13. A. S. TETELMAN and A. J. McEVILY, Jr., "Fracture of Structural Materials", (John Wiley & Sons, New York, 1967) p.62.
14. M. KUNA, thesis, Halle (1977).
15. L. L. HENCH, Private communication (1977).
16. D. M. MARSH, *Proc. R. Soc. London A* **279** (1964) 420.
17. F. M. ERNSBERGER, Xth International Congress on Glass, Prague 1977, Part I (ČVTS-Dum Techniky, Prague, 1977) p.293.
18. P. GRAU, Tagung "Strukturabhängiges Verhalten von Festkörpern", Dresden 1976 (Akademie Verlag, Berlin) to be published.
19. F. FRÖHLICH, P. GRAU and W. GRELLMANN, *Phys. Stat. Sol. (a)* **42** (1977) 79.
20. V. SCHMIDT, J. HOPFE and G. KÄSTNER, VIII. Arbeitstagung Elektronenmikroskopie, Berlin, 1975 (Phys. Ges. der DDR, Berlin, 1975) p.361.

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Thermal decomposition of $CaCO_3$ and formation of β-Ca_2SiO_4

β-Ca_2SiO_4 is an important cementing mineral of ordinary Portland cement (OPC) and has the potential to improve the quality of OPC by suitable modification of its structure, leading to partial or complete replacement of the most important high temperature cementing material, Ca_3SiO_5, in OPC. Examples are available where OPC of Indian and other origins show high early strength properties in spite of its low Ca_3SiO_5 content, mainly due to the presence of reactive β-Ca_2SiO_4, which was formed rather accidentally and thus could not be produced under controlled conditions.

Synthesis of β-Ca_2SiO_4 of reactive nature have recently been reported [1, 2]. In this communication it is intended to report the preliminary results on the decomposition of $CaCO_3$ and on the formation of β-Ca_2SiO_4 in the presence of NaF under different thermal treatments. The main objectives are:

(1) to improve the kinetics of the reaction between SiO_2 and CaO and increase the yield of the reaction product at a lower temperature with a low retention time

(2) to synthesize reactive β-Ca_2SiO_4 using normal raw materials

In doing so, the important steps taken consisted of (i) decomposing $CaCO_3$ at a lower temperature in the presence of SiO_2 + NaF and (ii) firing the products thus obtained to different temperatures adopting different heating schedules as suggested in [3, 4].

Reagent grade $CaCO_3$ and NaF were used with silica gel of fairly high purity for the synthesis of β-Ca_2SiO_4. The ratio of $CaCO_3$:SiO_2 was maintained approximately at 2:1. The materials were ground to powder (–325 mesh) before and after firing. Pelleting to a pressure of about 700 kg cm^{-2} was done for some of the mixes. The mixes were fired in a Pt-crucible in an electric furnace. The analysis of the materials was performed using differential thermal analysis (DTA apparatus, MoM, Hungary), X-ray diffraction (XRD apparatus, Phillips, Holland), and infra-red spectroscopy (i.r. apparatus, Perkin Elmer 621).

The effect of the addition of NaF on the decomposition of $CaCO_3$ can be seen in Figs. 1 and 2. The decrease in the decomposition temperature of $CaCO_3$ with increasing amount of NaF is considerable, although there is a sudden change in the mechanism of formation of compounds as is evident from Fig 2. The change in the slope of the curve at 10% NaF indicates the change in the compound formation or solid solution, the exact nature of which is yet to be established. The mix samples containing 6% or 12% NaF heated to 530 or 510° C (below the decomposition of $CaCO_3$, an endothermic DTA peak has been observed at this temperature, the intensity of which increases with increasing NaF content in the mix) showed quite interesting XRD patterns compared to that obtained at room temperature (Fig. 3). The XRD lines (2θ) at 26.1°, 27.1°, 45.9°, 50.1°, 52.4° and 52.9° of the mix at room temperature disappear completely from those of the heated samples. These lines are due to the presence of aragonite. The NaF line

