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Thermal studies of Cr_2O_3 doped $CaCO_3$–SiO_2 (2:1) system

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Mixtures of $CaCO_3:SiO_2$ in 2:1 molar ratio were subjected separated to thermal analysis with varying concentration of Cr_2O_3 (0.1 to 5%) as dopant. The activation energy (E_a) and enthalpy (ΔH) shows a decreasing trend with 0.1 to 1% Cr_2O_3 and attains a minimum value with 1% dopant. 0.1 to 0.5% Cr_2O_3 helps in the formation of β and γ C_2S, (Cement Chemistry notations, C = CaO, S = SiO_2) phases at 1400° C and above but 1% Cr_2O_3 stabilizes β-C_2S phase along with a little free lime and $CaCrO_4$. A small quantity of $CaCrO_4$, Cr_2SiO_4 and α-C_2S are also formed along with the major phases with 5% Cr_2O_3 indicating that Cr^{3+} can substitute both Ca^{2+} and Si^{4+} ions in the C_2S lattice.

1. Introduction

The effect of minor constituents on the structural properties of portland cement clinker has been the subject of interest for many years [1–6]. The effects of Cr_2O_3 on the early strength development have been reported [7–9]. Investigations on the effect of Cr_2O_3 on the formation of di- and tri-calcium silicate phases have also been carried out [10–13]. However, little work has been done on the thermal behaviour of Cr_2O_3 doped mixture of 2:1 molar $CaCO_3:SiO_2$, although the above mix is relevant for the synthesis of dicalcium silicate, an important mineral constituent of clinker.

This work aims to evaluate the thermodynamic and kinetic parameters of the decomposition of $CaCO_3$ in Cr_2O_3 doped 2:1 molar $CaCO_3$–SiO_2 mixture and on the early formation of dicalcium silicate phase. From the industrial point of view, the study is also important since the chromium acts as a mineralizer in the early formation of cement constituents [10, 13] and accelerates the assimilation of CaO and SiO_2.

2. Experimental details

2.1. Materials and sample preparation

To the 2:1 molar mixture of reagent grade $CaCO_3$ and quartz powder (purity > 99.9%), varying amounts of Cr_2O_3 (0.1 to 5%) were added. The resulting mixtures after thorough mixing, grinding and passing through a 100 μm sieve, were shaped in the form of nodules with small amounts of distilled water. The samples after drying at 100 ± 5° C (2 h) were tested for quantitative estimation of $CaCO_3$ to ensure complete homogenization. These dried samples were stored for the experimental work.

2.2. Thermal analysis

The measurements were made by Mettler thermal analyser (TA-1), which simultaneously records the differential thermal analysis (DTA) differential thermal gravimetric (DTG) and thermal gravimetric (TG) curves. The samples (60 mg) were heated to 1450° C at a rate of 8° C min^{-1} in a platinum crucible of the thermal analyser. α-Al_2O_3 (previously burned to 1500° C for 30 min) was used as the reference material.

The activation energy (E_a) of $CaCO_3$ decomposition was calculated from the DTG curve [14]. The enthalpy (ΔH) and the shape index were determined from the DTA curve [15, 16].

2.3. X-ray diffraction studies

The samples for analysis were powdered to pass through a 45 μm sieve and pressed into a sample holder. The instrument used was Philips model PW 1120. The diffraction patterns were recorded using copper target and nickel filter.

2.4. Examination of the intermediate phases

The samples in the form of nodules were heated in a quench furnace at the rate of 8° C min^{-1} in a platinum bucket to the temperature where the DTA peak ends, retained for 30 min at that temperature and immediately quenched in liquid nitrogen. Thus the likelihood of the reversibility of the reaction was prevented.

2.5. Estimation of free lime

The free lime in the final products (obtained after heating to the final DTA peak temperature for 2 h) was estimated by titrating the ethylene glycol extract against standard HCl [17].

