Journal of Thermal Analysis, Vol. 35 (1129–1136

THERMAL ANALYSIS OF SPURRITE FROM A ROTARY CEMENT KILN

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A number of samples from the pre-burning zone of a wet-process cement rotary kiln were examined by combined DTA/TG and XRD for estimation of spurrite ($2Ca_2SiO_4 \cdot CaCO_3$). It was found that decarbonation temperatures of spurrite range from 1130 to 1190 K and they are 45 to 75 K higher than that of calcite occurring in the same sample. In the TG curves calcite and spurrite can be easily distinguished and accordingly both can be estimated from the same TG scan. Combined DTA/TG, supplemented by XRD, is a very effective method for qualitative and quantitative estimation of spurrite in cement rotary kiln materials.

The mineral spurrite, $2Ca_2SiO_4 \cdot CaCO_3$ is generally reported to be present in the coating rings formed in the pre-burning zone of the rotary cement kiln. Occasionally its presence has also been reacorded in the cement kiln materials [1–3]. As spurrite may cause excessive ring formation and thus affect the clinker output, its estimation is very essential in the cement manufacturing process. Consequently in recent years, the formation of spurrite, either from industrial cement kiln feed or from cement clinker components has been examined extensively [4–8]. In most of these investigations spurrite is identified by XRD and microscopic methods. Thermal analysis has been applied very rarely for the quantitative estimation of spurrite. Hung Chen [3] examined spurrite in cement kiln materials by DTA and TG separately and showed that by determining $CaCO_3$ in the acid extracted part of the material, the quantity of spurrite in the original sample could be determined by TG. In the present study combined DTA/TG has been used for both qualitative and quantitative estimation of spurrite in the samples collected from different points in a wet-process cement kiln. Thermal analysis has been supplemented by XRD.

Experimental

A 165 m long, 700 tons per day (tpd) wet-process rotary cement kiln was stopped during normal operating conditions, allowing the kiln materials to remain in

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original positions. A number of samples were collected from different points in the kiln, out of which samples at 120 to 150 m from the feed-end were taken for the present investigation. This part of the rotary cement kiln may be termed as pre-burning zone.

Simultaneous DTA/TG of the samples was carried out in a Netzsch Simultan Thermo Analyzer, Model 429 with potentiometric recorder in air. The rate of heating was kept constant at 10 deg per minute; ΔT sensitivity was 0.05 mV/F.S. and Δwt. sensitivity was 50 mg/F.S. The weight of the sample taken for analysis in all cases was 100 mg. Al_2O_3 was taken as reference material. The chart speed was kept at 120 mm/hour.

XRD patterns of the samples were obtained in a Philips X-ray Diffractometer, PW–1730, using CuK_α radiation with Ni-filter under identical conditions (40 kV, 20 mA) in 1000 range.

Results

Figure 1 shows DTA curves of two consecutive samples from the kiln. Sample No. 1 shows 2 endothermic peaks at 846 and 1153 K for $\alpha-\beta$ quartz

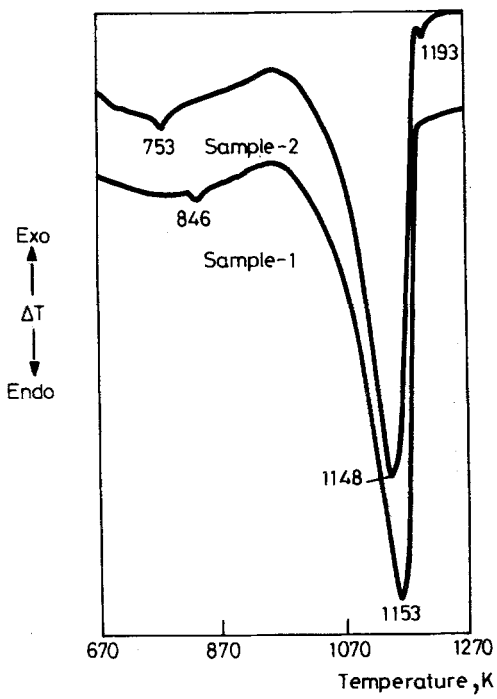

Fig. 1 DTA curves of cement kiln materials showing the appearance of spurrite in sample No. 2