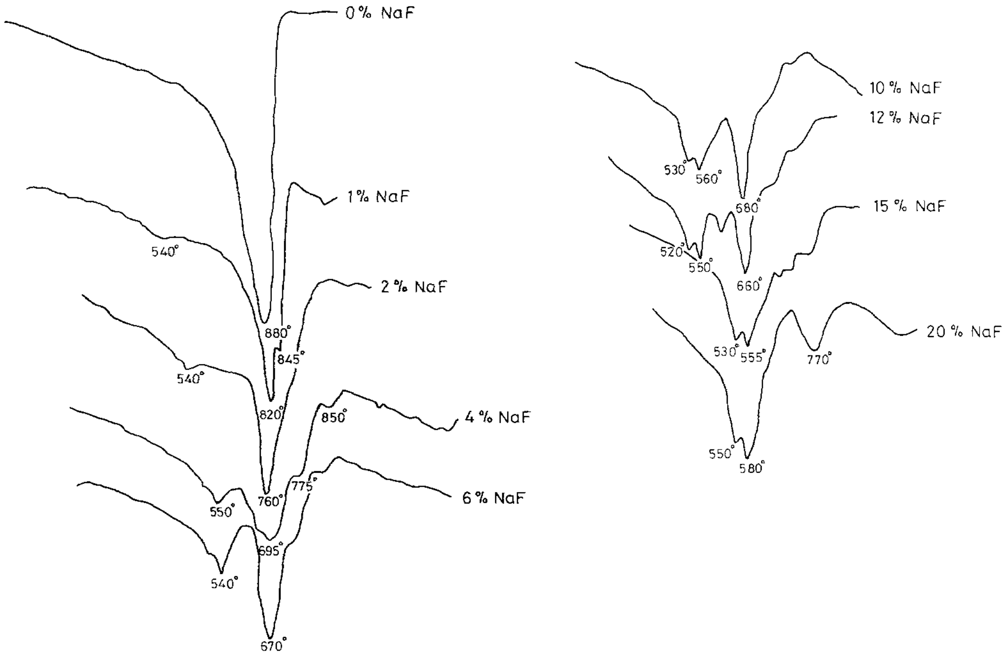

Figure 1 DTA curves of mixes containing $CaCO_3$, silica and NaF.

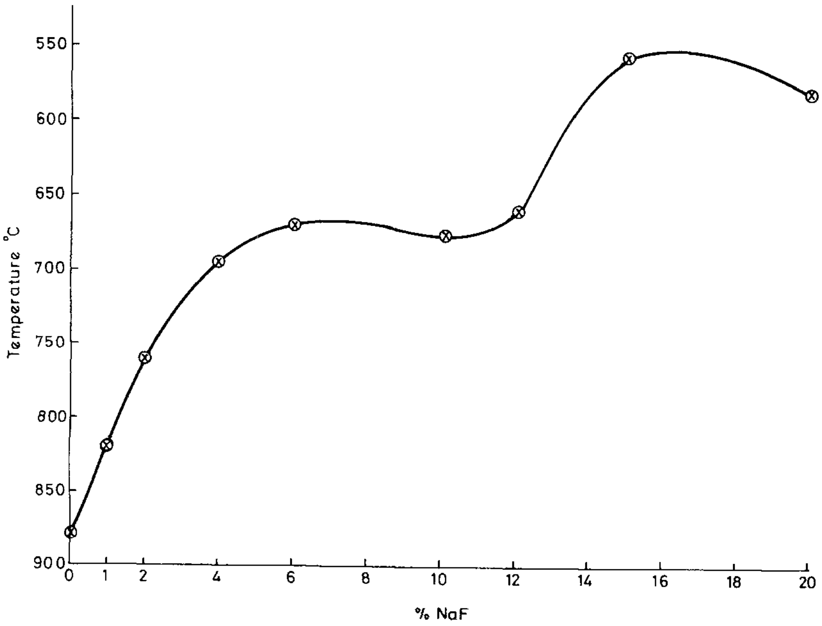

Figure 2 Variation of decomposition of temperature of $CaCO_3$ with amount of NaF.