3. Results and discussion

A broad exotherm in the DTA curve was observed for all samples in the region 100 to 200° C (Fig. 1), which could be assigned to heat capacity changes since no features are observed in the DTG curve. An endothermic peak at 575° C due to α–β quartz transformation is not influenced by the presence or concentration of the dopant. The initial, peak and termination temperatures (T_i, T_d and T_f respectively) of the DTG peak

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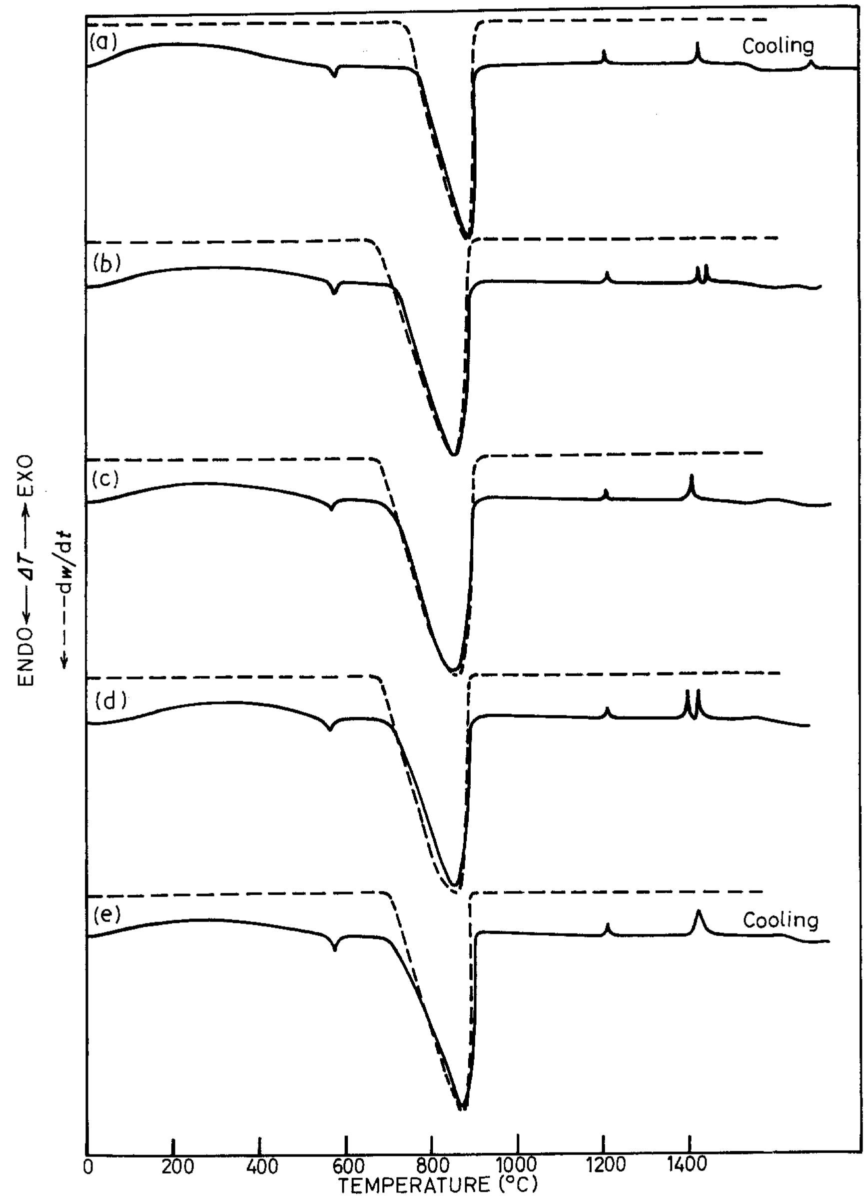

Figure 1 Thermal curves of (a) $2CaCO_3:SiO_2$; (b) $2CaCO_3:SiO_2$ + 0.1% Cr_2O_3; (c) $2CaCO_3:SiO_2$ + 0.5% Cr_2O_3; (d) $2CaCO_3:SiO_2$ + 1% Cr_2O_3; (e) $2CaCO_3:SiO_2$ + 5% Cr_2O_3 (– – –) DTG curve, (——) DTA curve.

for decomposition of $CaCO_3$ and the activation energy (E_a) are given in Table I. The enthalpy (ΔH) and shape index (Fig. 2) determined from the DTA curves are also given in the table. The dopant reduces the values of T_i, T_d and T_f but the effect of concentration variation is not significant. As the amount of dopant increases from 0.1 to 1.0%, the E_a and ΔH values progressively decrease, but for 5% concentration these values show an increase. The shape index shows an increasing trend with increasing concentration of the dopant and the value of the reaction kinetics approaches one.

