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FUTURE TECHNOLOGICAL OPTIONS : PART II

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ABSTRACT

This is the second part of the paper. While the first part dealth with the basic concepts and the technologies involving natural raw materials, this part attempts to highlight the 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 in terms of their durability and energy-saving potential has been examined. Finally, a picture of the future potential of this class of binder has been culled out.

Introduction

The distinctive roles of Alite and Belite in Portland Cements and the anticipated durability of high-Belite cements of the Indian origin as evident from the long-term hydration data generated in the author's laboratory have been discussed in Part I of this article. Of the three different types of technologies being developed in various laboratories for making reactive Belites, the process involving natural raw materials, chemical stabilizers and rapid cooling has also been dealt with in the first part of this article. The present part discusses the outlines of sol-gel processing and hydrothermal treatment for making reactive Belites, studies relating to the production of blended Belite cements and certain recent findings on the durability aspects of high-Belite cements.

Sol-gel Type of Processing

One of the early attempts of producing reactive C_2S phase at lower temperature than, what is achieved through the previously reported chemical stabilisation routes, was by Roy and Oyefesobi (27) who adopted the preparation of gel and spray-drying techniques. They used $Ca(NO_3)_2$ solution mixed in measured proportions with 1 M solution of a stabilised aqueous sol of SiO_2. The spray-dry technique involved spraying droplets of the solution into a vertical tube furnace preheated to temperatures usually between 750°C and 940°C. While 3:2 C/S compositions reacted at 750°C, 2:1 C/S compositions reacted at 940°C.

For gel preparation, the solutions were mixed thoroughly in the appropriate proportion and dehydrated at about 70°C. This dried gel was heated to 760°C for 1 hour.

TABLE 10
Illustrative Compressive Strength Properties of Sol-gel Derived Belite Powders

Sample	Composition %				Compressive Strength, MPa			
	SiO_2	Al_2O_3	CaO	C/S	1-D	3-D	7-D	28-D
1	34.1	0.3	63.1	1.98	2.5	12.5	17.0	32.0
2	34.0	0.8	62.8	2.01	3.9	4.4	6.6	32.8

In both gel and spray-dry routes, ß-Belite phase was obtained with BET surface area range of 7.43-12.94 m^2/g. The He pycnometer density was of the order of 3.15 g/cm^3 The hydration studies of these powders was carried out in 12.7 x 12.7 mm cylinders by hot pressing (150°C) or ambient pressing at 25,000 psi pressure for 1/2h. The compressive strength values were 48-90 MPa in the case of hot pressing and 41-68 MPa in the event of ambient pressing. Another comparative study of hot pressing of ß-C_2S prepared by this route showed a compressive strength of 62 MPa against identical hot pressing of a commercial ß-C_2S powder which showed only 41 MPa.

In another study (28) powders in CaO-SiO_2 system with surface areas greater than 50 m^2/g even after calcination at 700°C were synthesized by metallorganic decomposition. Pure ß-C_2S was obtained when C/S ratio was equal to or less than 2. The powders showed high hydraulic reactivity.

A more comprehensive investigation has been carried out at the author's laboratory (29). The gels were prepared by non-aqueous route from calcium nitrate as a source of lime and tetraethoxysilane (TEOS) as a source of silica using ethanol as a solvent. The proportions of a calcium salt and TEOS were adjusted in such a way to obtain the desired levels of C/S ratio in the sinters. Hydrolysis was carried out by addition of water to this solution along with the use of a small amount of acid catalyst. Similar studies were carried out by the aqueous route. The starting raw materials used in this were salts of calcium or calcium hydroxide and the aqueous solution of silica sol for the source of silica. The strength properties of some sintered Belite powders are given in Table 10 and the progressive formation of the ßC_2S-

