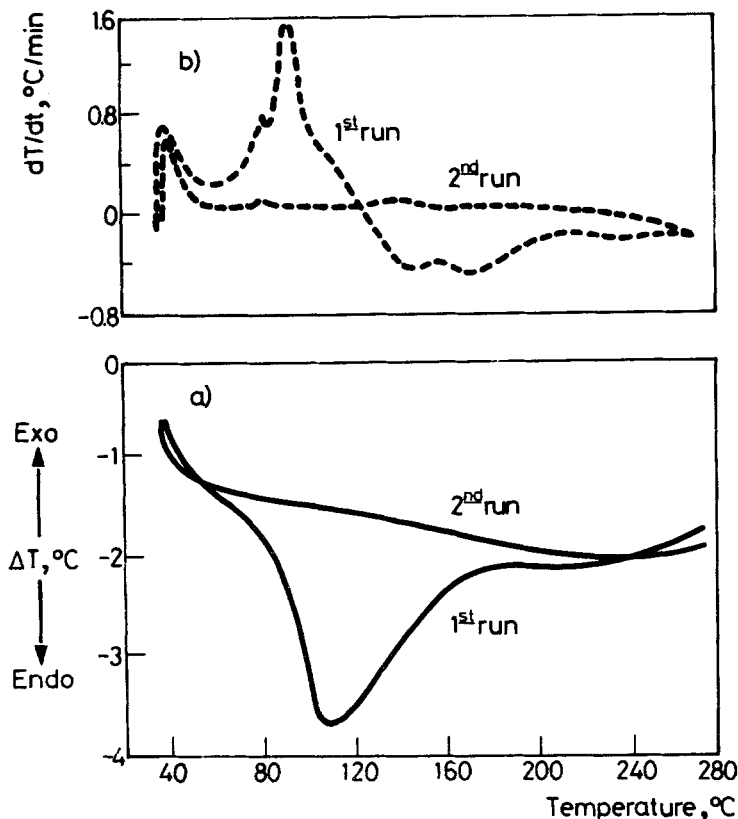
Fig. 5 DTA curve of endellite. *a)* ΔT vs. T; *b)* dT/dt vs. T

fluid form, but rather, the molecules of water lie in a definite orientation between the clay particles. In some clay compounds, water is believed to be in the form of crystalline water rather than directly bonded between the particles [13]. The percentage of the water removed from the samples up to $100°$ ($\approx 4\%$) is in good agreement with the value reported for endellite (4.45%) at $105°$ [13]. As a result of the water expulsion from the clay compound, a volume shrinkage of about equal to the volume of the lost water should occur. Simply, the 4% weight loss of water from the endellite clay corresponds to a volume shrinkage $\left(\dfrac{\Delta V}{V} \% \right)$ of $\approx 7.7\%$, and

since, $\dfrac{\Delta V}{V} = 3 \dfrac{\Delta L}{L}$, where $\dfrac{\Delta L}{L} \%$ gives the length shrinkage, then, immediately, the

length shrinkage of the endellite clay mineral has the value of 2.56%. This value is smaller than the reported values of length shrinkage for kaolinite (3–10)% and

endellite (7–15)% obtained after annealing the sample for 5 hours at 105° [13]. In contrast, the length shrinkage of our material is considerably larger than the value of 0.5–1% obtained at 200° by Khajuria et al. [3, 4]. This discrepancy is due to the existence of nonclay minerals as impurities in different percentages as the oxides of Ca, Na, K, Fe, Ti and Cu etc., and their presence tends to reduce the drying shrinkage depending on their content, shape, particle size and distribution. This explanation agrees well with the high content of impurities ($\approx 10\%$) reported in Ref. [3, 4] and the low impurity content in our material ($\approx 1.7\%$ and $\approx 1.26\%$) given in Ref. [13].