The thermal curves of these samples show an exotherm at 1210° C, which could be attributed to the transformation of quartz into cristobalite and formation of some β and γ-C_2S phases. This is confirmed by the X-ray diffraction (XRD) pattern of the liquid nitrogen quenched sample heated to 1220° C (with 30 min retention).

0.1% doped Cr_2O_3 sample gives an exothermic peak

TABLE I* Thermal analysis data of Cr_2O_3 doped $CaCO_3:SiO_2$ (2 : 1) system

Concentration of Cr_2O_3 by weight in $CaCO_3:SiO_2$ (2 : 1) system	Temperature of decomposition of $CaCO_3$ and other kinetic parameters						Exothermic peak observed by DTA after decomposition of $CaCO_3$ (° C)
	Threshold (T_i) (° C)	Peak (T_d) (° C)	Termination (T_f) (° C)	Activation energy E_a (kJ mol^{-1})	Enthalpy ΔH (kJ mol^{-1})	Shape index from DTA	
0.0	740	885	910	247	160	0.143	1425
0.1	655	860	885	225	146	0.250	1420 1440
0.5	680	860	900	216	142	0.307	1410
1.0	680	860	890	202	139	0.360	1400 1420
5.0	700	870	890	210	156	0.419	1420

*An endotherm at 575° C and an exotherm at 1210° C comon to all curves are not given in the table.

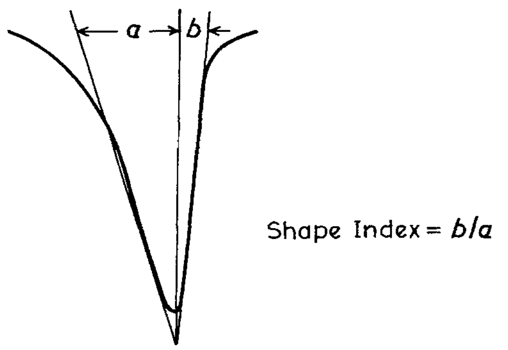

Figure 2 Shape index of the decomposition peak (DTA).

at both 1420 and 1440° C. The sample heated to 1430° C (30 min retention) and quenched in liquid nitrogen shows the presence of β and γ-C_2S phases with high free lime as discerned by XRD. The same mix on heating to 1450° C (30 min retention) gives mostly γ-C_2S and small amounts of β-C_2S phases. The mix on firing for 1 h at 1450° C gives the same pattern with a constant value of free lime (0.8%).

0.5% Cr_2O_3 gives an exothermic peak at 1410° C. The sample heated to 1420° C and quenched in liquid nitrogen gives again a mixture of β and γ-C_2S phases with an increase in β-C_2S phase. Longer heating of the sample at this temperature does not change the XRD pattern or the free lime content (0.6%). 1% Cr_2O_3 gives two exotherms at 1400 and 1420° C and the liquid nitrogen quenched sample heated at 1410° C (30 min retention) gives β-C_2S phase along with small amounts of free lime (0.5%) and Cr_2SiO_4. This is inferred from the increase in the intensities of peak for free lime at *d* nm 0.24. This position is also reported for Cr_2SiO_4 along with other *d* values (0.27, 0.16 and 0.20 nm). γ-C_2S phase is not observed. This is in accordance with the study done by Pashchenko *et al.* [18]. DTA of 5% Cr_2O_3 doped sample gives an exotherm at 1420° C. XRD pattern of the liquid nitrogen quenched sample gives the most predominant β-C_2S phase along with small quantity of α'-C_2S phase. Some of $CaCrO_4$ and Cr_2SiO_4 are also formed as discerned from the lines of the XRD pattern. Free lime content remains the same (0.5%). The final products so formed are given in Table II. The XRD pattern of the phases formed at the final DTA peak temperature are shown in Fig. 3.

