Pergamon

Cement and Concrete Research, Vol. 28, No. 11, pp. 1585–1594, 1998

0008-8846/98 $19.00 + .00

PII S0008-8846(98)00140-9

VOLUME STABILISATION OF HIGH MgO CEMENT: EFFECT OF CURING CONDITIONS AND FLY ASH ADDITION

M.M. Ali[1] and A.K. Mullick
National Council for Cement and Building Materials, New Delhi, India 121 004

(Received November 13, 1997; in final form August 27, 1998)

ABSTRACT

Hydration of high MgO cement paste under autoclave conditions causes the rapid formation and crystallization of magnesium hydroxide and leads to the creation of larger pore sizes. This results in the loss of mechanical strength and higher expansion values. Under ambient water curing, precipitation and distribution of gelatinous calcium silicate hydrates into the finer network causes a homogeneous morphology and the development of smaller pores. The resultant higher mechanical strength associated with partial hydration of MgO yields reduced expansion. High MgO cement paste containing fly ash also showed considerable pore refinement and improved hydrate morphology favouring volume stability under both autoclave and ambient water curing. *© 1998 Elsevier Science Ltd*

Introduction

The hard burnt MgO present as periclase in cement is known to affect the volume stability of the cement paste as the hydration of MgO into $Mg(OH)_2$ leads to molar solid volume expansion of 117%, which causes expansive stresses. As the expansive stresses exceed the tensile strength of cement paste, cracking occurs, resulting in higher expansion (1).

To ascertain cement soundness due to MgO expansion, accelerated hydration in an autoclave is specified in cement standards in many countries and the expansion limit specified is 0.8%. The limit of MgO content is set at 6% in cement specification of India and some other countries (2). Studies have shown that the amount of free MgO, its crystal size, and distribution affect expansion significantly and beyond 1.2% MgO as periclase, a steep rise occurs in autoclave expansion (3). Therefore, the cement samples containing up to 6% MgO but low periclase content with smaller size crystal can satisfy requirements of soundness in autoclave test.

The hydration of periclase under ambient conditions is very slow and occurs to an insignificant extent compared to autoclave curing. In addition, during accelerated hydration in the autoclave the cohesive forces present in normally hardened cement pastes are not available. Under such conditions, the performance of cement in service could not be correlated with the performance in the autoclave test and criticisms have been reported on the

[1]To whom correspondence should be addressed.

TABLE 1
Chemical analysis of cement and fly ash.

Constituent oxides (%)	OPC	Fly ash
LOI	1.56	2.80
SiO_2	21.48	59.06
Al_2O_3	4.50	28.25
Fe_2O_3	3.40	6.05
CaO	60.03	1.91
MgO	6.08	0.58
SO_3	1.73	0.16
CaO_f	0.20	—

validity of this test (4). Studies have shown that cement samples containing not more than 6.5% total MgO are sound under normal curing over longer ages (5,6). However, cement with higher MgO reported loss in strength after 5 to 10 years in normal conditions (7). At higher doses of MgO, silicious additions were found to provide volume stability to the cement under both autoclave and normal conditions (6,8).

The reported mechanisms on volume stabilization of high MgO cement in the presence of silicious additions are based on blocking periclase hydration through formation of a CSH gel coating, partial conversion of free MgO into magnesium silicate hydrates (9), and formation of 11 Å tobermorite during autoclave curing (3,10). A recently proposed mechanism of periclase expansion leading to unsoundness in high MgO cement is based on crystal growth pressure due to rapid formation of $Mg(OH)_2$ on the contacting particles, which causes expansion of hydration voids resulting in increase in volume of the hardened cement paste (11).

