

## PII S0008-8846(96)00099-3

# HIGH BELITE CEMENTS—PRESENT STATUS AND FUTURE TECHNOLOGICAL OPTIONS : PART I

# A.K. Chatterjee

The Associated Cement Cos. Ltd. Research & Consultancy Directorate Thane 400 604 India

(Refereed) (Received February 16, 1995; in final form May 20, 1996)

#### ABSTRACT

Interest in high-Belite cements, perhaps, owes its origin to the scientists' early expectation of saving energy in their manufacture. But as the experimental studies gradually revealed that the conventional approaches of making high-Belite cements may not lead to conservation of energy, there was an apparent waning in the active pursuit of this research. In recent years, there has been a revival of interest due to labscale successes of synthesizing reactive Belites at low temperatures through non-traditional approaches like sol-gel processing, hydrothermal treatment, etc. Further, the real value of the reactive Belite cements has also been seen to be their durability and not only the energy-saving potential. In the context of these conceptual changes, an attempt has been made here to review the status of development of high-Belite cements, share some of the Indian experiences and results, and draw up a picture of the future potential of this class of binder.

#### Introduction

Portland cement clinkers are characterised by the four principal mineral phases known as Alite, Belite, Celite and Brownmillerite which are structurally and chemically modified versions of Ca<sub>3</sub>SiO<sub>5</sub>(C<sub>3</sub>S),Ca<sub>2</sub>SiO<sub>5</sub>(C<sub>2</sub>S),Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>(C<sub>3</sub>A) and Ca<sub>2</sub>(Al,Fe)O<sub>5</sub>[C<sub>2</sub>(A,F)] respectively with incorporation of different foreign ions. Alite, capable of contributing to the strength development of cement at ages upto 28 days, is the most important constituent of all Portland cement clinkers, of which it constitutes 50-70%. On the other hand, Belite constitutes 15-30% of normal Portland cement clinkers and contributes little to the strength during the first 28 days and substantially at later ages. High-Belite cements are those in which there is a reversal in the preponderance of Alite by Belite without sacrifice of early age strength in mortar and concrete. Since this implies higher levels of early reactivity in belite, such cements are also known as Reactive or Active Belite Cement. When, however, the silicates pair of Alite and Belite is broken and replaced by Calcium Sulphoaluminate (CSA) and belite, a modified Portland cement is obtained.

Interest in high-Belite cements dates back to perhaps early seventies. The interest intensified due to the global energy crunch as it was expected that the production of Belite-rich cements would be less energy-intensive due to the minimisation of the Alite phase which in

accordance with phase equilibria principles requires at least a temperature of 1250°C for its formation. In some of the countries, the interest in high-Belite cement is from the point of view of raw materials conservation, as limestones with relatively lower carbonate content could be used in the production process. The growing preference for high-Belite cements in recent times is, however, related to the focus that engineers are now placing on "structural durability" as the basis of constructional design, rather than the traditional concept of "strength". It is believed that Belite produces a more durable hydrated matrix than Alite-rich Ordinary Portland Cements.

The present article is an attempt to review the developmental status of high-Belite cements, their durability features and future technological options. For constraints of space, the article restricts itself to only high-Belite Portland Cements without encompassing modified CSA-Belite varieties.

# Comparative Roles of Alite and Belite in Some Commercial Cements

In a simplistic way, the hydration reactions of  $C_3S$  and  $C_2S$  can be represented as follows (1):\*

$$2C_3S + 7H - C_3S_2H_4 + 3CH$$
,  $\Delta H = -1114 \text{ Kj mol}^{-1}$   
 $2C_2S + 5H - C_3S_2H_4 + 3CH$ ,  $\Delta H = 43 \text{ Kj mol}^{-1}$ 

It is well known that these reactions do not describe the stoichiometry exactly because the calcium silicate hydrate does not have the exact composition C<sub>3</sub>S<sub>2</sub>H<sub>4</sub> Designated as C-S-H, it is non-crystalline and variable in composition. In contrast, calcium hydroxide (CH) is crystalline and of fixed composition.