Fig. 4 shows the ratio of phases (γ-C_2S/β-C_2S) formed at 1450° C by addition of the different percentage of Cr_2O_3 dopant (XRD line intensity ratio has been used). It is clear from the figure that ratio of γ to β dicalcium silicate phase decreases with increasing percentage of chromium oxide.

4. Conclusion

Smaller concentration of Cr_2O_3 (0.1%) favours the formation of γ-C_2S phase. Higher percentages (0.5 to 5%) lead to the formation of the more desired β-C_2S phase. 1% Cr_2O_3 is found to be most effective in the decomposition of $CaCO_3$ (minimum activation energy) and formation of β-C_2S with complete elimination of γ-C_2S phase. 5% Cr_2O_3 gives most predominantly β-C_2S phase along with some α'-C_2S, $CaCrO_4$ and Cr_2SiO_4. This implies that Cr^{3+} causes a hole defect by replacing Ca^{2+} and Si^{4+} ions from the C_2S lattice. The temperature of β-C_2S formation is not affected by any concentration of Cr_2O_3.

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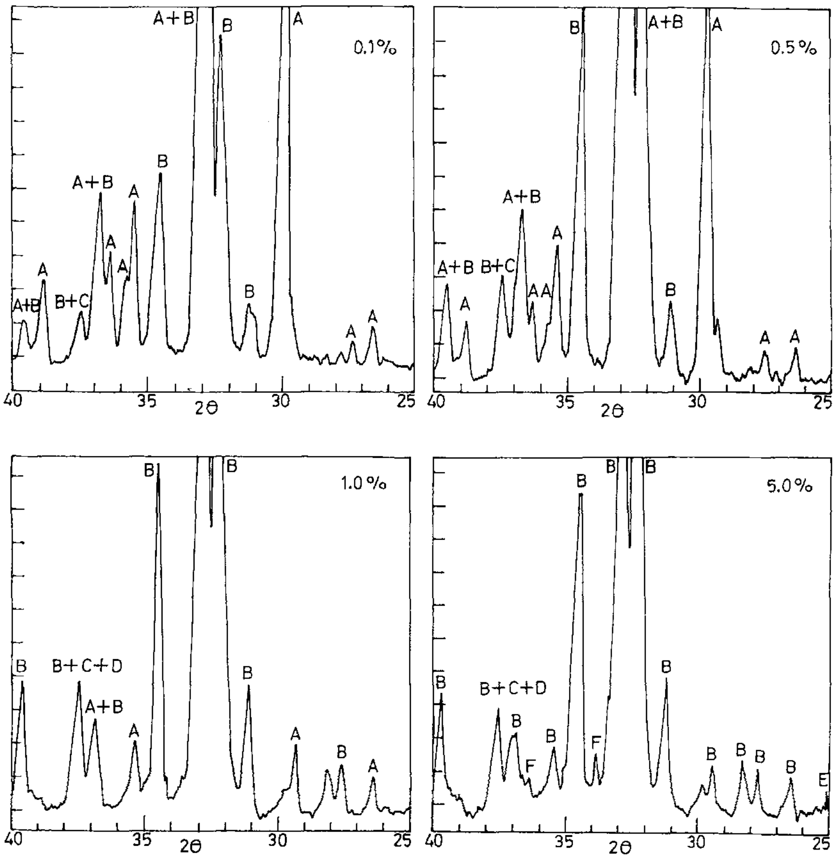

Figure 3 X-ray diffraction of chromium doped dicalcium silicate phase: A = γ-C_2S; B = β-C_2S; C = free lime; D = $CaCrO_4$; E = Cr_2SiO_4; F = α'-C_2S.