Although the problems of unsoundness of cement due to MgO, its implications, test procedures, and mechanisms of expansion have been well attended, further investigations are required to rationalize the mechanism of volume stabilisation. In the present investigation, a Portland cement containing ~6% MgO was subjected to hydration under autoclave conditions as per ASTM C 151–93a and ambient water curing up to 3 years. The effect of various amounts of fly ash addition was studied on the development of hydration products, porosity, pore size distribution, morphological developments, compressive strength, and linear expansion. A mechanism of volume stabilisation is proposed in terms of effects of curing conditions and fly ash addition on pore refinement and morphological improvements.

Experimental

The samples of ordinary Portland cement prepared and fly ash taken were analysed for constituent oxides using chemical analysis (Table 1).

The amount of periclase and its grain size distribution was determined by optical microscopic study of clinker specimen of high MgO cement using the point counting method (Fig. 1).

The physical characteristics of the cement are given in Table 2. Fineness of fly ash was 500 m^2/kg (Blaine).

To optimize the dosage of fly ash for controlling expansion within the permissible limit,

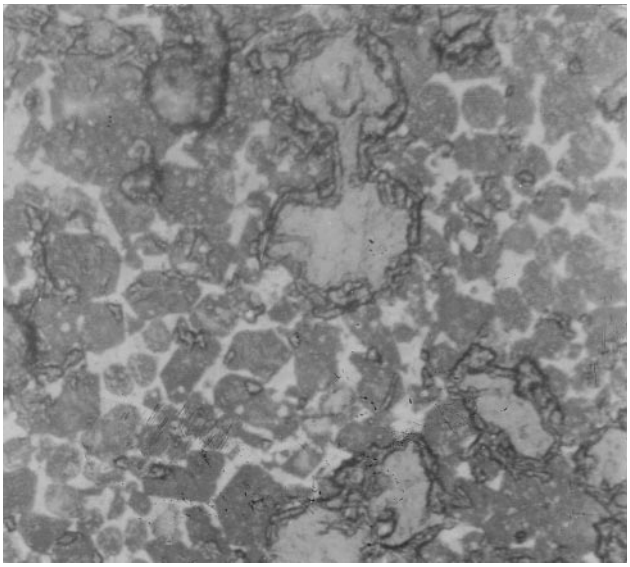

FIG. 1.
Microstructure of high MgO clinker.

blends containing 5%, 7%, 10%, 15%, and 20% fly ash by weight of cement were prepared. The plain cement and the blends were cast into specimens of size 25 × 25 × 280 mm using ~27% water content. Specimens were demoulded after 24 h of curing in 90% humidity and used for both autoclave test and ambient water curing for long ages. To determine compressive strength, the cement paste samples were cast as 25-mm cubes and cured in similar conditions.

TABLE 2
Physical characteristics of cement.

Properties	Values
Fineness	280 m^2/kg (Blaine)
Consistency	27%
Setting time (min)	
Initial	70
Final	400
Compressive strength (N/mm^2)	
3 days	28.0
7 days	34.5
28 days	50.0
Soundness	
Lechatelier	1 mm
Autoclave	10%

TABLE 3
Effect of curing conditions on linear expansion.

Curing condition	Paste					
	OPC	OPC + 5% FA	OPC + 7% FA	OPC + 10% FA	OPC + 15% FA	OPC + 20% FA
Autoclave	10.00	4.0	0.94	0.64	0.16	0.13
In water (12 months)	0.14	0.14	0.126	0.124	0.121	0.11

The autoclave test was carried out at a pressure of 21 kg/cm^2 and temperature of 215°C for 2 h. The linear expansion was measured using a length comparator. The porosity and pore size distributions of paste specimens were determined using a mercury porosimeter up to a pressure of 22,500 psi. Mineral phases in hydrated samples were determined using an x-ray diffractometer (Rigaku model using Co-target) and differential thermal analyser (Mettler unit). Morphological features were studied on fracture surfaces of hardened cement paste using scanning electron microscopy.

Results and Discussion

Effects on Linear Expansion

Linear expansion observed in ambient cured and autoclaved samples are shown in Table 3.

