

Cements, Glasses, Ceramics

**SIMULATING MINERALS PYROPROCESSING BY
THERMAL ANALYSIS**
Clinkerisation of cement raw mixes

A. Bhattacharya

17, PUSHPARAG, GOSHALA ROAD, MULUND (WEST) BOMBAY 400 080, INDIA

TG and DTA studies on laboratory cement raw mixes and raw dolomite have been extensively reported in the literature. This paper discusses four aspects. (1) Calcination kinetics of raw mix by isothermal TG and calculation of rate constants to derive activation energy by Arrhenius plots. (2) Quantification by TG of minerals in Indian laterites. The amount of goethite appears to influence burnability of raw mix. (3) Determination of practical heat of clinker formation from DTA studies and establishment of enthalpy temperature relationship of raw mix for heat transfer studies in rotary kilns. (4) Prediction of material temperature profile in a dolomite kiln from DTA studies of raw dolomite.

Keywords: calcination kinetics, cement, clinkerisation, dolomite

Introduction

A cement raw mix typically consists of 75–85% limestone, 15–20% clayey materials, the balance being corrective materials, and has a fineness of 85% less than 90 μm size particles. The raw mix is progressively heated to about 1450°C such that partial fusion occurs, followed by rapid cooling of the product, termed clinker.

Thermogravimetric measurements followed by evaluation of reaction kinetic parameters have found interesting applications for ascertaining the reactivity of limestone, which has a decisive influence on the sinterability of the raw mix to produce cement clinker. Waechtler [1] carried out non-isothermal TG studies on

limestone and calculated activation energies using the Coats and Redfern equation. He classified limestone deposits for cement making into four categories as under:

Category	Mean activation energy /kJ·mol ⁻¹	Reactivity
I	>180	Poor
II	180–130	Medium
III	130–80	Good
IV	80–30	High

Theoretical consideration and experimental

Calcination kinetics of cement raw mix by isothermal TG

The major early-stage reaction undergone by the raw mix is the decomposition of calcite, involving a weight loss of 36–37% mainly due to the reaction $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ over the temperature range 500°–900°C.

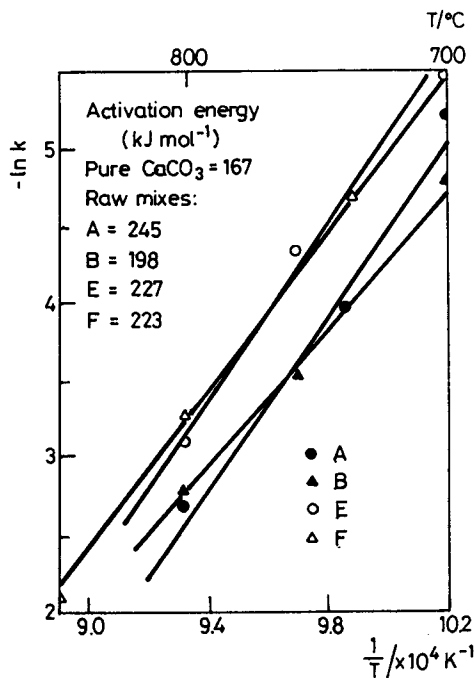


Fig. 1 Arrhenius plot for determination of activation energies for four raw mixes

Bhattacharya *et al.* [2, 3] carried out isothermal TG runs in static air at temperatures between 700° and 850°C on four raw mix samples. The rate constant for each temperature was calculated from the equation

$$1 - (1 - \alpha)^{1/3} = kt$$

assuming that limestone particles follow a contracting sphere model, whereby α = fractional decomposition, $k = V/r$, V = velocity of contraction and r = radius of spherical particles. For values up to 80% the plots of $1 - (1 - \alpha)^{1/3}$ vs. t showed good linearity. Activation energy values were then determined from the temperature dependence of rate constants using the Arrhenius equation, $k = Ae^{-[E_a/RT]}$. The results are shown in Table 1; E_a values ranged between 198 and 245 kJ/mol of limestone for the four raw mixes studied. E_a of pure CaCO is 167 kJ/mol [4].

