Thermochimica Acta, 75 (1984) 43–50
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL BEHAVIOUR OF SOME RAW MATERIALS AND CERAMIC MIXES

DOREYA M. IBRAHIM, ATIA M. KABISH and NABIL GHONEIM

Ceramic Department, National Research Centre, Dokki, Cairo (Egypt)

(Received 1 November 1983)

ABSTRACT

The effect of rate of heating on the decomposition reactions of some raw materials, namely: kaolinite; $CaCO_3$; dolomite; magnesite; and mixes of these, was followed by DTA. Two different rates of heating (20 and 50° min^{-1}) were chosen for the scanning. The time of the reaction was controlled. From the isothermal runs it was possible to obtain a factor ($A = cal/T^{-2}$) which is dependent on the rate of heating and the material under investigation. It was found that the amount of heat absorbed is dependent on the rate of heating. The temperature of the peaks of the main reactions were shifted by about 50°C.

INTRODUCTION

The raw materials normally used in once-fired ceramic bodies may contain components with a lower or higher content of carbonates, iron compounds and organic matter. The physical and chemical reactions taking place during firing (i.e., loss of lattice water, combustion of organic matter and dissociation of carbonates present) are influenced by time. When operating with a fast firing technique time is limited, although certain periods of time are necessary for the completion of these reactions. Meanwhile, these reactions are accompanied by the evolution of considerable amounts of gaseous by-products. Harms [1,2] has shown that the vapour released from the destruction of the clay mineral lattice exerts forces at the surfaces of the products. However, this pressure has no effect because it is distributed over a wide temperature interval between 450 and 700°C. $CaCO_3$, however, may raise problems if the dissociation process takes place suddenly when the surface of the products has already started the sintering process.

Apart from the dissociation reactions, the products produced may initiate a number of fairly complicated diffusion processes which are frequently simultaneous. These reactions are accompanied by a change in energy state (either absorption or evolution of heat) that can be readily detected by DTA. Thus, a DTA curve with an upward or a downward deflection indicates whether exothermic or endothermic reactions are taking place.

0040-6031/84/$03.00

TABLE 1

Chemical analysis of the raw materials

Constituent elements	China clay	Raw $MgCO_3$	Dolomite
SiO_2	54.78	0.9	0.42
Al_2O_3	32.22	1.04	0.63
Fe_2O_3	0.45	0.01	0.14
CaO	0.15	4.47	30.59
MgO	0.28	45.57	20.89
Na_2O	0.09		
K_2O	0.29		
Loss on ignition	11.73	48.01	47.39

Lehman [3] has shown that the rate of heating affects the intensity and temperature at which these reactions occur. He concluded that heating a clay sample at a rate of 30° $\min^{-1}$ gives an exothermic reaction with a peak 15 times that found for a rate of 2° $\min^{-1}$. Also, the temperatures of the endothermic and exothermic peaks are shifted by 170 and 80°C, respectively.

In the present study DTA is used to determine the effect of the rate of heating on the dehydroxylation reaction of china clay. Thus, two rates of heating (20 and 50° $\min^{-1}$, representing firing schedules of 2 h and 50 min, respectively, and recommended in the literature for a fast firing technique [4,5]) were used. The different components that could be added or may be present in the raw materials are studied separately and in mixes.

EXPERIMENTAL

Raw materials

China clay, basic $MgCO_3$ (Merck), pure Aswan quartz (99.65%), raw dolomite and magnesite were used. Chemical analysis of the raw materials is represented in Table 1.

Thermal analysis

The powder samples were scanned in a 1200°C DuPont DTA cell. The run was carried out against standard a-alumina as reference using platinum crucibles. Rates of heating were 20 and 50° $\min^{-1}$, sensitivities were 1, 2 and 0.5° $in.^{-1}$. Two procedures were carried out.