The values of autoclave expansion were 4.0%, 0.94%, and 0.64% with addition of 5%, 7%, and 10% fly ash, respectively. Only at 10% fly ash addition was the expansion within the stipulated limit of 0.8%. At higher doses of fly ash, expansion was further reduced. Ambient water curing of high MgO cement paste for 1 year showed expansion of only 0.14%, which was found to be 0.12% in presence of 10% fly ash.

Hydration Phases

Main phases observed in x-ray diffraction of samples cured in autoclave and water curing are shown in Table 4. Autoclave curing resulted in complete hydration of periclase both in plain cement paste and in the presence of fly ash. Crystalline magnesium hydroxide (MH) was seen along with C_2SH phase in autoclaved samples. Calcium hydroxide (CH) was a predominant phase in plain cement paste, which was reduced with the increase in amount of fly ash added. Formation of crystalline and low lime CSH phase (11 Å tobermorite) was seen in sample containing fly ash. Unhydrated C_2S phase also was present in all the autoclaved samples.

Samples cured in water showed presence of periclase along with unhydrated C_2S. Samples containing fly ash also showed formation of ettringite along with CSH (Table 4).

Differential thermal analysis curves of 1- and 3-year water-cured cement paste samples are given in Figure 2, which indicate presence of ettringite, $Mg(OH)_2$, $Ca(OH)_2$, and $CaCO_3$. In

TABLE 4
Main phases identified in hydrated cement samples.

OPC autoclaved	OPC + 10% FA autoclaved	OPC 3 years water cured	OPC + 10% FA 3 years water cured
CH	C_2S	CH	CH
C_2S	CH	C_2S	C_2S
MH	CC	MgO	CC
C_2SH	MH	CC	MgO
	CSH*	CSH gel	$C_6A_2\bar{S}_3H_{32}$
			CSH Gel

CH: $Ca(OH)_2$; MH: $Mg(OH)_2$; CC: $CaCO_3$; $C_6A_2\bar{S}_3H_{32}$: ettringite; CSH: calcium-silicate-hydrates.
* CSH: 11 A° Tobermorite.

3-year hydrated cement, the amount of $Mg(OH)_2$ was determined based on thermogravimetric weight losses, which showed hydration of about 80% periclase.

Porosity and Pore Size Distribution

Cement hydrated under autoclave yielded a porosity of 29.65%. Pore sizes were found to vary from 0.005 to 20 μm. In the presence of fly ash, autoclaved samples showed comparable porosity but narrower pore size distribution ranging from 0.005 to 0.5 μm. Thus, larger pores

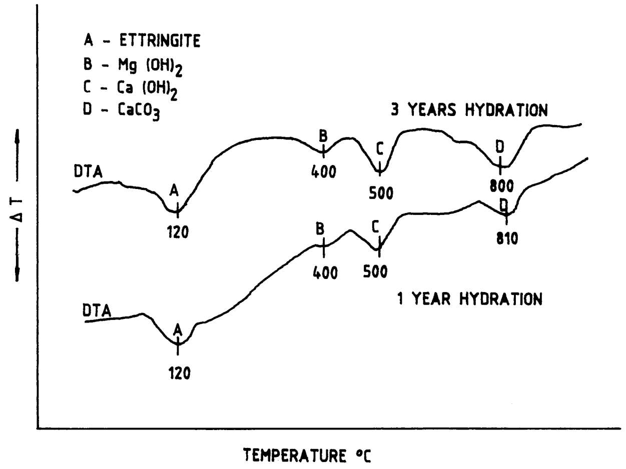

FIG. 2.
Differential thermal analysis of hydrated cement paste.