For the four raw mixes the authors attempted to correlate E_a values with the raw mix reactivity, which is generally defined as the overall transformation of the raw mix to clinker. This is primarily a function of the minerals present in the constituents which on thermal decomposition yield active oxides for the solid-state melt phase reactions. The reactivity was expressed as the heat required for reactions from ambient to 1350°C as determined by DTA. Bhattacharya and Co-workers observed that for raw mixes with higher E_a values the decomposition rate is higher at higher temperatures and that reactivity increases with decrease in activation energy values.

Table 1 Results of kinetic study

Raw mix	$T / ^\circ\text{C}$	Rate constant	$E_a / \text{kJ}\cdot\text{mol}^{-1}$
A	710	0.0054	245
	750	0.0211	
	800	0.0676	
B	710	0.0084	198
	760	0.0286	
	800	0.0637	
C	710	0.0043	227
	760	0.0135	
	800	0.0454	
D	740	0.0093	223
	800	0.0381	
	850	0.1251	

Minerals in Indian laterites

In the manufacture of Portland cement, laterite is extensively used in small quantities as a corrective material to balance the aluminium and iron contents of the raw mix feed. Anandakumaran and Bhattacharya [5] investigated the influence of minerals present in Indian laterites on the pyrolysis of raw mix using TG and DTA. Based on minerals identified by DTA runs to 1000°C, 15 laterite samples were classified in three groups (Fig. 2). For approximate quantification of major minerals they conducted TG analysis to 950°C taking one sample from each group, after first determining major-element chemistry. Hematite and free silica detected by XRD were calculated by difference. Major minerals identified from DTA peaks and XRD as well as their approximate composition are given in Table 2.

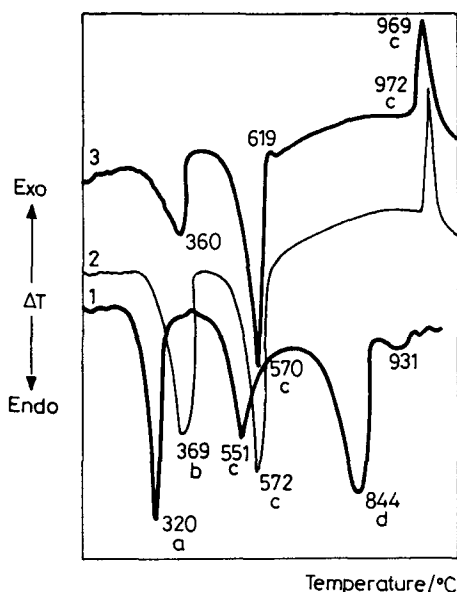


Fig. 2 DTA curves of laterites, 1,S; 2,N; 3,JM

The authors also conducted TG runs to 950°C and DTA runs to 1400°C on three raw mixes proportioned with two grades of limestone and 3% laterite to theoretically yield 75% C₃S in the sintered products. Using raw mix pellets, burnability experiments were carried out following well established methods.

The authors concluded that laterite containing goethite as the major iron-bearing mineral seemed to influence the solid-state reactions both during calcination and sintering. In the temperature range 700°–840°C goethite retarded the rate of

calcite decomposition in limestone. The sintering reaction seemed to have proceeded faster with Fe_2O_3 decomposed from goethite rather than Fe_2O_3 present in hematite.

Table 2 Quantitative mineralogy of laterite samples

Minerals	DTA peak	$T / ^\circ\text{C}$	Approx. %		
			1.S	2.N	3.JM
a. Gibbsite	endo	320	19.5	—	—
b. Goethite	endo	320–360	—	58.1	45.5
c. Kaolinite	endo	550–575	35.8	34.9	42.4
	exo	950–980	—	—	—
d. Calcite	endo	840–900	15.7	—	—
Hematite	XRD	—	28.0	1.4	8.0
Free silica	—	—	—	1.1	—

Practical heat of clinkerisation by DTA

For the design and operation of a minerals pyroprocessing system knowledge of the practical heat requirement to bring the feed material to its burning temperature is essential. DTA provides a direct and practical method as reported in several Indian publications.