Isothermal scan

This procedure was performed on the kaolin samples in the temperature range 300–700°C representing the temperature interval at which the de-

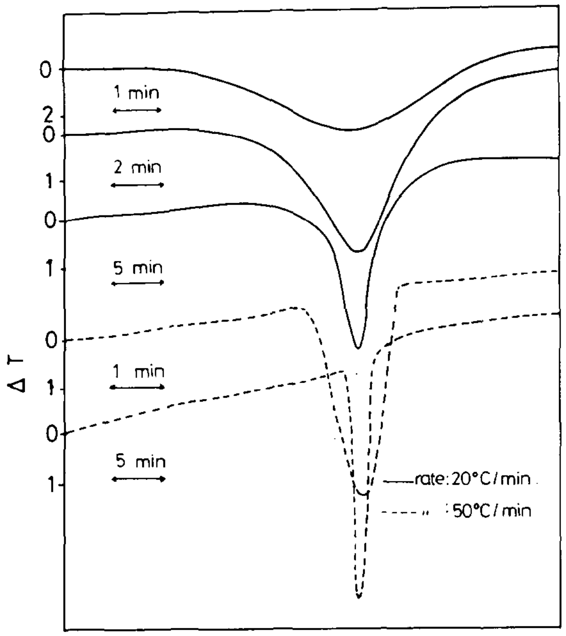

Fig. 1. Effect of rate of heating and time base of scan on the dehydroxylation reaction in kaolin.

hydroxylation reaction occurs and the formation of metakaolin takes place. The reaction was traced for constant specimen weights of 30-mg heated at the two rates (20 and 50° min^{-1}) and with three different time base settings (1, 2 and 5 min in.$^{-1}$). The curves obtained are shown in Figs. 1 and 2.

Normal thermal scan

Powder samples (10–30 mg) were scanned up to 1000°C at the rates

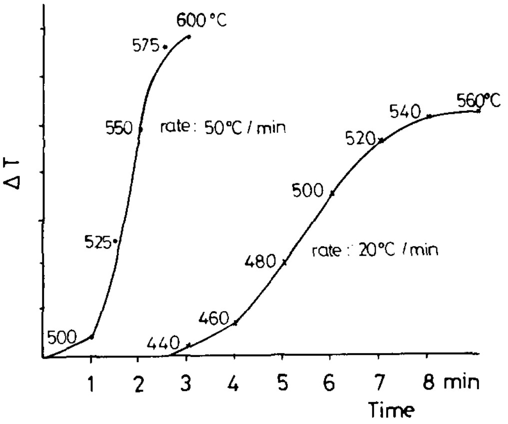

Fig. 2. Effect of rate of heating on the dehydroxylation peak of kaolin.

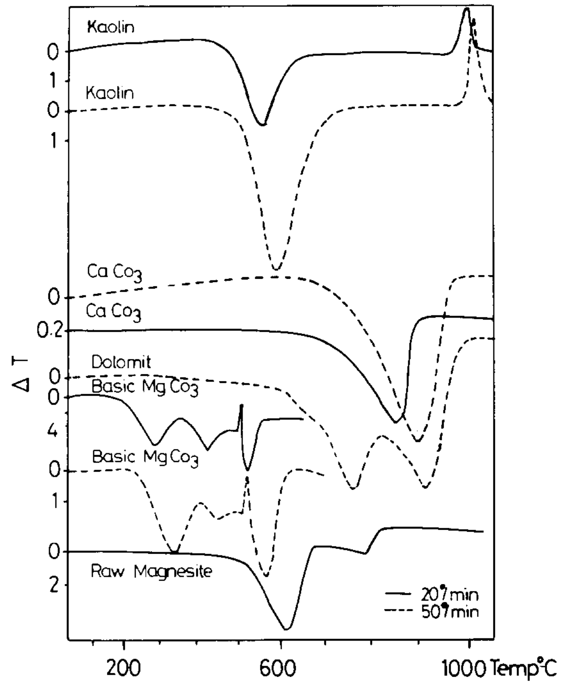

Fig. 3. DTA of raw materials.

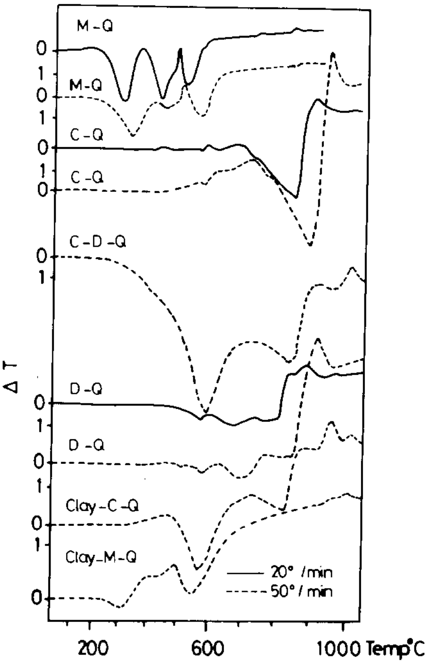

Fig. 4. DTA of the different mixes.

above. Mixes presented in Table 2 were also scanned under the same conditions. Results obtained are shown in Figs. 3 and 4.