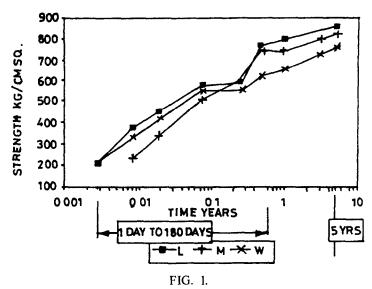
The hydration of  $C_2S$  is apparently characterised by the same hydration products but with much lower evolution of heat and smaller quantities of CH formation, which is a necessary evil in cement hydration. It is required for pH maintenance and consolidation of CSH gel

TABLE 1 Comparative Theoretical Porosities in  $C_3S$  and  $C_2S$  on Hydration

Parameters	C <sub>3</sub> S	C <sub>2</sub> S
Wt. of solids, g	456	344
Vol. in cm³ water Reactants Combined water Free water Voids Total Pores	182.4* 270.7 126 56.4 23.7 50.1	103.2* 197.5 90 13.2 17.8 31.0
% Porosity by volume	29.6	15.7

<sup>\* 40% (</sup>wt.) of solids in the case of C<sub>3</sub>S and 30% in the case of C<sub>2</sub>S

<sup>\*</sup> NOTE: References are included at the end of Part II



Compressive Strength development patterns of Alite and Belite-rich Portland Cements (Five year hydration)

but, being susceptible to sulphate and carbonate attacks, it also introduces weakness in mortar and concrete. By a very approximate quantitative computation of the aforesaid reactions, one may find that while 100 g of C<sub>3</sub>S produces only 79 g of CSH gel and 49 g of CH crystals, an equal weight of C<sub>2</sub>S is likely to produce 105 g of gel and 21.5 g of CH crystals, which itself is an indicator of higher durability of matrix in high-Belite mortars.

In similar lines of approximate quantification and following the three-decades-old assumptions of Hansen (2), one may also compare the porosity by volume in  $C_3S$  and  $C_2S$  hydration (Table 1). This also hints at lower volume of porosity in  $C_2S$  hydration as compared to  $C_3S$ .

In search of some phenomenological evidences of the above theoretical indications of the superiority of C<sub>2</sub>S as a binder, a series of long-age hydration studies of Alite-rich and Beliterich commercial Portland cement samples have been commissioned in the author's laboratories. The comparative strength development pattern spanning over five years are shown in Fig.1 and the compositional features and microstructural observations are given in Table 2. Quite in line with the expectations, the high-Belite cement mortars (L and M) have shown much higher strength gains beyond 28 days as compared to W. The microstructural studies had also revealed that the matrix densification is also better in high-Belite mortars. The measured porosity by volume after 5 years of hydration is relatively higher in Alite-rich mortar. It is interesting to note that although in the unhydrated cement, the Belite phase in both M and L specimens was present in β and a' forms, the unreacted Belite phase in them after 5 years is only the a' variety, signifying uninhibited early reactivity of β-Belite grains in these cements, which is apparently contradictory to many observations. The high proportions of unreacted cement particles in the samples are due to their clustered occurrence and indicate the potential of further strength gains, although at a slower rate.

The relative superiority in terms of expected durability of the moderately high-Belite cements being produced in India has, thus, been experimentally confirmed.

TABLE 2
Composition and Microstructure of Cements on Long-Term Hydration

Parameters	L	М	W			
Unh	ydrated Cement	ts	,			
Alite %	42	41	59			
Belite %	32	33	14			
Belite Polymorph	ß + a'	ß + a'	a' + a			
After	After 5-year Hydration					
Capillary porosity, vol %	24.5	24.0	30.0			
Matrix Densification	Very High	High	Moderate			
Proportions of unreacted cement particles	Low	High	Moderate			
Nature of unreacted cement particles	a'-Belite	a' - Belite	Alite a - Belite a' - Belite			

Note: Mortars cast in accordance with the Indian Standard Test Method using wat required for standard consistency.

The production and use of similar types of moderately high-belite cements with good properties on a regular basis is also known in Poland (3). These cements are reported to contain 35-45% Alite and 35-45% Belite of compositions given in Table 3.

#### Belite as a Clinker Phase

It is a common knowledge that there are five polymorphs of C<sub>2</sub>S at ordinary pressures, viz.