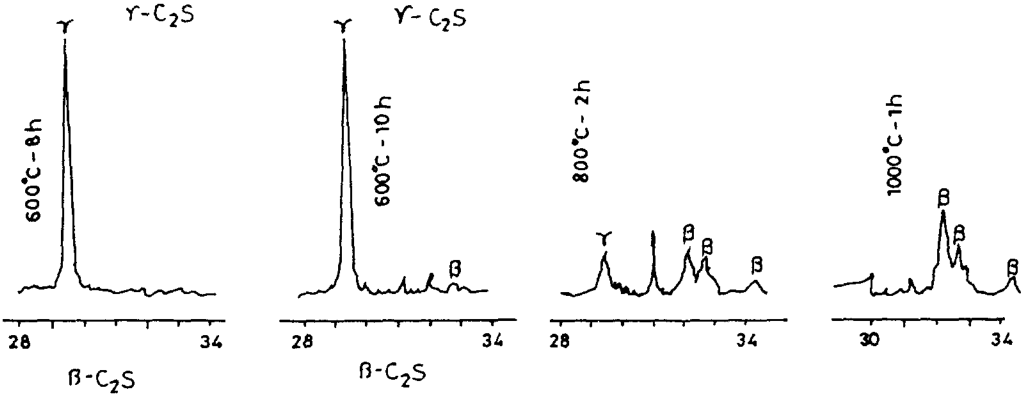

FIG. 4.
Progressive formation of C_2S obtained by the sol-gel process at different temperatures.

phase at low temperatures has been shown in Fig. 4. Some anomalies in the strength gain upto 7 days were characteristic in these samples.

Hydrothermal Processing

The feasibility of producing reactive ß-C_2S through hydrothermal processing has been receiving wide attention in the recent past. This route consists of first making C-S-H through hydration, which is then subjected to hydrothermal treatment and finally to low-temperature firing to obtain reactive Belite phase.

Yang et al (30) used analytical reagent CaO and aerosol silica as starting materials. A mixture of CaO/SiO_2 with mole ratio of 2 and W/S ratio of 5-10 (by wt.) was treated hydrothermally under 100°C and 1 atm for several hours, then dried and heated at 850°C, 1000°C, 1200°C and 1300°C separately followed by air quenching. The products were characterised by very fine grain size in the range of 0.27 - 2.7 mm and specific surface area of 10-24 m^2/g. The $[SiO_4]^{4-}$ tetrahedra in these ß-C_2S particles are situated in very poor symmetry and Ca^{2+} ions are irregularly distributed in the crystal lattice sites. The amount of combined water on hydration increased significantly with decrease of heating temperature, which is in line with particle size distribution, crystal defects and molecular distortions of corresponding samples.

Ishida et al (31) attempted to synthesize the stable and pure ß-C_2S at room temperature without any stabiliser by dehydration below 800°C of calcium silicate hydrates having Ca/Si ratio of 2.0. These are a-C_2S hydrate $Ca_2(HSO_4)(OH)$, hillebrandite $Ca_2(SiO_3)(OH)_2$ and dellaite $Ca_6(Si_2O_7)(SiO_4)(OH)_2$, which give dehydroxylation at 400 - 450°C, 520-540°C and 640-700°C respectively. Out of these, hillebrandite can be purely made by using various forms of silica with lime in hydrothermal suspensions at temperatures of 200°C - 250°C and decomposed easily to ß-C_2S on heating at 600°C. The ß-C_2S is thus obtained as fibrous thin crystalline aggregates with specific surface area of more than $6m^2/g$, similar to that of hydrothermally formed hillebrandite. This ß-C_2S is highly reactive and completes hydration in 28 and 14 days with W/C = 0.5 and 1.0 at 25°C respectively. The C-S-H has a Ca/Si ratio as high as 1.95 and contains almost no $Ca(OH)_2$.

A similar approach of hydrothermal processing was also adopted by Jiang and Roy (32), although for a different purpose of utilising fly ash in making a cementious product. The starting materials used are class F fly ash and analytical reagent grade CaO. The samples were prepared with a Ca/Si molar ratio of 2 and a synthesis route as depicted by Fig.5 was adopted. The main hydration products of fly ash-lime mixes are C-S-H and C_3AH_6. After hydrothermal treatment, the reaction product was heated dry. The mineralogical compositions of reaction products generated were ß-C_2S and $C_{12}A_7$ as well as $CaCO_3$. The mortar specimens, prepared with the above reactive fly ash cement, shows comparable compressive strength patterns as those of C_3S (Fig.6), which is an evidence of better reactivity of the ß-C_2S phase obtained through this route.