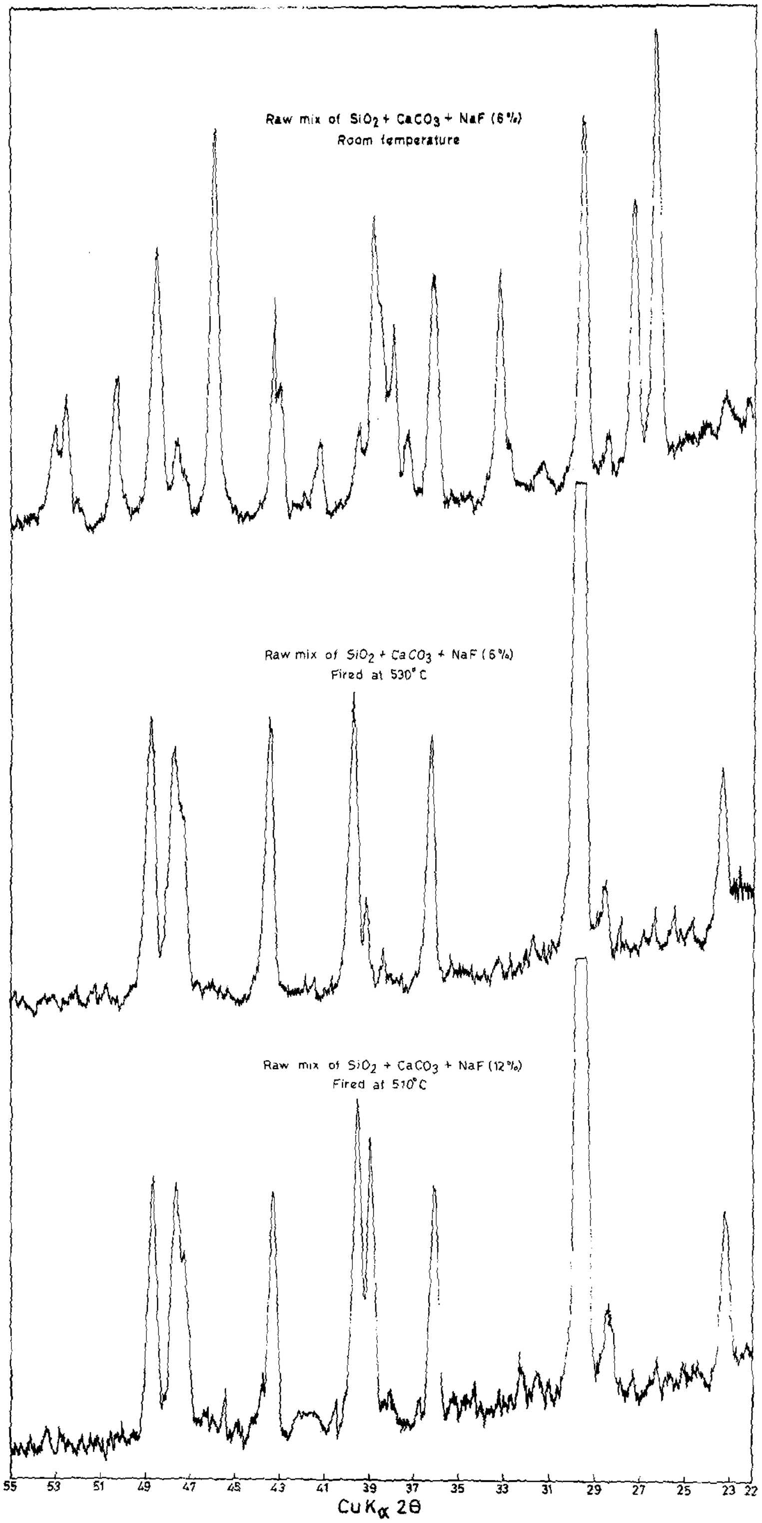

Figure 3 X-ray diffraction patterns of mixes heated to temperatures of compound formation.