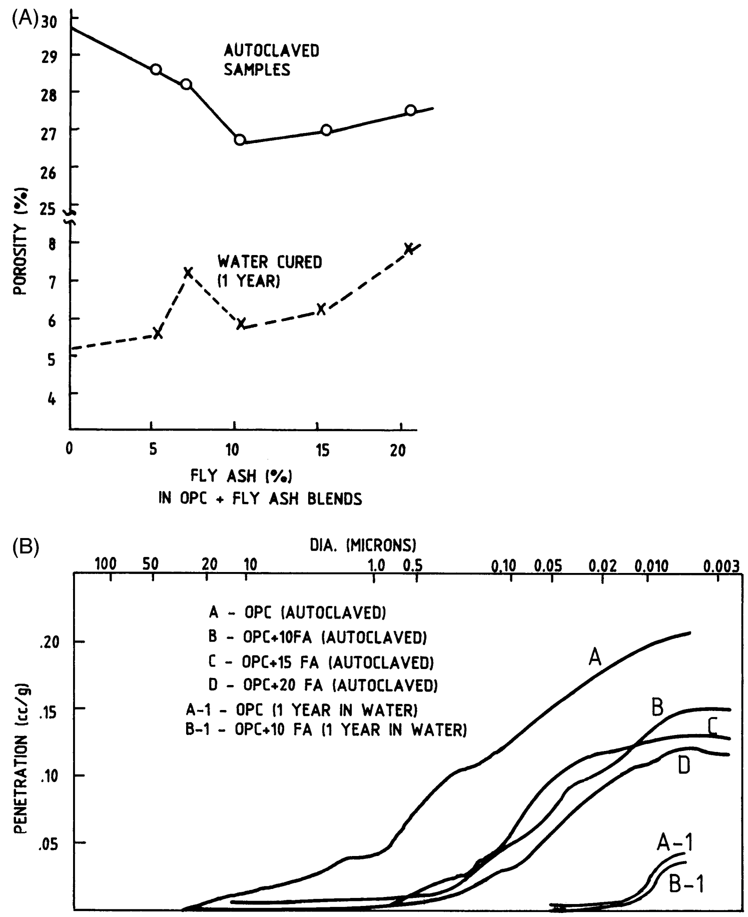

FIG. 3.

Porosoity (*A*) and pore size distribution (*B*) of hydrated cement pastes.

were eliminated in the presence of fly ash. Under water curing, the porosity observed at 1 year was $<$6% in both cases, and pore sizes were reduced considerably ranging, from 0.005 to 0.02 μm (Figs. 3A and 3B).

Morphological Developments

Morphological developments in high MgO cement paste hydrated in autoclave and ambient water curing without and with fly ash are shown in Figure 4. The autoclaved plain cement paste showed the presence of large voids and inhomogeneity in microstructure that, in the presence of fly ash, were homogeneous. Distinct large size crystals growing in the interparticle spaces were seen bridging the pores. Portland cement paste steam cured under high pressure is reported to show presence of tobermorite phase, $Ca(OH)_2$, and dicalcium silicate hydrates (12). The homogeneous and denser morphology in presence of fly ash is probably