Blended Belite Cement

Quite different from the approaches narrated so far to obtain a reactive Belite phase approximating the properties of Alite, Mikoc and Matkovic (33) suggested that the addition of

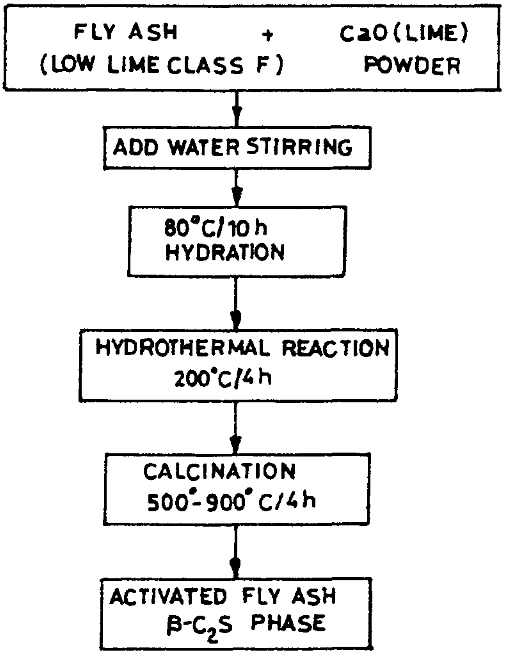

FIG. 5.
Hydrothermal processing of flyash to make β-C_2S cement.

silica fume, calcium sulphoaluminate, gypsum and a superplasticiser to a Belite cement would accelerate the strength development significantly. This is a concept which is different from producing CSA-Belite cement at the same time. The authors produced a clinker with 2.9% $BaSO_4$ doping in a pilot rotary kiln with simple air cooling. The microscopic examination showed C_3S 1.7%, C_2S 84.5% and matrix 13.7%. The C_2S phase was in the β-state. The clinker was ground to 3500 cm^2/g fineness and the blended mortars were cast with 20-30% silica fume with or without 3% C_4A_3S and varying proportions of gypsum along with classified sands and naphthalene sulphonate condensate as plasticiser. The test results are given in Table 11. The prewetting of the ground clinker was done to avoid the fast reaction of C_3A. The best strength gain was observed with simultaneous addition of silica fume and C_4A_3S and was comparable to reference OPC sample.

It may be worthwhile to mention here that, unlike many other countries, in India blended cements are commercially produced in some of the plants using high-Belite clinkers and pozzolana or granulated blast furnace slags. The long-term strength properties of some of these cements in mortar and concrete are quite interesting, when compared with the properties of blended cements obtained from high-Alite clinkers. Some typical data are furnished in Table 12. Excepting the early mortar strength, the pozzolanic cement based on clinker with higher Belite content is quite comparable in properties to the Alite cement.

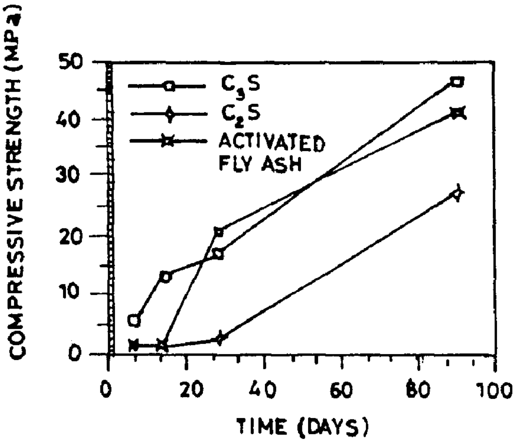

FIG. 6.
Compressive strength patterns.

Durability of High-Belite Cement Mortar and Concrete

The acceptance of high-Belite or Reactive Belite cements would strongly depend on the durability data of mortars and concretes produced with these kinds of cements. The experience of using moderately high-Belite cements produced commercially in countries like India, Poland, etc. as mentioned earlier, and the long range strength data furnished for the moderately high-Belite cements produced in India, provide enough confidence base about the durability of high-Belite cement concretes.

This has been further reinforced by the studies of Muller and Stark (34) on the durability of a concrete road made with Reactive Belite cement in 1984. Four-year old drill cores from

TABLE 11
Composition and Properties of Blended Belite Cements

Binder Composition, Wt %				Compressive Strength	
Clinker	Silica Fume	C_4A_3S	CSH_2	28-day	90-day
96	-	-	4	2	13
76	20	-	4	6	25
66	30	-	4	24	68
66	20	3	11	100	128
86	-	3	11	13	nd
66*	30	-	4	101	122

* OPC for ref.