Hex	Ortho	Ortho	Mono	Ortho
1425°C	1160°C	630-680°C	<500°C	780-860°C
a	а' <sub>н</sub>	a' <sub>L</sub>	ß	a t
(2.94)	(3.11)	(3.14)	(3.20)	(2.94)
(H=high; L=1)	low, specific g	ravity in bracket	)	

The structures of  $a_H$ ,  $a_L$  and  $\beta$  polymorphs are derived from that of a-C<sub>2</sub>S by progressive decreases in symmetry which take place due to changes in the orientation of the SiO<sub>4</sub> tetrahedra and small movements of Ca<sup>2+</sup> ions. The higher temperature polymorphs cannot normally be preserved on cooling to room temperature unless stabilised by foreign ions.

Clinker belites typically contain 4-6% of impurity, of which the chief ones are usually Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>. It has generally been observed that C<sub>2</sub>S takes up a greater proportion of foreign ions such as Al, Fe, B, K, Na, P, Ba, Sr, Ti, V and Cr into solid solution than C<sub>3</sub>S.

Belite C	ompositio	n (Minor C	omponent	•	sn Mode		gn-Bente
	Belite Type	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na₂O	K₂O	MgO	TiO₂
	l	1.44	0.50	0.05	0.66	0.40	0.30
	ш	3.19	0,50	0.08	0.93	0.30	0.40

TABLE 3
Belite Composition (Minor Components) in Polish Moderately High-Belite Cement

Belites are optically distinguished as dark, small, rounded grains invariably with characteristic striations. Based on striations, they are distinguished as Type I (two sets), Type II (one set) and Type III (no striations). In Type I, the striations normally indicate  $a - a'_H$  and  $a'_L$ - $\beta$  transitions as  $a'_H - a'_L$  transitions do not leave any mark of different orientation. In Type II Belites, the striations arise from  $a_L - \beta$  transformation. Belite forming in clinker at lower temperatures may not show any striations.

From these microstructural features, it is evident that clinkers mostly contain more than one polymorph of Belite, β-polymorph being predominant followed by a and a' varieties.

In 1985, Von Lampe et al. for the first time reported an unusual  $\beta$ -polymorph obtained under extremely rapid cooling which they designated as  $\beta^*$  (4). The same school later established that  $\beta^*$  can be distinguished from normal  $\beta$  phase by shifts and intensity changes in the x-ray pattern, viz. the 4th strongest  $\beta$ -C<sub>2</sub>S reflection (103, d=2.612) moves towards higher d-spacings (2.63 - 2.64).  $\beta^*$  C<sub>2</sub>S also has a reversible transformation to a'C<sub>2</sub>S in the temperature range of 390-400°C. The differential calorimetric behaviour of  $\beta$  and  $\beta^*$  variations is also different.

On simple thermodynamic considerations, one expects that the high-temperature apolymorph would exhibit the greatest reactivity but in practice, the picture is more complex. In fact, totally contradictory observations are noticed in published literature. Further, one comes across situations where the same polymorph stabilised by two different chemicals display significantly different reactivity.

In this context, the study of Yang and Song (5) is quite relevant. The authors studied the structure and properties of hydration of dicalcium silicates with 2:1C/S ratio doped separately with 3% MgO, 2% K2O and 2% BaSO4 and came to the conclusion that the following factors changed the hydraulic behaviour of the resultant phases: lattice distortion, crystal size, intercrystalline imperfections, crystallo-chemical environment, and chemical shifts of the electron binding energies of Ca and Si atoms. Needless to mention, that such sensitivities make the production technology of reactive Belite more complicated.

### Stabilisation Technologies for Belite

Based on the plethora of publications made during the last two decades or so on the formation of stabilised reactive Belites, one may selectively classify three approaches:

- a) Technology involving the use of natural raw materials, chemical stabilisation and rapid cooling techniques.
- b) Sol-gel type of processing
- c) Hydrothermal treatment

The salient features of these technologies are highlighted below.

<u>Chemical Stabilisation and Rapid Cooling</u>. From some of the relatively more comprehensive studies such as those carried out at Weimar Institute in Germany (6) and in the author's laboratory in India (7), it is, perhaps, possible to take note of the following technical and technological aspects.

<u>Chemical Considerations.</u> For high Belite cements, the range of Lime Standard or equivalent LSF has been defined as 0.78 to 0.83. It may be worthwhile to mention that this kind of delineation of LSF is related to the essentiality of presence of some quantity of Alite phase. The studies indicate that about 10-20% of the Alite phase may make the high-Belite cements more acceptable. In some of our studies, it has also been found that the chemical stabilisation does not show any significant improvement in raw mixes with LSF below 0.78.