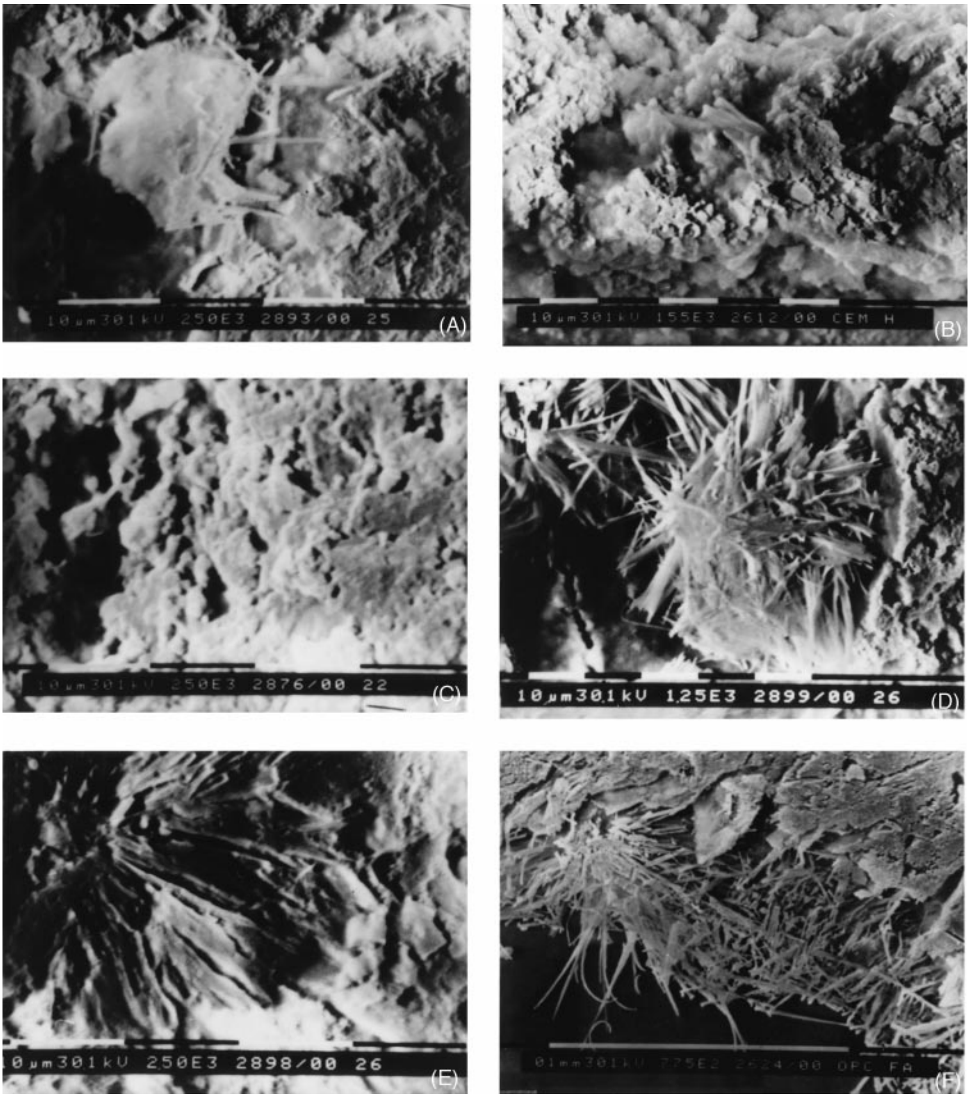

FIG. 4.
(*A*) Ordinary Portland cement (OPC) autoclaved, (*B*) water cured 1 year, (*C*) water cured 3 years, (*D*) OPC + 10% fly ash (FA) autoclaved, (*E*) OPC + 20% FA autoclaved, (*F*) OPC + 20% FA, water cured for 3 years.

due to greater amounts of the calcium-silicate-hydrate formed by pozzolanic reaction of fly ash. This is evident from observed decrease of $Ca(OH)_2$ and increase in peak intensities of calcium silicate hydrates in autoclaved samples containing fly ash.

Under water curing, formation of the gelatinous hydrate is seen in fracture surface morphology. In the presence of fly ash, ettringite formation was seen leading to needleshaped structures. Gelatinous calcium-silicate-hydrates along with other hydrates developed uniformly over later ages, leading to denser morphology with finer pores.

Development of Compressive Strength

High MgO cement pastes without and with different amounts of fly ash hardened in ambient for 24 h appeared to be weak and, therefore, the compressive strengths were determined after autoclave curing as shown in Figure 5A.