TABLE 12
Properties of Commercially Processed Blended Cements Made From High Belite Clinkers

Source Designation	Belite % in clinker	% Blend component	Mortar or concrete (M30)	Compressive Strength, MPa				
				3-D	28-D	180-D	1 Y	2 Y
J	35%	50% slag	Mortar	24	37	46	49	52
			concrete	15	27	32	33	33
M	30%	12% Pozzolana	Mortar	22	56	72	74	77
			Concrete	15	36	50	55	60
W	15%	15% Pozzolana	Mortar	40	60	72	76	76
			Concrete	20	42	55	55	57

this concrete road were tested for depth of carbonation, porosity, water impermeability, compressive strength and frost resistance in comparison with Ordinary Portland Cement concrete. The authors concluded through quantitative measurements that the Reactive Belite cement concrete is quite at par with Ordinary Portland Cement concrete virtually in all respects. As an illustration, the comparison of pore size distribution in the two concretes is shown in Fig. 7.

The durability of reactive Belite cements in comparison with commercial Alitic cements or cement with high non-activated Belite content has been investigated in (35, 36). The clinker phase compositions of the cements studied are given in Table 13. Clinkers designated as BL, BAL and BSL are high-Belite laboratory-made ones with no sulphate/alkali activation, with only alkali incorporation and with both alkali and sulphate incorporation respectively, while PZL and PZ are commercially available Portland clinkers. The compressive

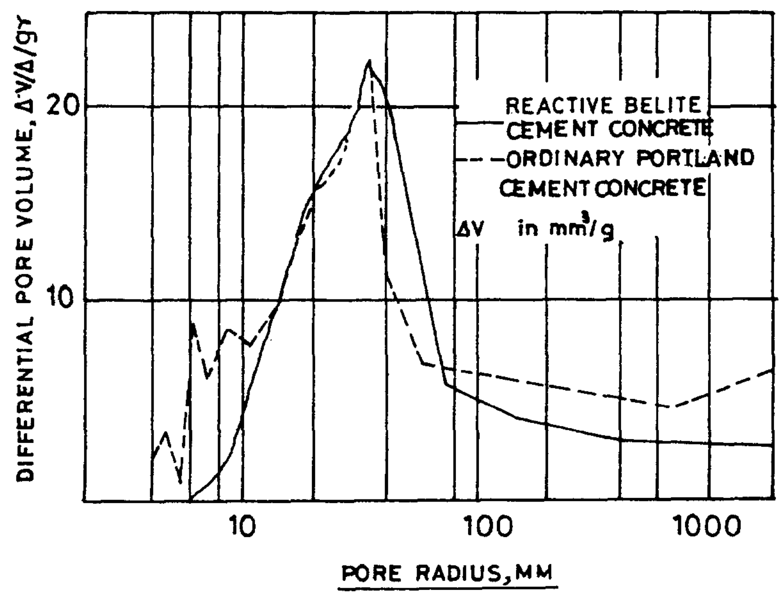

FIG. 7.
Comparative pore size distribution of reactive Belite Cement and Ordinary Portland Cement Concretes.

TABLE 13
Quantitative Clinker Phase Content Microscopically Determined by the Point Counting Method

		Quantitative clinker phase content (wt.%)			
Specimen	SL	Alite	Belite	Aluminate	Ferrite
BL	80	21	60	12	8
BAL	80	23	52	20	5
BSL	80	13	67	14	6
PZL	88	54	29	0	16
PZ	93	60	24	9	7

strength data, the depth of carbonation and porosities of these five clinkers were studied in cement mortar samples, after converting all the clinkers to cements of same fineness (3000 and 4000 cm^2/g) and sulphate content (3.2%). The results of investigations are given in Figs 8 & 9 and Table 14. From the results, it is evident that the reactive Belite cements (BAL/BSL) have shown better strength development, lower depth of carbonation and higher impermeability with respect to non-activated Belite cement and also the commercial Alitic cements. It has also been established that the alkali-activated reactive Belite clinker does not result in high alkali content in pore fluid. As a result, the chances of alkali aggregate reaction for reactive Belite cement are no more than for Portland Cement.