TABLE I Reaction of calcium carbonate with silica in the presence of sodium fluoride (2%)

Materials	Slow heating (10° C min^{-1})		Abrupt heating	
$CaCO_3$ + SiO_2 (2:1) and 2% NaF	Raw mix fired slowly at 800 and 1000° C (retention time = ½ h)		Raw mix decarbonated at 800° C, pelletized and fired abruptly at 850, 900, 950 and 1000° C (retention time = ½ h)	Raw mix pelletized fired abruptly at 1000° C and 1200° C (retention time = ½ h)
	At 800° C – sharp XRD lines of β-C_2S, free lime > 5% : indications of spurrite phase (small amount)	At 1000° C – sharp XRD lines of β-C_2S, free lime ≈ 2% and no reduction in free lime even on increasing retention time	At 850 and 900° C – sharp XRD lines of β-C_2S, no appreciable change in free lime contents	At 1000° C – sharp XRD lines of β-C_2S, free lime < 2%
			At 1000° C – sharp XRD lines of β-C_2S, free lime < 2%	At 1100 and 1200° C white spots in the matrix, sharp XRD lines of β-C_2S and free lime content increases with temperature

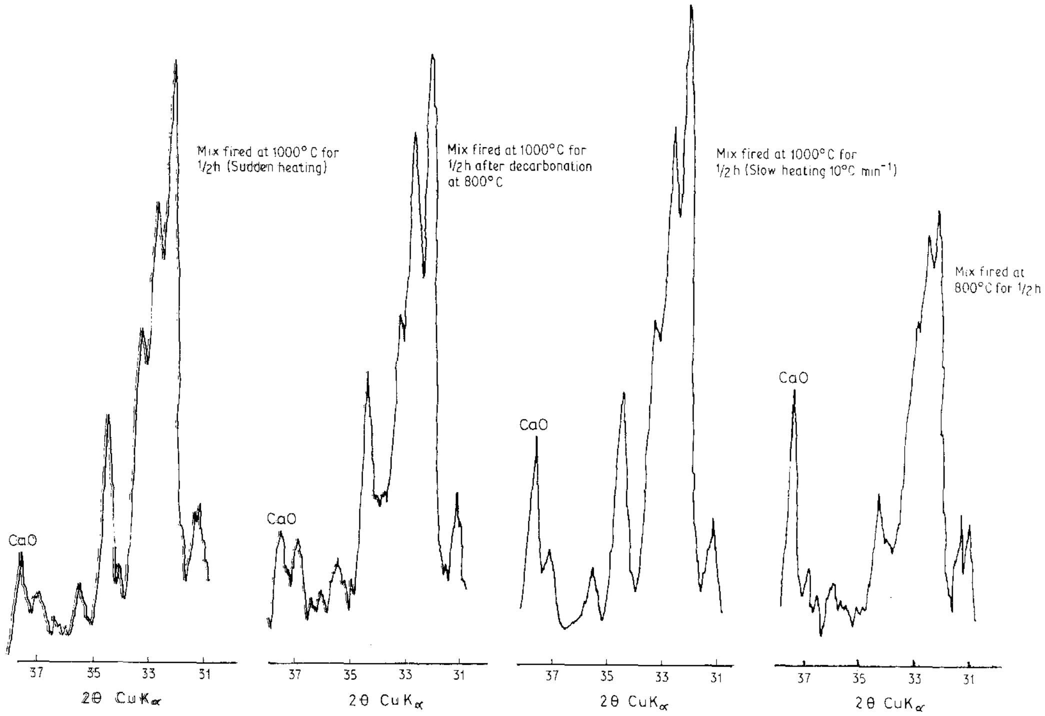

Figure 4 X-ray diffraction patterns of mixes fired at different temperatures.