So far as the chemical stabilisations are concerned, the recent studies show the preference for  $K_2O$ ,  $Na_2O$ ,  $SO_3$ ,  $B_2O_3$ ,  $Fe_2O_3$ ,  $Cr_2O_3$  and BaO. Although  $Fe_2O_3$ ,  $Cr_2O_3$  and BaO have given some interesting results, as evident from Table 4 (8-10), there is overwhelming preference for  $K_2O$ ,  $Na_2O$ ,  $SO_3$  (11-14). Based on some studies in the author's laboratory, the relative effectiveness of  $K_2O$  and  $B_2O_3$  as dopants can be seen from Table 5 (7). From the above tables, it appears reasonable to conclude that

- (a) Fe<sub>2</sub>O<sub>3</sub> below 1% level, although making the Belite phase relatively less-reactive for early strength, may ultimately be more effective for later-age strength gains.
- (b) Cr<sub>2</sub>O<sub>3</sub> is effective at doses upto 7% studied, although the optimum proportion appears to be about 5%.
- (c) BaO at 0.5% really introduces improvement in strength properties in cements of lower LSF only.
- (d) B<sub>2</sub>O<sub>5</sub> at 0.5% level is as effective as K<sub>2</sub>O at 1.0% level and under certain circumstances, the former seems to be more effective.

So far as the alkalies are concerned, it is now increasingly clear that in the low LSF raw mixes in the absence of sulphur, a large proportion of alkalies gets incorporated in the main Belite phase. Raising the alkali content in Belite phase leads to the stabilisation of hydraulically more active phases and of higher temperature forms a and a'. Needless to mention, rapid cooling assists in such stabilisation (11).

The relationship amongst the phase composition, cooling rate and alkali content in Belite has been studied fairly extensively in (12). The studies are based on comparative behaviour of two clinkers - one with Lime Standard of 70 and another of 80 with other moduli values remaining the same in both the clinkers. The total alkalies as Na<sub>2</sub>O were varied in the range of 0.4 - 4.3% and the cooling rates from 3000°C to 20°C/min. The study showed that for the clinker of LS 80, the stability fields of a-form corresponded to both high content of alkalies and high rate of cooling while the β-phase stabilised over the entire range of alkalies with lower rates of cooling. The intervening fields were characterised by mixed belite phases. With lower LS of clinker, the overall pattern of stabilization of Belite polymorphs did not change radically, although the mixed fields of stability of a' phase increased towards lower cooling rates.

**B-Belite** 

0.7% Fe<sub>2</sub>O<sub>3</sub>

1.0% Cr<sub>2</sub>O<sub>3</sub> 2.4% 4.9% 7.3%

0.5% BaO

0.5% BaO

Ė	Effects of Bente Doping with Some Oxides						
	Compre	ssive Streng	Special Relevant Features				
	3-day	7-day	28-day				
	0.28 (0.30)*	5.2 (4.0)*	43.0 (20.0)*	Grain size reduced from 11-19 microns to 5-15 on doping.			
	18.0 19.0 27.3 23.0	26.0 26.0 33.0 27.0	34.0 33.0 46.0 38.0	Properties are for cements with near-zero Alite, 5% gypsum and 3000 cm <sup>2</sup> /g SSA			

54.9

(58.2)\*

22.0

(15.6)\*

Cement with LSF

Cement with LSF

70, 5% gypsum and

3000 cm<sup>2</sup>/g SSA

3000 cm<sup>2</sup>/g SSA

90, 5% gypsum and

TABLE 4
Effects of Belite Doping with Some Oxides

33.5

(33.0)\*

10.0

(7.6)\*

On the other hand, with no alkalies, when SO<sub>3</sub> is increased, the Alite phase further decreases in quantity, thus lowering the early strength (13). The strength, however, at 28 and 90 days shows considerable improvement. These effects are pronounced with rapid cooling of clinkers. It has also been reported that SO<sub>3</sub> in Belite, in the absence of alkalies, occurs in

46.8

(46.2)\*

22.0

(12.6)\*

TABLE 5
Comparative Efficacy of K<sub>2</sub>O and B<sub>2</sub>O<sub>3</sub> as Dopants