RESULTS AND DISCUSSION

Isothermal reactions

The shape of the peak of the dehydroxylation reaction in kaolin, due to the destruction of the lattice and loss of the OH group, is greatly affected by the rate of heating and schedule of scan (time base chosen). The area under the peak was calculated from measurements of the peak height and peak width at half height and by weighing after cutting it from the curve. The values obtained were inserted in the following relation taking into consideration that the conditions of the experiment are constant for the same cell.

$$\Delta H/T = A \times (\text{area/wt.}) \times (\text{scale, }^{\circ}/\text{in.}) \times (\text{rate, }^{\circ}/\text{in.}) \times (\text{time, min/in.}) \times (1/\Delta T)$$

The results obtained give a constant value for each rate (Table 3). A cumulative plot for ΔT against time was obtained by measuring peak height at different temperatures and time intervals (Fig. 2). The results show the

TABLE 2

Results of normal thermal scan for raw materials and mixes

Raw material or mix	Peak temperature		Type of reaction	Remarks
	20° min^{-1}	50° min^{-1}		
China clay	550	590	endothermic	loss of OH
	990	1010	exothermic	
$CaCO_3$	860	900	endothermic	loss of CO_2
$MgCO_3$ (basic)	300	340	endothermic	loss of H_2O
	425, 500	450, 515	endothermic	loss of H_2O
	530	565	endothermic	loss of CO_2
Dolomite	ND	765	endothermic	loss of CO_2
		920	endothermic	loss of CO_2
Raw magnesite	573	ND	endothermic	quartz inversion
	610		endothermic	loss of CO_2
	790		endothermic	loss of CO_2
Mixtures				
M–Q magnesite (50%) and quartz (50%)	300	340	endothermic	loss of H_2O
	450 sh	450 sh	endothermic	loss of H_2O
	520	570	endothermic	loss of CO_2
	850	870	exothermic	$MgO \cdot SiO_2$
C–Q $CaCO_3$ (50%) and quartz (50%)	573	573	endothermic	quartz inversion
	850	900	endothermic	loss of CO_2
	915	955	exothermic	$CaO \cdot SiO_2$
D–Q dolomite (50%) and quartz (50%)	573	573	endothermic	quartz inversion
	670	700	flattened endothermic	loss of CO_2
	810	850	flattened endothermic	loss of CO_2
	890	915	sharp exothermic	

ND, not determined; sh, shoulder.

TABLE 3

Results of isothermal scan for the dehydroxylation reaction of kaolin

Rate of heating (° min^{-1})	Time base (min in.$^{-1}$)	Sensitivity (° in.$^{-1}$)	Peak area/wt. (cm^2 g^{-1})	Temp. interval (°C)	Value calculated
50	1	1	1455.33	475–625	485
50	5	1	291.66	450–600	486
20	2	1	1080	440–660	196.3
20	1	2	746.66	430–580	199.1
20	5	1	456	425–650	202.6

effect of the rate of heating on the time of completion of the dehydroxylation reaction. Thus, 3 min were enough to end the reaction with the fast rate (50° min^{-1}) compared with 10 min for the slower rate (20° min^{-1}).

These results indicate that the procedure carried out could be reliable. Thus, the calculation of $\Delta H/T$ for the destruction of kaolin and the formation of metakaolin in the temperature interval 300–700°C was carried out using the thermochemical constants [6] and the following equation [7]

$$H_T^0 = H_{298}^0 + a(T-298) + \tfrac{1}{2}b(T^2 - 298^2) - c(1/T - 1/298)$$

where:

	H_{298}^0 (kcal mol^{-1})	a	b	c
Kaolin	−964.47	65.49	33.17×10^{-3}	-14.9×10^5
Metakaolin	−792.7	54.84	8.8×10^{-3}	-3.48×10^5

The results obtained were: for kaolin $H_{700}^0 = 29152$ kcal mol^{-1}; and for metakaolin $H_{973}^0 = 39189.722$ kcal mol^{-1}.