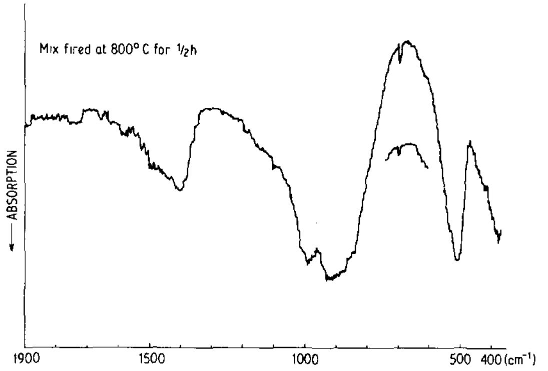

Figure 5 An infra-red spectrum of a mix heated to 800° C.

at 38.82° (2θ) decreases in intensity at 6% NaF and increases with increasing percentage of NaF (12%).

The i.r. band at $1400\,\text{cm}^{-1}$ becomes broader with splitting in the spectrum of the sample containing 12% NaF in comparison to that of samples containing 6% NaF.

For the synthesis of β-Ca_2SiO_4, mixes containing 2% NaF were selected for the present study. The details of heating schedule and analysis of the products are given in Table I. It appears that β-Ca_2SiO_4 is formed even when the sample is fired at 800° C. Formation of spurrite is observed in this product (Figs. 4 and 5). The spurrite XRD lines at 23.4° (2θ) and the carbonate bands at 1400 and $695\,\text{cm}^{-1}$ in the infra-red spectrum can be seen.

From the studies carried out so far, the following observations have been made:

(1) The kinetics are very fast for the reaction to occur at 1000° C, even with a retention time of 30 min or so. Increase of retention time to 90 min increases the yield very little, as was deduced from the XRD line at 37.4° (2θ) for CaO.

(2) Higher temperature 1100, 1200° C etc. did not help the reaction to proceed further, to the contrary, it increases the uncombined CaO content.

(3) Sudden heating of the mix to 1000° C for $\frac{1}{2}$ h appears to have the same result as against the decarbonated mix (800) heated to 1000° C.

Using NaF as mineralizer and adopting rapid heating techniques the kinetics of formation of β-C_2S can be increased substantially. It is, therefore, possible to produce β-Ca_2SiO_4 under controlled conditions with substantial heat economy. However, a certain amount of α'-C_2S phase formation cannot be avoided.

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References

1. D. M. ROY and S. O. OYEFESOBI, *J. Amer. Ceram. Soc.* **60** (1977) 178.
2. B. S. RANGNAKAR, V. R. G. SRINIVASAN and V. N. PAI, the VIth International Congress on the Chemistry of Cement, Moscow, September 1974.
3. Y. M. BUTT, V. V. TIMASHEV and A. P. O. SOKIN, the VIth International Symposium on the Chemistry of Cement, Moscow, September 1974.
4. V. I. KORNEEV and E. B. BYGALINE, Proceedings of the Fifth Symposium on the Chemistry of Cement, Tokyo 1968, Vol. I, Part I, p. 285.

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The effect of ambient atmosphere on the gold-to-alumina solid state reaction bond

In a recent paper by the authors [1], the effect of a number of factors on the bonding of gold to alumina in an air atmosphere was discussed. In that paper, a detailed discussion was given of the preparation of the bonding materials, the actual bonding process, and the evaluation of the bonds. This paper reports the results of an experimental programme to study the effect of using non-air atmospheres in the formation of this bond. Data are presented for bonds formed in air, oxygen, nitrogen, argon, hydrogen and vacuum.

Briefly, bonds consist of a "sandwich" of two 10 mm diameter rods of Coors polycrystalline