Thus, based on the available information, one may note very positive indications about the durability of high-Belite cements.

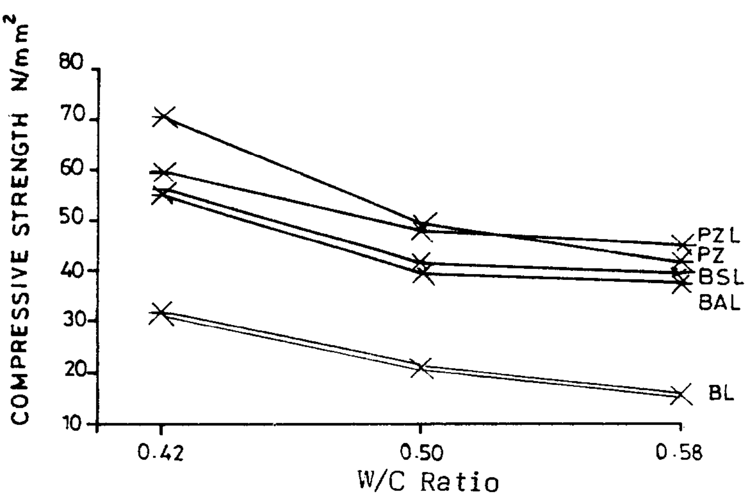

FIG. 8.
Compressive strength cement mortars after 28 days as a function of the water/cememt ratio (4000 Blaine, 27 d water storage).

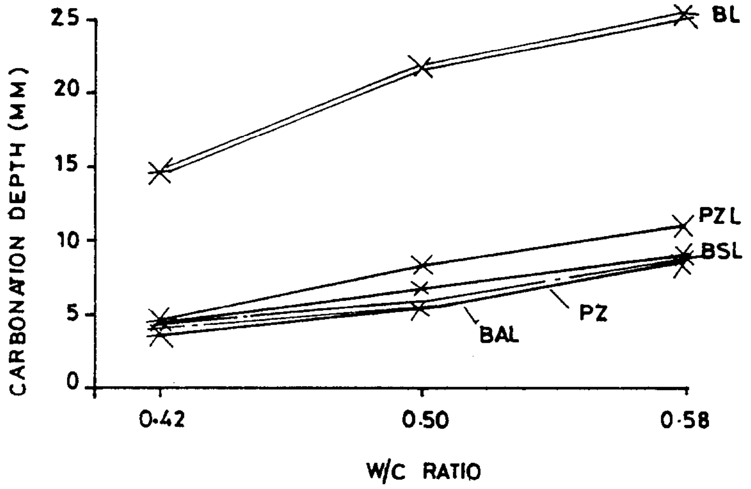

FIG. 9.
Depth of carbobation of the cement mortar prism after 90 days eposure in vol% CO_3.

Technological Imperatives

From the above discourse, it is evident that the high-Belite cements hold real promise more in terms of their anticipated durability and ultimate strength gain than in respect of their energy or cost saving potential in manufacture. But, if both the advantages could be combined, the high-Belite cements may well be the binders of the future. Towards this objective, the available technology options have already been discussed. The technological imperatives that are becoming increasingly evident through various pilot or plant scale trials are perhaps the following:

a) The process route of chemical stabilisation to make reactive Belite cement needs to be looked at from the point of non-traditional engineering as it involves three critical elements - fast firing, rapid cooling and use of dopants or stabilisers which are mostly volatile in nature. The standard practices of using rotary kilns and grate coolers may posepose limitations in achieving the desired degree of 'fast firing' and 'rapid cooling'. In addition, the rotary kiln system is likely to introduce operational impediments in cases like alkali activation due to generation of internal volatile cycles.
b) The issue of proper selection of a quenching medium is also related to the engineering of an appropriate system. Although "air' as the medium appears more easily implementable, the other possibilities should not be foreclosed.
c) The use of dopants or stabilisers in the process is generally small and the feeding arrangements in such small doses as well as their uniform dispersion in total raw mixes offer problems in present-day large-scale trials.
d) The other two process routes, viz. the Sol-gel and Hydrothermal are just perhaps coming out of the lab-scale to pilot level of experimentation. Although, prima-facie, these processes offer positive indication about low temperature operations, which perhaps may be below even 1100°C, the cost implications of these processes would be more related to