In the case of the endellite clay, the contribution of the electrons in the specific heat is completely absent, and the lattice contribution cannot be easily represented by the specific heat function (Debye) due to the complex lattice vibration. On the other hand, the molecular theory and the Neumann–Kopp rule [14], $\left(C_p = \sum_{i=1}^{N} g_i C_i \right)$, cannot be used to calculate the specific heat of the clay compound because of the different contents in the compound.
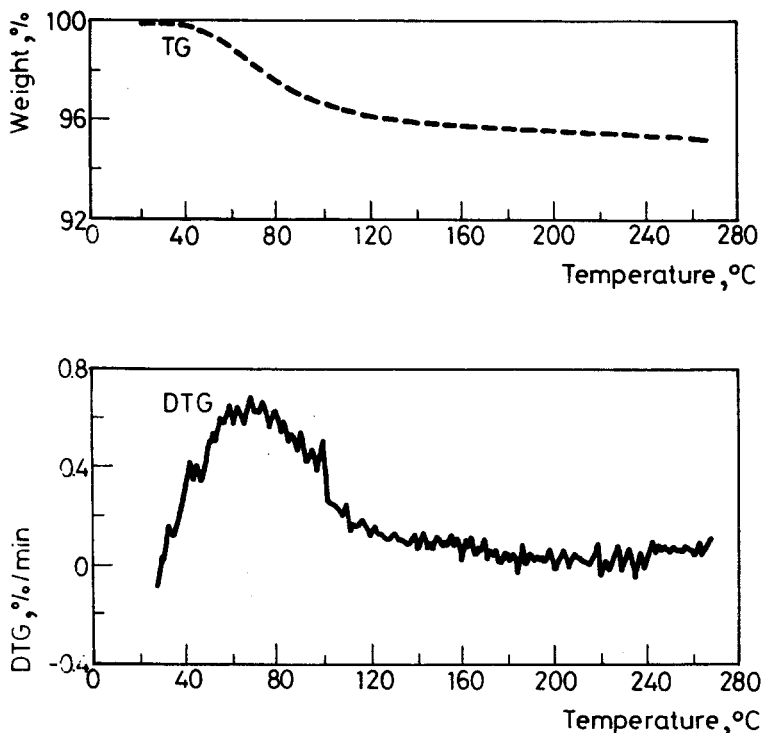

Fig. 6 TG and DTG curves of endellite

Of particular interest here to notice is that the thermal diffusivity, a (Fig. 3), exhibits nearly similar behaviour with temperature as the specific heat, Fig. 2. The observed variation of a may be due to the variation of the macrostructure of the compound. This is attributed to the fact that the thermal diffusivity is a parameter sensitive to the variation of the macrostructure. The steep decrease of a as the specimen is heated above room temperature to about 100° has occurred as a result of the removal of absorbed and combined water from the material. As the dehydration process is completed, a stable value of the thermal diffusivity of $(5 \pm 0.18) \times 10^{-4}$ cm²/sec is attained. In principle, the concept of diffusivity is inapplicable to heterogeneous materials. However, in practice, this material is never homogeneous, as point defects, dislocations, grain boundaries, pores and cracks..., etc. are present even in the so-called homogeneous material [15].

The steep decrease of the thermal diffusivity at the initial stage of heating and then the attainment of a stable value has been reported also in the case of some clays and rocks as corundum, the garnet group, granite, limestones, marbles, olivine, crystalline rock salt and sandstones [2]. Of particular importance is the fact that the above mentioned clays and rocks are similar in behaviour but different in values, in comparison with our clay compound. Moreover, the values of the thermal diffusivity of the above rocks are greatly different at the corresponding temperatures [2].

The steep decrease of the thermal diffusivity with temperature seems to follow an exponential function of the form $a = A e^{-BT}$, where both A and B are constants. From the plot of (ln a) against temperature (T) up to 100°, Fig. 7 the constants A and B were determined to be $A = 1 \cdot 294 \times 10^{-3}$ cm²/sec, $B = 0.0095$ deg⁻¹. Thus, the thermal diffusivity a can be determined at a given temperature from the relation $a = 1.294 \times 10^{-3} \exp(-0.0095\ T)$, $R.T. \leqslant T \leqslant 100°$. The above equation is, of course, not applicable for all clay compounds but only for endellite, as this equation depends strongly on the quantity of the combined water in the material.

