Thermochemical effects on the formation of Ca_3SiO_5

Ca_3SiO_5, the principal cementing phase in ordinary Portland cement, starts forming at about 1280° C during the formation of Portland cement clinker [1]. The reaction occurs in two stages, i.e.,

$$2\,CaO + SiO_2 \rightarrow Ca_2SiO_4$$

$$Ca_2SiO_4 + CaO \rightarrow Ca_3SiO_5$$

The kinetics of formation and the stability of this phase depend on a number of parameters [2–6]. Similar to our earlier work on Ca_2SiO_4 [7], the present communication is based on further study of the synthesis of Ca_3SiO_5 using thermochemical methods.

The chemical doping agents used in this investigation were CaF_2, NaF, $CaHPO_4$, CrO_3, $CaSO_4 \cdot 2H_2O$, $CaF_2 + CaHPO_4$ (1:1) and $CaF_2 + CaHPO_4 + CaSO_4 \cdot 2H_2O + CrO_3$ (1:0.5:0.5:0.5). About 2% of each of these chemicals was used. A mix of 5 g containing finely ground silica gel (passing 40 μm and major fraction was estimated to pass 20 μm – milled in a jar mill) and $CaCO_3$ in the ratio 1:3 was made for each firing. Necessary corrections were made for the presence

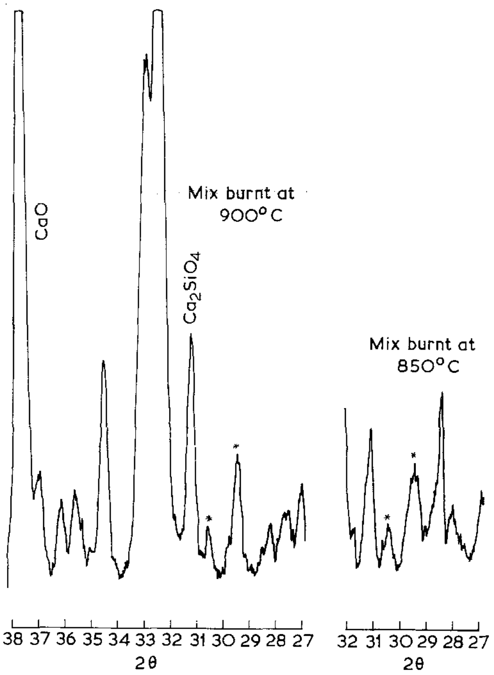

Figure 1 XRD traces of mix containing CaF_2 fired at a lower temperature. The marked lines are due to Ca_3SiO_5.

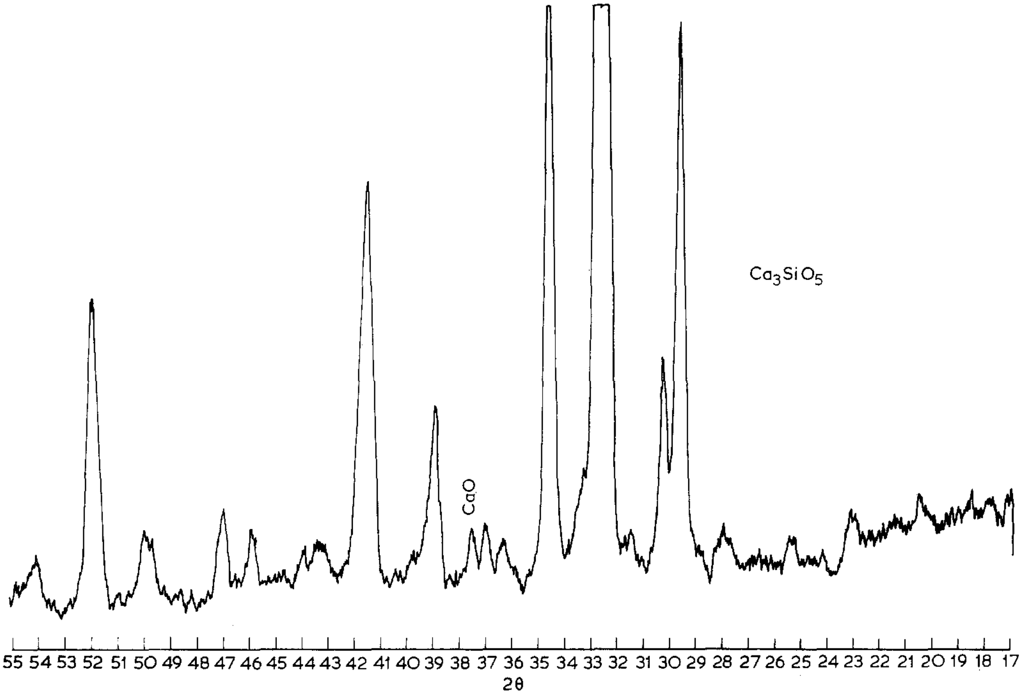

Figure 2 An XRD trace of a refired mix containing CaF_2; firing temperature 1400° C and retention time 2 h.