TABLE 14

Properties of various Hardened Cement Pastes after 90 days, arranged by decreasing porosity, with varying water cement ratios and a Specific Surface of 3000cm^2/g

Specimen	W/C ratio	Porosity		Capillary related to total porosity
		Total (vol%)	Capillary (vol %)	
BL	0.42	26.7	18.5	69.3
	0.50	30.8	22.4	72.8
	0.58	34.4	24.5	71.2
PZL	0.42	25.1	15.0	59.8
	0.50	29.1	18.3	62.9
	0.58	34.0	22.0	64.6
PZ	0.42	20.0	11.9	59.5
	0.50	22.2	13.3	59.9
	0.58	25.9	16.0	61.8
BAL	0.42	19.6	10.3	52.3
	0.50	20.4	11.7	57.4
	0.58	23.2	13.3	57.3
BSL	0.42	16.4	7.4	45.4
	0.50	18.3	8.9	48.6
	0.58	23.0	13.3	57.8

the purity of raw materials used, scale of operation feasible, adoption of continuity in the operations, etc.

e) Ultimately, it is necessary to conceptualise three upscaled system designs for effective comparison of energy and cost.

f) Apart from the focus on the manufacturing processes, it is realised that continued efforts will have to be laid on generating further durability data on concretes produced with reactive Belite cements containing over 60% Belite obtained through bulk production routes.

g) The data on the blendability of high-Belite cements with microfine substances like Silica fume and other pozzolanic materials are rather limited and for practical demands of concreting, this sort of data base will have to be built up.

Conclusion

The current research trends indicate that Portland type of cement with Alite phase restricted to 20% or so and Belite phase close to or in excess of 60% with a partially glassy matrix containing low proportions of tricalcium aluminate and fine crystallites of aluminate and ferrite will get wider acceptance as a 'High-Belite' or 'Reactive-Belite'cements. These kinds of binders can be produced through three alternative routes: Chemical stabilisation through conventional firing or fast firing but always with rapid quenching, sol-gel type of processing and hydrothermal treatment. In the last two routes, the operating temperatures are low and no chemical stabilisation is necessary. The development scale for the first process is certainly much higher than the latter two. However, the conceptual design of all the three processes for scale-up operations is yet to be undertaken and then only, the relative cost-benefit picture of the three processes would emerge. The energy advantage of the processes vis-a-vis the present day production of Portland cement is a moot point in favour of high-Belite cements, which is yet to be established. The durability and strength gain features of moderately high-Belite cements commercially produced in countries like Poland and India are indicators for the expected performance superiority of high-Belite cement mortars and concretes. Some data have been generated and more studies will obviously reinforce the concept. The technical feasibility of making blended high-Belite cement with silica fume has been indicated. More studies in this direction will certainly help expanding the application of high-Belite cement.