It is noticed that there is an accordance between the temperature dependence of the thermal conductivity (Fig. 4), the specific heat (Fig. 2) and the thermal diffusivity (Fig. 3). The behaviour of the thermal conductivity with increasing temperature is similar to a group of clays and rocks as muscovite at specific orientations [16], and basalt, calcite, corundum, granite, rocks, limestones, muscovite, olivine, quartzite and sandstones [2]. Similar to the case of thermal diffusivity, the thermal conductivity diminishes exponentially with temperature $(R.T. - 100°)$. Namely, the thermal conductivity of endellite clay can be determined at a given temperature according to the relation $K = 2.2 \times 10^{-3} \exp(-0.228\ T)$, $R.T. \leqslant T \leqslant 100°$. Above 100°, the stable value of the thermal conductivity of $(2.2 \pm 0.18) \cdot 10^{-4}$ cal/cm·sec·deg, lies in the range of the usual values of K for thermal insulating materials. The thermal conductivity of thermal insulating
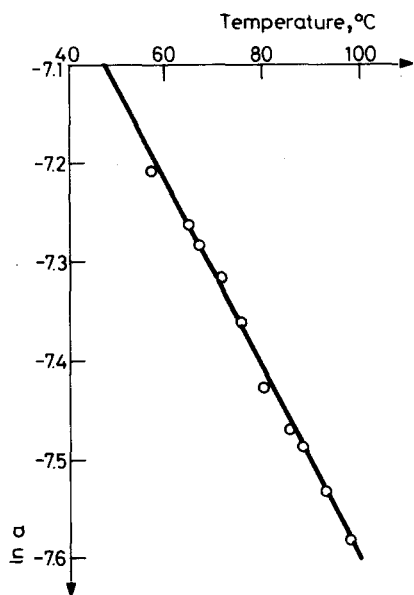
Fig. 7 (ln a) as a function of temperature
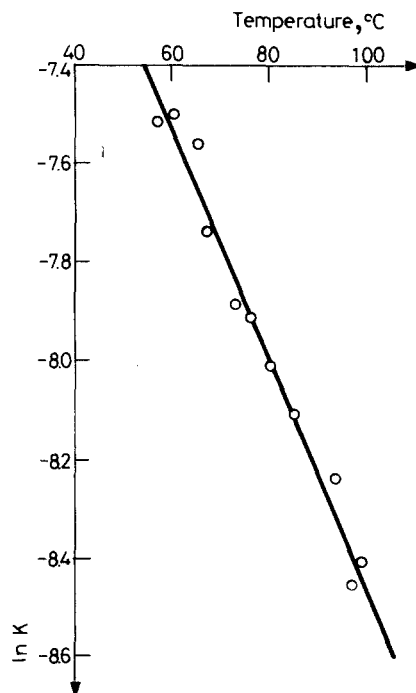
Fig. 8 (ln K) as a function of temperature

materials is essentially given by the sum of the lattice conduction (K_L) and the radiation conduction (K_{rad}). In the low temperature range, K_{rad} is negligible. A more detailed understanding of the conduction mechanism of this kind of compounds requires a knowledge of the shape, size, location and the conductivity of each particle in the system, together with the interactions among the particles.

Conclusions

From the experimental results of the present study we conclude that:

(1) The clay compound under investigation (endellite) is a thermal insulating material, especially above 100°, and has a conductivity of $(2.2 \pm 0.18) \cdot 10^{-4}$ cal/cm·sec·deg. The specific heat of the dehydrated material is nearly constant with temperature (0.22 cal/g·deg or mass corrected value $C_p = 0.234$ cal/g·deg). The value obtained for the thermal diffusivity of the water-free samples is about 5×10^{-4} cm²/sec.