TABLE I Formation of silicate phases at different temperatures using mineralizers (2%)

Temperature of heating (° C)	CaF_2			NaF			$CaSO_4 \cdot 2H_2O$			$CaHPO_4$			CrO_3			$F^- + PO_4^{3-}$			$F^- + PO_4^{3-} + SO_4^{2-} + CrO_3$		
	C_3S*	C_2S*	Free lime	C_3S	C_2S	Free lime	C_3S	C_2S	Free lime	C_3S	C_2S	Free lime	C_3S	C_2S	Free lime	C_3S	C_2S	Free lime	C_3S	C_2S	Free lime
1200	Good	Weak	Low	Good	Very weak	High	Weak	Fair	High	–	–	–	Weak	Weak	High	Weak	Fair	High	Weak	Fair	High
1300	Very good	Weak	Low	Very good	Very weak	Moderately low	Weak	Fair	High	Weak	Weak	Very high	Fair	Weak	High	Good	Weak	Moderately low	Good	Weak	Moderately low
1350										Good	Weak	Very high	Very fair	Weak	High						
1400	Very good	Weak	Very low	Good	Very weak	Moderately low	Weak	Fair	High	Good	Weak	Very high	Weak	Weak	High	Good	Very weak	Low	Good	–	Low

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*$C_3S = C_3SiO_5$; $C_2S = C_2SiO_4$. The relative data obtained from XRD traces.

of calcium in the doping agent. Pellets were made of the mix containing the doping agent at a load of 5000 kg. The pellets were introduced directly into a quench furnace in a Pt crucible at a temperature ranging from 800 to 1400° C. The retention time was normally one hour. The samples were air-quenched.

A semi-quantitative estimation of the mineral phases, Ca_3SiO_5 (29.54, 30.2, 36.90), Ca_2SiO_4 (31.1, 39.48 and 44.90) and CaO (37.36 and $56.86 - 2\theta$ values) were undertaken on the basis of the intensity of the X-ray diffraction (XRD) lines (Philips, CuKα) characteristic of the phases. Chemical analysis, microscopic analysis and differential thermal analysis (DTA) of some samples were carried out. Table I gives the qualitative information on the formation of the mineral phases at 1200, 1300 (1350) and 1400°C. Although some formation of Ca_3SiO_5 at a temperature as low as 850° C (retention time of 2 h) was observed (Fig. 1), with the fluoride doping agents sizeable amounts of Ca_3SiO_5 formed at about 1300° C. The formation of Ca_3SiO_5 with other mineralizers was poor even at 1400° C. The decomposition of $CaCO_3$ in the presence of the mineralizers was studied by DTA. The temperature of decomposition was lowered in the case of NaF (765° C) and CaF_2 (865° C) compared to pure $CaCO_3$ (885° C). The effectiveness of these agents in the formation of Ca_3SiO_5 are given in the following (decreasing effectiveness) order:

$$CaF_2, NaF, CaF_2 + CaHPO_4 + CaSO_4 \cdot 2H_2O + CrO_3, CaF_2 + CaHPO_4, CaHPO_4, CrO_3 \text{ and } CaSO_4 \cdot 2H_2O.$$

The percentages of free lime were found to be 3.94 (1300° C), 2.13 (1350° C) and 2.32 (1400° C) in samples fired with CaF_2. Certain XRD lines at 31.6, 33.3 and 43.5 (2θ) appeared in the diffractogram of the sample, containing CaF_2, which, however, disappeared or became weak on refiring (Fig. 2). It appears that these lines are due to Ca_2SiO_4 although they are slightly shifted.

The kinetics of formation and the stability of the Ca_3SiO_5 phase is enhanced by fluorides and sudden heating to sintering temperature, leading to a high yield of this phase in a single firing. The temperature of initiation of the reaction for the formation of this phase has been lowered considerably.

References

1. F. M. LEA, "The Chemistry of Cement and Concrete" (Edward Arnold, London, 1970).
2. Yu. M. BUTT and V. V. TIMASHEV, Chemistry of Cement Congress (Moscow, 1974).
3. T. HAHN, W. EYSEL and E. WOERMANN, Proceedings, Chemistry of Cement, Vol. 1 Part 1 (1968) p.61.
4. W. GUTT, *ibid.* p. 93.
5. K. MOHAN and F. P. C. GLASSER, *Cement Concrete Res.* 7 (1977) 373.
6. B. V. VOLKINSKY, S. D. MAKASHEV and N. P. SHTEJERT, *Tsement* 74 (1974) 17.
7. S. N. GHOSH, A. K. PAUL and A. K. THAKUR, *J. Mater. Sci.* 13 (1978) 1602.

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