References

1. I. Jawed, J. Skalny and J.F. Young, Hydration in Portland Cement, in "Structure and Performance in Cements" Ed. P.Barnes, p. 237, Applied Science publishers, London, 1983.
2. W.C. Hansen, Discussion on "Portland-Pozzolon Cement" by G. Malquori, Proc. 4th Intern'l Symp. Cement Chem., Vol. II, Washington, p. 1800, 1960.
3. Su Muchen, W. Kurdowski and F. Sorentino, "Development in non-Portland Cements", 9th ICCC, Vol. I, NCB, New Delhi, p. 317, 1992.
4. F. Von Lampe and R. Seydel, Cem. Concr.Res., 19, p. 509-518, (1989).
5. Yang Shuzhen and Song Hantang, 9th ICCC, Vol.IV, p. 391, NCB New Delhi, 1992.
6. Jochen Stark, Anette Muller, et al, Pt 1-3, Silikatechnik, 30, p. 357 (1979), 31, p. 50 31, 168 (1980).
7. S.V. Karkhanis, C.H. Page, B.K.G. Rishi, P.S. Parameswaran and A.K. Chatterjee, 2nd Intern'l Symposium on Cement and Concrete, Vol. 2, p. 377, Beijing, (1989).
8. Ram Prakash, S.C. Ahluwalia and J.M. Sharma, 9th ICCC, Vol. IV, p. 397, NCB, New Delhi, 1992.
9. V.V. Subba Rao and K.C. Narang, ZKG Intern'l, 40, p. 434 (1987).
10. K. Rajczyk and W. Nocum-Wczelik, 9th ICCC, Vol. II, p.250, NCB, New Delhi, (1992).
11. A. Gies and D. Knofel, Cem. Concr. Res., 16, p. 411, (1986).
12. K.H. Jost, R. Seydel, A. Muller and J. Stark, ZKG Intern'l, 41, p. 169, (1988).
13. A. Gies and D. Knofel, Cem. Concr. Res., 17, p. 317, (1987).
14. H.C. Visvesvaraya, S.J. Raina and S.N. Ghosh, Proc. MRS Intern'l Meeting on Advanced Materials, 63, Advanced Cements and Chemically Bonded Ceramics, ed. by M. Doyama et al, p. 45, Tokyo, 1989.
15. Ingo Mielke, Anette Muller and Jochen Stark, 9th ICCC, Vol. II, p. 399, NCB, New Delhi, 1992.
16. M. Munteau, M. Dinuleseu, M. Bedo and F. Paul, 9th ICCC, Vol. III, P. 406, NCB, New Delhi, 1992.
17. S.N. Ghosh, A.K. Paul and A.K. Thakur, J. Materials Sci., 13, p. 1602, (1978)
18. V.K. Mathur, R.S. Gupta and S.C. Ahluwalia, 9th ICCC, Vol. II, p.406, NCB, New Delhi, 1992.
19. V.K. Mathur, R.K. Goswami and K.M. Sharma, Proc. 3rd NCB Intern'l Seminar on Cement and Building Materials, 4, p.37,(1987).20. N.B. Singh, S.P. Singh and A.K. Shukla, 9th ICCC, Vol. II, p. 101, NCB, New Delhi, 1992.
21. Jan Majling, Peter Znasik and Josef Lasek, Stavivo, 68, p. 100, (1990).
22. B.S. Rangnekar, V.R.G. Srinivasan and V.V. Pai, Proc. 6th ICCC, Vol. I, p. 197, Stroiizdat, Moscow, 1976.

23. Anette Muller, HAB Weimar Wissenschaftsbereich Baustoffe, Germany, Personal Communications, 1993.
24. V. Carin, R. Halle and B. Matkovic, Ceram.Bull., AcerS, 70, p. 251, (1991).
25. R. Bei and U. Ludwig, ZKG Intern'l, 43, p. 506 (1990).
26. R.V. Hargave, R.D. Shaha, A.K. Chatterjee and B.S. Rangnekar, Proc. 4th Intern'l Conf. Cem. Microscopy, p. 110, USA 1982.
27. D.M. Roy and S.O. Oyefesobi, J. Amer. Ceram. Soc., 60, p. 178 (1977).
28. T. Nagira, S.A. Warner, J.J. Mecholsky and J.H. Adair, Proc. MRS Intern'l Meeting on Advanced Materials, Vol. 13, p.255, Tokyo, 1989.
29. C.H. Page, C.H. Thombare, R.D. Kamat and A.K. Chatterjee, Advances in Cementitious Materials, ed. by S.Mindess, p. 643, Amer.Ceram.Soc., Ohio, 1991.
30. Yang Nanru, Zhang Hua and Zhang Beiquian, 9th ICCC, Vol. IV, p. 285, NCB, New Delhi, 1992.
31. H. Ishida, K. Sasaki, Y. Okada and T. Mitsuda, 9th ICCC, Vol. IV, p. 76, NCB, New Delhi, 1992.
32. W. Jiang and D.M. Roy, Ceram. Bull., AcerS, 71, p. 642, (1992).
33. M. Mikoc and B. Matkovic, Ceram. Bull., AcerS, 71, p. 1131,(1992).
34. A. Muller and J. Stark, ZKG Intern'l 43, p. 160, (1990).
35. D. Knofel and C. Fuhr, Advances in Cementitious Materials, ed. by S.Mindess, p. 715, Am.Ceram. Soc., Ohio 1991.
36. C. Fuhr and D. Knofel, 9th ICCC, Vol.V,p. 32, NCB, New Delhi, 1992.