CaO%	61.4	61.8	60.9	62.4	62.6	62.6
K <sub>2</sub> O%	0.38	0.41	0.62	0.39	0.39	0.64
B <sub>2</sub> O <sub>3</sub> %	-	0.7	_	-	0.8	-
Fineness cm²/g	4210	4280	4300	4250	4397	4434
	(	Compressive	Strength (mo	ortar) MPa		
3-day	70	90	160	85	145	190
7-day	140	250	280	200	360	295
28-day	430	515	555	450	675	560

Note: The sulphate content in the cements maintained at the same level of 2.5%

<sup>\*</sup> Results of samples without doping

CaSO<sub>4</sub> state. No a and a' modifications are known to occur even upto 1.5% incorporation of SO<sub>3</sub>. It is generally agreed that an optimum SO<sub>3</sub> content in clinker is in the range of 0.6 -0.8%, which results in lattice distortions and improved hydraulic properties. In this paper, the combined effects of alkalies and sulphates have also been examined through a systematic study of the effects of alkalies and sulphates in the range of 0 to 1.5% by manipulating the relative proportions of K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and CaSO<sub>4</sub>.2H<sub>2</sub>O in a clinker of Lime Standard 80, silica modulus 2.4 and alumina modulus 2 and having phase composition of 20% Alite, 56% Belite, 13% Aluminate and 11% Ferrite. From the results, it has also been concluded that when simultaneously present, K<sub>2</sub>O and SO<sub>3</sub> do not get incorporated in clinker so easily due to preferred formation of K<sub>2</sub>SO<sub>4</sub>. On the other hand, when Na<sub>2</sub>O and SO<sub>3</sub> are present together, Na<sub>2</sub>O is preferably incorporated in the Belite and Aluminate phases and the formation of Na<sub>2</sub>SO<sub>4</sub> turns out to be secondary. Cements with 1.3 - 1.6% K<sub>2</sub>O and 1.0 - 1.2% SO<sub>3</sub> with little Na<sub>2</sub>O (0.04%) have shown relatively better strength levels at all ages upto 90 days, when compared generally with other combinations of alkali and sulphate incorporation. The alkali and sulphate activation in Belite cements has also been dealt with in (14, 15) with similar findings.

The effects of sulphates of Mg, Ca or Ba in making white Belitic Portland cement have been specifically reported in (16). LSF of 80, use of BaSO<sub>4</sub> in preference and quenching of clinker in triethanolamine solution have been indicated as the desirable steps in obtaining good properties and requisite whiteness in these cements.

In the context of stabilisation of Belite by doping alkalies and sulphates, it may be interesting to look at the conditions of stabilisation of  $\beta$ \* mentioned earlier. It has been reported (4) that in clinkers with K > Na, a and  $\beta$  modifications of Belite do not coexist. When cooling rates were as high as 20,000 to 50,000°C/min, a-Belite prevailed at more than 1.49% alkalies. With lower cooling rates, more and more alkalies were needed to arrest a-polymorph (viz. more than 2.63% alkalies, when the cooling rate was about 3600°C/min, and more than 5% alkalies, when the cooling rate was 1000°C/min). The appearance of the  $\beta$ \* form is apparently related to these high ranges of alkalies and cooling rates but any accurate delineation of the stability field of  $\beta$ \* has not yet been reported in the literature. Nevertheless, the relationship of this phase with strength development can be appreciated from

TABLE 6
Relationship Amongst the Belite Polymorphs, Cooling Rate & Strength

Belite Polymorph at 80%	Cooling rate, °C/min	Compressive Strength, MPa			1Pa
		3-day	7-day	28-day	90-day
a	50,000	3.1	8.9	20.9	29.6
a'	3,000	1.4	2.0	6.7	14.0
ß*	50,000	2.0	2.8	8.2	21.8
В	40	2.2	2.3	3.9	8.3
B* transfor- med into a'	Annealed at 800°C for 2	1.4	2.0	2.4	13.5

Table 6. From the table, one may observe the dramatic fall in strength levels, when  $\beta^*$  form transforms into a' by annealing.

While on the subject of synthesizing reactive Belite cement through chemical stabilization, it may be relevant to mention other studies involving the use of stabilisers like NaF, Li<sub>2</sub>CO<sub>3</sub>, TiO<sub>2</sub>, MnO, etc. (17-19) on the one hand, and different raw materials (20, 21) on the other. Since these studies are now at a level of scientific curiosity, no detailed reviews are made here.