(2) Specific values of the above thermal parameters at room temperature cannot be safely reported, as these parameters depend strongly on the combined or/and

crystalline water that exists in the clay structure. The dependence of the thermal conductivity at room temperature of some sandstones on the quantity of the matrix and pore water has been achieved [2].

(3) The drying shrinkage of clays varies effectively with the mineral impurity content, i.e., the drying shrinkage decreases as the mineral impurity content increases.

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References

1 G. W. Brindley and G. Brown, Crystal Structures of Clay Minerals and their X-ray Identification, Mineralogical Society, London, 1980.

2 Y. S. Touloukian, W. R. Tudd and R. F. Roy, Physical properties of rocks and minerals, McGraw-Hill Book Company, New York 1981.

3 H. R. Khajuria, S. K. Mehta and Ashok K. Gupta, J. Thermal Anal., 31 (1), (1986) 15.

4 H. R. Khajuria, S. K. Mehta and A. Kalsotra, J. Thermal Anal., 32 (1987) 749.

5 R. D. Cowan, J. Appl. Phys., 32 (1961) 1363.

6 O. A. Kreav, Studies at High Temperatures, Nauka, Novosibirsk, 1966.

7 M. J. Wheeler, J. Appl. Phys., 16 (1965) 365.

8 L. P. Fillippov, Teplifizika Vysokikh Temperature, 2 (1964) 817.

9 M. M. Mebed and A. Gobrial, Proc. Math. Phys. Soc. Egypt, 44 (1977) 19.

10 M. M. Mebed and S. Saknidy, Bull. Assiut Univ., 6 (1977) 177.

11 M. S. Mostafa, PhD Thesis, Assiut Univ., Assiut, Egypt, 1983.

12 M. S. Mostafa and A. Gaber, Indian J. Pure & Appl. Phys., 24 (10) (1986) 493.

13 Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd Ed., Vol. 6, John Wiley & Sons, New York, 1979.

14 R. A. Swalin, Thermodynamics of Solids, John Wiley & Sons Inc. 1962.

15 R. Taylor, High Temp. High Pressure, 15 (1983) 299.

16 B. N. Egorov, V. P. Konderatenkov and I. N. Anikin, High Temperature, 10 (1) (1972) 68.

Zusammenfassung — In einem Temperaturbereich zwischen Raumtemperatur und 280 °C wurde die Temperaturabhängigkeit der thermischen Eigenschaften (spezifische Wärme C_p, Temperaturleitfähigkeit a, Wärmeleitfähigkeit K) von Endellittonerde untersucht. Die Ergebnisse zeigen, daß sowohl a als such K im ersten Abschnitt der Temperaturzunahme mit steigender Temperatur bis 100 °C exponentiell abnehmen. Oberhalb 100 °C erreichen die Parameter stabile Werte: $C_p = 0,22 \pm 0,008$ cal g^{-1} deg^{-1}, $a = (5,0 \pm 0,18) \cdot 10^{-4}$ cm^2 sec^{-1} und $K = (2,2 \pm 0,16) \cdot 10^{-4}$ cal cm^{-1} sec^{-1} deg^{-1}. Die Erklärung der Ergebnisse wurde unter Zuhilfenahme von DTA und TG durchgeführt.

Резюме — Методом плоской температурной волны изучена температурная зависимость термических свойств (удельная теплоемкость C_p, термический коэффициент диффузии a и термопроводимость K) глины энделлит в области температур комнатная температура $\leqslant T \leqslant 280°$. Экспериментальные результаты показали, что на начальной стадии поднятия температуры до $100°$ обе величины a и K экспоненциально уменьшаются. Выше $100°$ термические параметры достигают постоянных значений равным $C_p = 0,22 \pm 0,008$ кал·г$^{-1}$·град$^{-1}$, $a = 5,0 \pm 0,18 \cdot 10^{-4}$ см^2·сек$^{-1}$ и $K = 2,2 \pm 0,16 \cdot 10^{-4}$ кал·см$^{-1}$·сек$^{-1}$·град$^{-1}$. Обсуждение результатов подтверждено ДТА и ТГ измерениями.