Bhaskara Rao *et al.* [6] proposed a method using simultaneous TG/DTA which consisted of the following steps:

1. Obtain two DTA curves, one for pure $\alpha\text{-Al}_2\text{O}_3$ and the other for the raw mix for the same heating rate of $16^\circ\text{C}\cdot\text{min}^{-1}$ under identical experimental conditions as that of reference material $\alpha\text{-Al}_2\text{O}_3$.

2. Obtain a DTA curve of standard CaCO_3 under similar conditions. The area of the endothermic peak is assigned an accepted heat equivalent of $164 \text{ kJ}\cdot\text{mol}^{-1}$, (S).

3. Superimpose Al_2O_3 DTA curve (A) on the raw mix DTA curve (B) to obtain two well defined areas (P = positive) and (N = negative) in a closed loop which includes the sensible heat, HA, of $\alpha\text{-Al}_2\text{O}_3$ calculated by a standard formula.

4. Measure areas of P , N and S and, using $S = 164 \text{ kJ}\cdot\text{mol}^{-1}$, calculate heat equivalent of P and N , namely HN and HP. The total heat requirement = $\text{HA} + \text{HP} - \text{HN}$. The advantage of this method is that it does not require chemico-mineralogical compositions of the raw materials.

DTA curves of Al_2O_3 and the raw mix are given in Fig. 3. The authors also devised a second method which requires determination of reaction heat from DTA curves by comparison with areas obtained from DTA curves of standard reference materials of known enthalpies, and adding sensible heat computed for the mineral

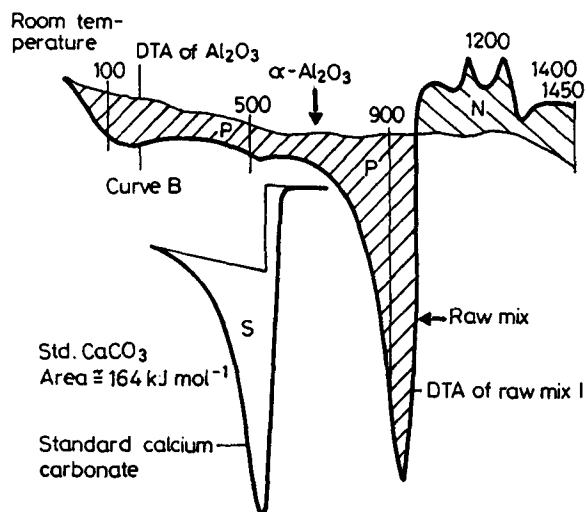


Fig. 3 DTA curves of cement raw mix and alumina (method 1)

phases determined by XRD in the raw mix and clinker. The heat required for clinkerisation of a raw mix by this method is reproduced in Table 3.

Table 3 Heat requirements for clinkerisation

Temp. range / °C	kJ/kg clinker		Total heat
	Sensible heat	Peak area heat	
25–200	261	167	428
200–400	341	–	341
400–600	354	25	379
600–800	360	195	555
800–1000	246	1492	1738
1000–1200	214	–	214
1200–1450	287	–78	209
	2063	1801	3864

Khadilkar and Hargave [7] followed the second method of earlier authors to calculate the reaction heat of clinker formation but not the total heat requirement. They investigated raw mixes of varying chemico-mineralogical compositions, including coal ash and compared the theoretical (Zur Strassen) heats of reaction with those experimentally determined by DTA. They concluded that raw mixes with unfavourable chemico-mineralogical compositions showed higher experimental heat of reaction and that higher reactivity is indicated by a lower heat

of reaction. Addition of a mineraliser such as CaF_2 reduced the experimental heat of reaction.

Raina *et al.* [8] later presented an experimental method based on DTA for estimating practical heat of reaction. Following the first method [6] they determined the total heat (A) required to bring the raw mix from ambient to burning temperature. From this the heat (B) recovered from the cooling of clinker (assumed to consist of the four conventional potential compounds) as well as the heat from gaseous products (C), H_2O and CO_2 , determined by TG and DTA, were subtracted to obtain the experimental heat of reaction. This compared well with the theoretical heat calculated by the Zur Strassen equations [9] valid for raw mixes with purer raw materials.