Pyroprocessing issues. In almost all the studies pertaining to the chemical stabilization of the reactive Belite phases as reported above, the sintering experiments have been carried out in either static furnaces or lab/pilot-scale rotary kilns. Generally, the stabilization of the phase has not been found to be sensitive with respect to the sintering temperature or soaking time at the peak temperature, as long as the latter is well above 1300°C.

In one of the studies carried out at the author's laboratory with  $K_2O$  stabilisation (22), it was demonstrated that if the pyroprocessing technology is not favourable for retention of the alkalies in the Belite phase, the ultimate reactivity of the phase may get affected severely. The experiments carried out in this regard are briefly reproduced here.

Raw mixes prepared from a low-grade limestone (74% CaCO<sub>3</sub>) were compacted in standard brick form with 0.35% void fraction. The bricks after drying were decarbonated in a

TABLE 7
Comparison of High-Belite Cements Obtained with Different Pyroprocessing Systems

Properties	Cement from Fast Heated Clinker	Cement from Slow Heated Clinker			
C <sub>3</sub> S%	10.1	16.5			
C₂S%	59.0	55.0			
C <sub>3</sub> A%	11.2	11.5			
C <sub>4</sub> AF%	10.6	10.3			
Free CaO%	1.06	0.14			
CaSO <sub>4</sub> %	2.99	4.73			
MgO%	1.11	1.04			
Na <sub>2</sub> O%	0.12	0.12			
K₂O%	1.62	0.20			
SSA, Blaines, Cm <sup>2</sup> /g	3200	3180			
Compressive Strength, MPa					
3-day	16.5	13.5			
7-day	33.0	18.6			
28-day	49.0	31.5			

heat-treatment furnace at 1050 - 1100°C and introduced into another gas-fired furnace whose walls were maintained at 1550°C. After seven minutes, the clinkering was complete and bricks were withdrawn and rapidly quenched in air. The cooled clinker was ground with gypsum to produce cement. This schedule of preparing reactive Belite cement has been designated as "Fast Heating".

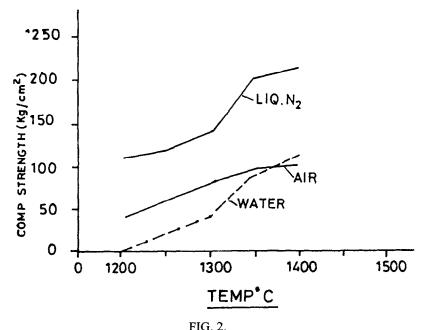
A companion lot of clinker was made by heating the same raw mix continuously in a gasfired furnace upto 1400°C, simulating the rotary kiln conditions. A cement was prepared from this clinker in the same manner as the previous lot. The comparative results are furnished in Table 7

From the table, it is evident that more  $K_2O$  has been retained in the 'fast-heated' clinker almost entirely in the belite phase, which is responsible for better properties of the finished cement, despite lower Alite content. This was further confirmed by us through another experiment in which raw mixes prepared from another low-grade limestone but with only  $0.10\%~K_2O$  were subjected to the similar 'fast-heating' schedule. The cement pastes prepared from such clinker, even after 7 days of hydration, remained soft and the x-ray examination indicated absence of any worthwhile hydration.

The above experiments, thus, reconfirmed the relevance of "fast heating", "rapid cooling", and "alkali retention" for activating the Belite phase.

Cooling media and systems. The essentiality of rapid cooling or quenching for the chemical stabilization of reactive Belite phases has already been highlighted. For all practical purposes, the previous studies indicate that in the temperature range of 1300°C - 850°C at least the rate of cooling should be 1000°C/min. or more.

So far as the cooling media are concerned, air, water, liquid nitrogen and carbon tetrachloride have been tried in the laboratory experiments by the author and others (6,7). As an



Effect of different quenching media on compressiver strengths at 1-day.