$\Delta H = H_{973}^0$ (for metakaolin) $- H_{700}^0$ (for kaolin)

$= 176.53 \text{ kcal g}^{-1} - 112.994 \text{ kcal g}^{-1} = 63.53 \text{ kcal g}^{-1}$

$\Delta H/T = 90.757 \text{ cal g}^{-1}\ {}^\circ\text{C}^{-1}$.

Therefore

For a rate of 50° min^{-1}, $A = 0.187$ cal $^\circ\text{C}^{-2}$

For a rate of 20° min^{-1}, $A = 0.45$ cal $^\circ\text{C}^{-2}$

These results show that the factor A representing the amount of energy consumed/temp.^{2} varies with the rate of heating. It is evident that this factor is relatively small for the fast rate (50° min^{-1}). The temperature difference (peak height) on the other hand is large. This explains the increase in peak height with an increase in the rate of heating observed by Lehman [3].

Results of normal scan

The effect of firing rate on the main reactions in the raw materials is shown in Fig. 3 and Table 2. The fast rate caused a shift in the peak temperature and in the intensity of the peak. Results of the two-component mixes of quartz (50%) with either dolomite, $CaCO_3$, or magnesite show the main peaks of the starting material, i.e., those of the decomposition reactions and the exothermic peaks of the new compounds formed. Thus, the reaction of quartz with magnesite gives enstatite, while the reaction of quartz with $CaCO_3$ gives wollastonite which is characterised by an exothermic reaction occurring at 915°C. As expected the fast rate shifted the peak temperature to 955°C. The three-component mixes of clay (50%), quartz (25%) with either dolomite, $CaCO_3$, or magnesite gave similar results (Fig. 4). The addition of magnesium carbonate greatly reduced the exothermic peak of the kaolin. This shows that part of the metakaolin formed entered into reaction with the magnesium compounds formed. Magnesium compounds end early in the reactions.

Discussion

The calculation of heats of reactions is based on the principle of conservation of energy [8]. In a given system, the heat consumed in the decomposition of a compound into its elements is equal to that evolved during its formation. Therefore, the resultant heat change accompanying the reaction is the same whether it takes place in one or several steps independent of the path (i.e., the net heat of reaction at constant pressure depends on the initial and final states and not on the intermediate states through which the system may pass). The heat change varies with temperature, therefore, the heat of reaction can be calculated from the thermochemical data.

Using the values obtained from the calculation of peak area and substituting in the relation

$$\begin{aligned}(\Delta H/\mathrm{d}T)_\mathrm{p} &= \Delta c_\mathrm{p}(T_2 - T_1)\\ &= A \times T/g\end{aligned}$$

where the factor A represents the amount of energy consumed in the reaction (cal T^{-2}). It is evident from the results that this factor depends on the rate of heating.

CONCLUSIONS

The rise in temperature accompanying fast rates of heating is accompanied by the absorption of a smaller amount of energy.

The amount of energy absorbed or evolved depends on the material scanned and the rate of heating. It can be estimated from the factor A (cal $^\circ C^{-2}$).

DTA can be used to calculate the amount of this energy carrying out the scan isothermally.

REFERENCES

1 W. Harms, Sprechsaal, 105 (1972) 765.
2 W. Harms, Interceram, 2 (1974) 1.
3 H. Lehman, Tonind. Ztg., Suppl. 1 (1954).
4 H. Mörtel, Ceram. Int., 3 (1977) 65.

5 Anonymous, In Fact, 86 (1972) 1.
6 S. Kienow and F. Harders, Feuerfestkunde (Herstellung, Eigenschaften und Verwendung feuerfesten Baustoffe), Springer, Berlin, 1960.
7 H. Salmang and H. Scholze, Keramik Teil I. Allgemeine, Grundlagen und wichtige Eigenschaften, 6th edn., Springer, Berlin, 1982.
8 S. Glasstone, Elements of Physical Chemistry, Macmillan, London, 1954.