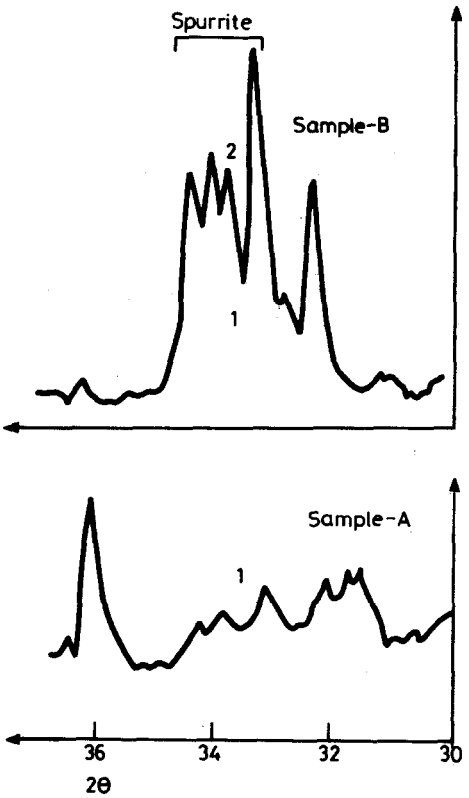

Fig. 2 XRD patterns of cement kiln materials showing the presence of different amounts of spurrite

transformation and dissociation of calcite, respectively. Sample No. 2 shows 3 endothermic peaks at 753, 1148 and 1193 K. The first endo peak at 753 K is identified as that for $Ca(OH)_2$ [9]. The third endo peak at 1193 K was not recorded in any of the samples examined from the feed-end side of the sample No. 2 and hence it was assumed to be due to a newly developed clinker phase. The XRD pattern of sample No. 2 shows the appearance of spurrite (Fig. 2, sample A). Accordingly the endo peak at 1193 K is identified as that for the dissociation of spurrite. The XRD pattern of a sample containing 40% spurrite is also shown in Fig. 2 (sample B).

DTA curves of some of the samples examined are shown in Fig. 3. They are numbered 1 to 4 in the order of increasing amounts of spurrite. It is found that the decarbonation temperture of spurrite is not a fixed one, but ranges from 1130–1190 K.

Figure 4 is a combined DTA/TG trace of a spurrite-containing material from the pre-burning zone of the kiln. Furthermore TG curves of cement kiln materials

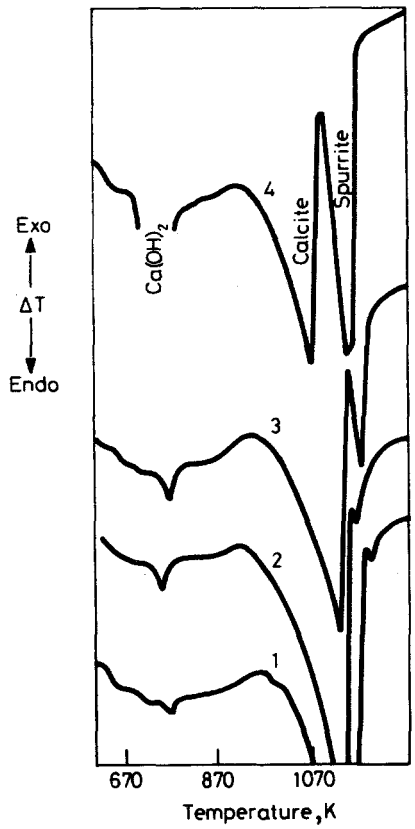

Fig. 3 DTA curves recording different temperatures of decarbonations of spurrite in cement kiln materials

containing different amounts of spurrite are shown in Fig. 5. Both figures show that mass loss due to decarbonation of spurrite can be clearly distinguished from that of calcit in the TG curve. So it is possible to estimate the spurrite content from the mass loss due to decarbonation of spurrite. ($2Ca_2SiO_4 \cdot CaCO_3$ contains 9.9% CO_2.) Spurrite contents, calculated from the mass loss in TG and respective pulse counts per second (PCS), for spurrites at *d* spacings of 2.701 Å (*hkl*–023, 22$\bar{2}$) are shown in Table 1. It is found that they are almost proportionate.

Discussion

The DTA curve and XRD pattern of the sample No. 2 (Figs 1–(2) and 2–(A) respectively) show that both methods are equally sensitive for a qualitative analysis

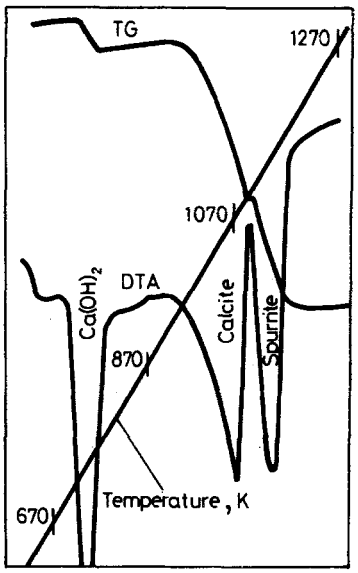

Fig. 4 Combined DTA/TG of a spurrite-containing cement kiln material

Table 1 Spurrite contents (by TG) and pulse counts per second (PCS) for spurrite at *d* spacings of 2.701 Å

Serial No.	Spurrite, wt.%	PCS
1	40	240
2	30	190
3	20	130
4	16	105
5	8	55
6	4	30

of spurrite. Neither XRD nor DTA could detect spurrite in any of the samples examined from the feed-end side of sample No. 2. Janko [10] reported the decomposition temperature of spurrite to be 1133 K for his samples collected from the coating of a pilot plant rotary kiln. Hung Chen's [3] DTA curves for spurrite recorded variable dissociation temperatures but invariably lower than 1123 K. In the present investigation they are found to range from 1130 K to 1190 K. Thus it is observed that spurrite samples even from the same kiln may show different temperatures of dissociation. This may be attributed to the different temperature and pressure conditions prevailing during the formation of spurrite.