Enthalpies for heating raw mixes from ambient to any intermediate temperature can be easily obtained from a plot of total heat against temperature, as determined by either of the above methods [6]. For suspension pre-heater kilns, enthalpies for material temperature from 800°C , assumed at the kiln entry, up to the burning temperature of approximately 1450°C , are shown in Table 4 for a raw mix with coal ash.

Table 4 Enthalpy values for raw mixes with increasing temperature

Temp. interval 25°C to	Enthalpy / $\text{kJ}(\text{kg clinker})^{-1}$	Temp. interval 25°C to	Enthalpy / $\text{kJ}(\text{kg clinker})^{-1}$
800	1324	1200	3211
900	1923	1300	3384
1000	3015	1400	3744
1100	3104	1450	3939

The non-flame zone of a kiln can be calculated by estimating the segmental heat for every 100°C rise in material temperature, starting with a solid temperature of 800°C and a gas temperature of 1100°C , up to a solid temperature of 1200°C which corresponds to a gas temperature of about 1900°C which approximates to the actual flame temperature. In a case study, the non-flame zone length was calculated to be approximately 56% of the total kiln length; the addition of the burner pipe projection, that is the precooling zone length and the flame length calculated by well established formulae, to the non-flame zone length gave the total kiln length [10] close to the design length.

Material temperature profile in dry process rotary kiln from DTA curves

Ludera [11] proposed a method for determining the approximate feed material temperature curve in a rotary kiln for any type of material. He cited an example of raw dolomite which was heated in a DTA furnace to 1400°C , over a period of

200 min. He assumed that all sintering processes above 1500°C occur only in the burning zone of the kiln, i.e. under the tip of the flame the material assumes its highest temperature. The DTA curve thus corresponds to about 80% of the kiln length.

As a reference point the ratio n of the DTA end temperature to the burning temperature is taken. For dolomite clinker burning at 1950°C and a DTA end temperature of 1400°C, $n = 1400/1950 = 71.8\%$. From the DTA curve:

	Temperature / °C		
	begins at	ends at	peak
Decomposition of first stage	440	760	740
Decomposition of second stage	780	950	860

Decomposition began at 60 min i.e. 30% of the test period and ended at 122 min (61% of the test period).

Thus, 740°C = 50% of time

780°C = 52.5% "

860°C = 59% "

Ludera also assumed that 15% of the length represented the burning and pre-cooling zone (estimated temperatures 1850–1900–1950), sintered product discharged to the cooler at 1500°C.

First reference point in the temperature/zone length diagram is $1400/1900 = 73.7\%$ as kiln length coordinate for 1400°C. Drying to 110°C takes about 10%, while heating and calcining take about 63% of the length.

It must be stressed that the method is only approximate, but it does replace the laborious arrangement of taking out material samples from running kilns to estimate material temperature along its length.

Conclusion

From discussions on the four selected applications of TG/DTA techniques it can be concluded that thermal analysis is a versatile technique for simulating pyroprocessing of minerals in rotary kilns.

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Zusammenfassung — TG- und DTA-Untersuchungen an Zementrohnmischungen und Rohdolomit wurden in der Literatur intensiv beschrieben. In dieser Arbeit werden vier Aspekte diskutiert: (1) Die Kalzinationskinetik von Rohgemischen mittels isothermer TG und der Berechnung der Geschwindigkeitskonstante, um in Arrheniusschen Diagrammen die Aktivierungsenergie zu erhalten. (2) Mittels TG die Quantifizierung von Mineralen in Lateriten aus Indien. Goethit scheint die Brennbarkeit von Laterit-Rohmaterial zu beeinflussen. (3) Bestimmung der Klinkerbildungswärme aus DTA-Untersuchungen und Feststellung der Enthalpie/Temperatur Beziehung von Rohgemisch für Wärmetransportuntersuchungen an Drehbrennöfen. (4) Vorhersage des Temperaturprofils des Materiales in einem Dolomitbrennofen anhand von DTA-Untersuchungen an Rohdolomit.