The cement sample without fly ash did not possess measurable strength and showed signs of disintegration on autoclave curing. However, by addition of 5%, 7%, 10%, 15%, and 20% fly ash, the compressive strengths were found to be 10, 37, 46, 48, and 51 N/mm^2, respectively. The compressive strengths of cement pastes cured in water for 1 year were higher and found to be 73.0, 76.0, 76.0, 76.6, 74.0, and 72.0 N/mm^2 in the presence of 0%, 5%, 7%, 10,% 15%, and 20% fly ash (Fig. 5B).

Mechanism of Volume Stabilisation

Hydration of high MgO cement paste in autoclave and ambient water curing as well as addition of fly ash to cement leads to major changes in porosity, pore size distributions, and the morphology of the hardened cement pastes. The hydration of MgO to $Mg(OH)_2$ in hardened cement pastes occurs with the formation of other hydrate phases, and the expansive stresses generated due to $Mg(OH)_2$ control the microstructural changes affecting the net expansion.

On autoclave curing, the accelerated rate of MgO hydration rapidly increases pore solution concentration with respect to Mg^{2+} and OH^- ions. As the particles of MgO are embedded in the 24-h hardened cement paste, rapid formation and crystallization of $Mg(OH)_2$ on autoclave curing produces expansive stresses on the surrounding particles, which consist of mainly C_2, CH, CAH, and unhydrated C_2S phases. The directional growth of these $Mg(OH)_2$ crystals lead to expansion of pore spaces, resulting in substantial change in microstructure that showed the presence of larger pores (11). Formation of C_2SH and presence of higher porosity with larger pore sizes cause poor mechanical strength of the autoclaved sample (12). As a result, restraint to the expansive stresses is reduced, which causes unhindered MgO hydration resulting in higher expansion values.

In autoclave curing of high MgO cement paste containing fly ash, although rapid hydration of MgO increases pore solution concentration with respect to Mg^{2+} and OH^- ions, the simultaneous release of alkali and silicate ions from fly ash consumes the available Ca^{2+} ions forming low-lime CSH (13) phases. This increases the rate of calcium silicate dissolution, increasing the amount of crystalline CSH that fills the pores and reducing porosity and pore sizes in hardened cement paste. Therefore, considerable improvements were seen in morphology of autoclaved samples containing fly ash. Formation of low-lime calcium-silicate-hydrates with improvement in microstructure results in higher compressive strength. Majumdar and Rehsi (3) also reported formation of 11 Å tobermorite on autoclave curing of cement containing fly ash leading to higher strength. According to them, higher strengths are utilized in counteracting the expansive forces due to periclase hydration and result in lower expansion values (10).

Under ambient water curing of cement paste, the hydration rate of periclase is very poor