From DTA and XRD studies of number of samples from different points in the kiln, it is found that the decarbonation temperature of spurrite is invariably higher

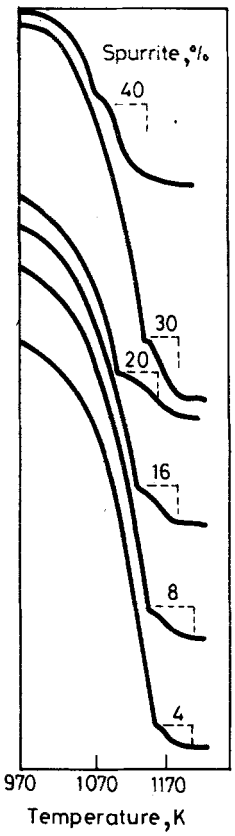

Fig. 5 TG curves of cement kiln materials containing different amounts of spurrite

than those of calcite present in the same material. Glasser [6] has also shown that at a given CO_2 pressure, the thermal stability of spurrite is greater than that of calcite. So, identification of spurrite in presence of calcite should not pose any problem. But in case of sample exhibiting only one peak in the temperature range of 1100 to 1190 K, it is desirable to check the sample with XRD.

As shown in Figs 4 and 5, the mass loss due to decarbonation of spurrite can be clearly distinguished from that of calcite in the TG curve. Accordingly, the quantities of both spurrite and calcite could be estimated from their TG curves. In the present study, it has been found that spurrite decomposes at temperatures which are 45 to 75 K higher than that for calcite. Glasser [6] has reported that, spurrite, decomposed at temperatures which were 25–50 K higher than that for calcite. In case of natural minerals this difference may be even higher than 100 K [11]. Hung Chen [3] could not get them separated in the TG curves, most probably because of the fact that the rate of heating of his samples was 20 deg/min and the TG sensitivity

was low (4–20 mg/FS). So, Hung Chen, had to analyze both the original and the acid extracted part of the samples separately to estimate the spurrite content. The present investigation shows that it is possible to estimate both spurrite and calcite from the same TG scan by employing proper instrumental conditions.

Conclusion

Combined DTA/TG, supplemented by XRD, is a very effective method for qualitative and quantitative estimation of spurrite in cement rotary kiln materials.

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The authors are very grateful to Mr. A. H. Dalmia, president, M/s. Orissa Cement Limited, Rajgangpur for allowing to collect the samples during the stoppage of the kiln and also for his permission to publish the paper.

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Zusammenfassung — Unter kombinierter Anwendung von DTA/TG und Röntgendiffraktionsverfahren wurde eine Anzahl Proben aus einem Vorkalzinator eines Drehrohrofens zur Zementherstellung nach dem Naßverfahren auf Spurrit ($2Ca_2SiO_4 \cdot CaCO_3$) untersucht. Es wurde festgestellt, daß die Temperatur für das Austreiben von CO_2 bei Spurrit zwischen 1130 und 1190 K und somit um 45–75 °C höher als bei in derselben Probe vorliegenden Kalzit liegt. Aufgrund der TG-Kurven können Kalzit und Spurrit leicht voneinander unterschieden und demzufolge mit einem einzigen TG-Scan bestimmt werden. Kombinierte DTA/TG, ergänzt durch Röntgendiffraktionsverfahren ist eine sehr leistungsstarke Methode zur qualitativen und quantitativen Bestimmung von Spurrit in Stoffen aus Zementdrehrohröfen.

Резюме — С целью установления спуррита ($2Ca_2SiO_4 \cdot CaCO_3$), комбинированным методом ДТА/ТГ и диффракцией рентгеновских лучей был исследован ряд проб, взятых из зоны

предобжига вращающейся цементной печи, работающей по мокрому способу. Найдено, что температуры декарбонизации спуррита находятся в области температур 1130–1190 К, что на 46–75 К выше чем для кальцита, находящегося в том же самом образце. Кривые ТГ для кальцита и спуррита могут быть легко разделены и поэтому обе кривые могут быть установлены из одного и того же ТГ измерения. Комбинированный метод ДТА/ТГ, дополненный рентгенодифракционным, является очень эффективным методом качественного и количественного определения спуррита в материалах вращающейся цементной печи.