TABLE 8
Effect of Different Cooling Rates on Matrix of High-Belite Cements

Sample No. & (Nature of cooling)	Matrix Charac- ter	Crystallite size of C <sub>3</sub> A, (microns)	Specific Surface cm²/g	W/C for normal consis- tency	Setting Time (I-F) Min.
1.(10°C/min to ambient)	100% crysta- lline	15	3592	0.62	16-22
2.(10°C/min to 950×C & air cooling)	-do-	15	4532	0.64	18-45
3.(10°C/min to 950°C & water cooling	-do-	15	4198	0.75	60-95
4.(10°C/min to 950°C & liquid N <sub>2</sub> cooling)	-do-	15	4714	0.89	45-65
5.(direct air cooling to ambient)	-do-	5-10	3412	0.56	16-27
6. (direct water cooling to ambient)	50% glassy	5	3404	0.37	85-180
7. (direct liq. N₂ cooling to ambient)	100% crysta- lline	5-10	3550	0.55	15-30

illustration, some comparative results are given in Fig.2, which shows the highest effectiveness of liquid nitrogen followed by air. The aqueous quenching was found to affect the strength properties, while the use of carbon tetrachloride led to complete shattering of the physical structure of the clinker phases.

In sum and substance, because of practical difficulties of using liquid nitrogen and reaction problems with water, ultimately the design of industrial systems would have to depend on air as the quenching media. A system design on a pilot scale has been attempted (23). A small rotary kiln of 60 kg/h capacity was modified with peripheral discharge of clinker at 1300°C into a fluidised trough cooler to cool clinker to 900°C. It is reported that this system has been subsequently upgraded to 20 TPD capacity range. An attempt has also been made to develop a hot clinker crusher which was installed at clinker discharge to take care of coarser (+12 mm) clinker grains before entry into the fluidised cooler for effective cooling.

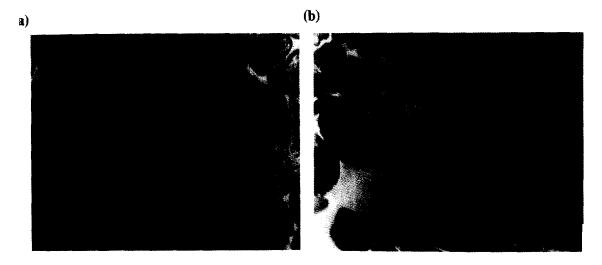
Rapid cooling to control  $C_3A$  effect in high-Belite cements. When high-Belite cements have enough crystalline  $C_3A$  in them, the experience shows that the addition of gypsum (even if

TABLE 9
High-Belite Cement Production Trial at a Wet Process Plant in India

C₃S%	44.69	26.47
C₂S%	44.38	67.78
C <sub>3</sub> A%	9.55	5.05
C <sub>4</sub> AF%	1.38	0.55
Na <sub>2</sub> O%	0.16	0.12
K₂O%	0.80	0.69
SSA Blaines,cm2/g	3255	3285
% SO <sub>3</sub>	2.5	2.4
Le-Chatelier Expn. mm	4.0	25
Comp.Strength MPa 3-day 7-day 28-day	26.0 41.0 59.9	15.0 23.7 39.3

the quantity is increased) cannot properly regulate the setting time because of flash setting tendencies (24). This is explained (25) by the increased quantities of ettringite and secondary gypsum formed in cements with low lime, resulting in stiffening and not rapid setting. Hence rapid cooling, which is so very essential for the reactive Belite phase itself, is also necessary to control the crystallinity of the matrix formed by C<sub>3</sub>A and C<sub>4</sub>AF. This is evident from the study reported in (24), involving the cooling of clinker with 71.2% Belite, 16.8% C<sub>3</sub>A and 10.7% C<sub>4</sub>AF at different rates and measurement of setting time of cements prepared with 3.5% SO<sub>3</sub> added to differently cooled clinkers (Table 8). From the data, it is evident that the clinker obtained by cooling through water quenching directly from kiln discharge has shown 50% glass formation in the interstitial phase with small crystal size in the balance crystalline matrix with resultant improvement in setting time. Similar results were perhaps expected from liquid nitrogen quenching but, according to the authors, the results were different perhaps due to the formation of insulating layers during quenching that inhibited glass formation.

In this table, the high expansion of the high-Belite cement is worth noting. During the run, many spot samples recorded even higher expansion as well as flash setting characteristics. The microstructural studies revealed abnormalities of the matrix (Fig.3 a). To rectify the situation, use of 5% gypsum as a mineraliser and 1.5% iron ore as a flux was resorted to and the Belite morphology and the matrix characteristics dramatically improved (Fig. 3b) and consequently, the expansion behaviour of the cement changed with LC expansion of 8-10 mm. The cement strength properties also registered significant improvement.



 $FIG.\ 3.$  Differences in Belite microstructure and matrix characteristicas without (a) and with (b) user of gypsum and iron ore.