TABLE II Products formed at the various exothermic peaks (observed by DTA) of thermal curves as discerned by X-ray diffraction

Concentration of Cr_2O_3 (%) by weight in $CaCO_3:SiO_2$ (2:1)	Exothermic peaks as shown by DTA (°C)	Compounds identified by XRD	Corresponding d values (nm)	d values as per the ASTM cards (JCPDS values)*
0.0	1425	β-C_2S (most predominant)	0.280, 0.274, 0.277, 0.261	0.280, 0.274, 0.278, 0.2608
		γ-C_2S (predominant)	0.430, 0.404, 0.381, 0.301	0.432, 0.405, 0.381, 0.301
		free lime (high)	0.277, 0.240, 0.170, 0.145	0.2778, 0.2405, 0.170, 0.145
0.1	1420	γ-C_2S (most predominant)	0.430, 0.404, 0.381, 0.301	0.430, 0.404, 0.381, 0.301
		β-C_2S (predominant)	0.280, 0.274, 0.277, 0.261	0.280, 0.274, 0.277, 0.261
		free lime (high)	0.277, 0.240, 0.170, 0.145	0.277, 0.240, 0.170, 0.145
	1440	γ-C_2S (most predominant)	0.430, 0.404, 0.381, 0.301	0.430, 0.404, 0.381, 0.301
		β-C_2S (predominant)	0.280, 0.274, 0.277, 0.261	0.280, 0.274, 0.277, 0.261
		free lime (0.8%)	0.277, 0.240, 0.170, 0.145	0.277, 0.240, 0.170, 0.145
0.5	1410	β-C_2S (most predominant)	0.280, 0.274, 0.277, 0.261	0.280, 0.274, 0.277, 0.261
		γ-C_2S (most predominant)	0.430, 0.404, 0.381, 0.301	0.430, 0.404, 0.381, 0.301
		free lime (0.6%)	0.277, 0.240, 0.170, 0.145	0.277, 0.240, 0.170, 0.145
1.0	1400	β-C_2S (most predominant)	0.280, 0.274, 0.277, 0.261	0.280, 0.274, 0.277, 0.261
		γ-C_2S (small amount)	0.430, 0.404, 0.381, 0.301	0.430, 0.404, 0.381, 0.301
		free lime (small amount)	0.277, 0.240, 0.170, 0.145	0.277, 0.240, 0.170, 0.145
	1420	β-C_2S (most predominant)	0.280, 0.274, 0.277, 0.261	0.280, 0.274, 0.277, 0.261
		$CaCrO_4$ (small amount)	0.362, 0.288, 0.268, 0.238	0.362, 0.288, 0.268, 0.238
		free lime (0.5%)	0.277, 0.240, 0.170, 0.145	0.277, 0.240, 0.170, 0.145
5.0	1420	β-C_2S (most predominant)	0.280, 0.274, 0.277, 0.261	0.280, 0.274, 0.277, 0.261
		α'-C_2S (small amount)	0.273, 0.266, 0.248, 0.206	0.273, 0.266, 0.2489, 0.207
		$CaCrO_4$ (small amount)	0.362, 0.288, 0.268, 0.238	0.362, 0.288, 0.268, 0.238
		Cr_2SiO_4 (small amount)	0.240, 0.270, 0.254, 0.204	0.240, 0.270, 0.254, 0.204
		free lime (0.5%)	0.277, 0.240, 0.170, 0.145	0.277, 0.240, 0.170, 0.145

*ASTM X-ray Powder Diffraction Files.

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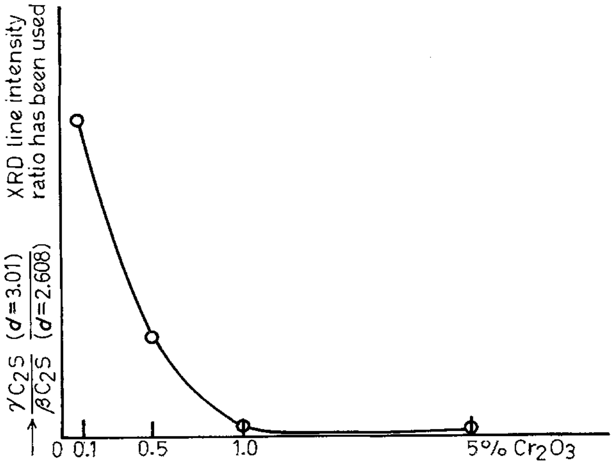

Figure 4 Ratio of γ-C_2S/β-C_2S against concentration of dopant.

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