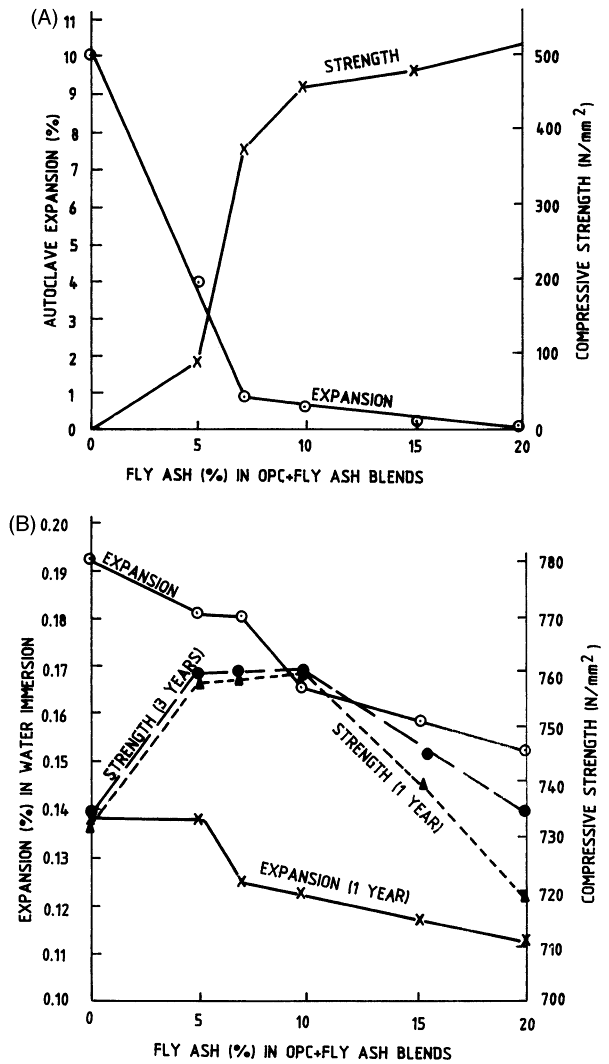

FIG. 5.

(*A*) Compressive strengths of autoclaved cement pastes. (*B*) Compressive strengths and linear expansions for water-cured cement pastes at 1 and 3 years.

and normal hydration of calcium silicate phase causes consistent formation of CSH gel, which is distributed uniformly in the finer network. Denser morphology with reduced porosity provide higher strength to restrain expansive stresses due to MgO hydration. Therefore, water-cured cement paste yields reduced expansion values. In the study carried out, cement paste showed compressive strength of 73 N/mm^2 with expansion of only 0.19%, although 80% of periclase content was hydrated at 3 years. In the presence of fly ash, the microstructures were found to be further densified due to additional formation of ettringite along with calcium-silicate-hydrates.

Conclusions

On autoclave hydration of Portland cement paste containing higher amounts of MgO as periclase, the rapid formation and crystallization of $Mg(OH)_2$ is associated with the formation of C_2SH phase, resulting in poor mechanical strength. The prevailing expansive stresses create larger pores ($>$20 μm) leading to inhomogeneous morphology and higher expansion values. In the presence of fly ash, pores $>$0.5 μm were eliminated and formation of low-lime and crystalline calcium-silicate-hydrate phases led to denser, homogeneous morphology and higher strength, resulting in low expansion.

Under ambient water curing of these cement pastes, the porosities were substantially low and pores $>$0.02 μm were not present. Microstructural homogeneity and higher strengths were observed. MgO hydration produced reduced expansive stresses due to the less formation of $Mg(OH)_2$. The large amount of hydration product was distributed in the finer network filling the pores. Consequently, the higher mechanical strength generated provided more restraint to the expansive stresses, resulting in reduced expansion at later ages.

Acknowledgment

This paper is based on the investigations carried out under a project at National Council for Cement and Building Materials and is being published with the permission of Director General.

References

1. C. Rod, et al., translation ZKG. 4/88, pp. 195–199.
2. A.K. Mullick, 10th ICCC, Vol. I, Plen. 1, 31 pp, Goteborg, 1997.
3. A.J. Majumdar and S.S. Rehsi, Mag. Concr. Res. 21, 141 (1969).
4. P.K. Mehta, Cement Standards—Evolution and Trends, ASTM publication.
5. H.F. Gonnerman, et al., PCA Bulletin, 45, June 1953.
6. Y.V. Nikiforov and R.A. Zozolya, 9th ICCC, Vol. IV, pp. 64–68, New Delhi 1992.
7. P.H. Bates, Proc. Am. Soc. Test. Mater. 27, 324, (1927).
8. S.S. Rehsi and S.K. Garg, 9th ICCC, Vol. IV. pp. 684–690, New Delhi, 1992.
9. J. Rosa, Proc. Eight Conf. on Silicate Industry, 1965.
10. NCB Technical Report, SP-6-73, Utilization of High Magnesia Limestone in the Manufacture of Cement.
11. S. Chatterjee, Cem. Concr. Res. 5, 51 (1995).
12. H.F.W. Taylor, The Chemistry of Cements, Academic Press, New York, 1964.
13. M. Deng, et al., Cem. Concr. Res., 25, 440 (1995).