Pergamon

Cement and Concrete Research 29 (1999) 355–359

CEMENT AND CONCRETE RESEARCH

Influence of titania on the formation of tricalcium silicate

N.K. Katyal [a],*, R. Parkash [b], S.C. Ahluwalia [c], G. Samuel [a]

[a]National Council for Cement & Building Materials, 34 KM Stone NH2, Ballabgarh, 121004 Haryana, India
[b]Punjab University, Chandigarh, India
[c]OCL Ltd. New Delhi, India

Manuscript received 13 July 1998; accepted manuscript 18 November 1998

Abstract

The effect of titania on clinker formation has been studied by many researchers [1–5]. Its effect on the formation of pure tricalcium silicate phase and the formation of titanium compounds at 1450°C, has rarely been investigated. The present work relates to the investigation of the formation of titanium compounds in the C_3S-TiO_2, system and to find the polymorphic forms of C_3S. The study also attempts to establish the limit of incorporation of TiO_2 in C_3S at 1450°C, at different levels of TiO_2 in the concentration range of 0.5–6% of TiO_2. It is found that TiO_2 affects the polymorphic form differently at different concentrations. Up to 2% TiO_2, triclinic form, 4–5% TiO_2 monoclinic, and with 6% rhombohedral form is stabilized. TiO_2 is incorporated into C_3S up to 4.5% at 1450°C and beyond this limit a compound $CaOTiO_2$ is formed. Techniques used for the investigations are X-ray diffraction, optical microscopy (OM), scanning electron microscopy, with energy dispersive analysis of X-rays (EDAX) and chemical analysis. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Ca_3SiO_5; Clinker; Crystal structure; X-ray diffraction; SEM

Titania is generally present in small amounts (approximately 0.2–0.3%) in all portland cements, being derived from the clay or shale bearing TiO_2. The influence of moderate additions of titania to common portland cement raw mixes is considered that of a mineralizer. Decarbonation in raw mix is enhanced, assimilation and binding of lime is accelerated, crystallization of alite to unusually large individuals (up to 120 μm in size) is favored [6]. In small concentrations (0.5–1.0%), titania is favorable for clinkerisation. It also forms solid solutions with $3CaOSiO_2$ and $2CaOSiO_2$ [6]. In the system $CaOTiO_2$, there is formation of $CaOTiO_2$ and $3CaOTiO_2$, possessing hydraulic properties [2].

The presence of a small quantity ($<5\%$) of TiO_2 increases the hydraulic activity of cement [1] because of the distortion of the crystal lattice of belite and alite as a result of substitution of the Si^{4+} ion by the Ti^{4+} ion and formation of corresponding solid solutions [2].

Kuhl [7] found that in portland cement the substitution of silica by titania in small amounts slightly increased the strengths, but that in larger amounts a reduction in strength occurred. The optimum content was found to be 4.5%. He suggested that a compound $3CaOTiO_2$ is formed, and early workers on the system CaO-TiO_2 claimed to have prepared both $3CaOTiO_2$ and $2CaOTiO_2$. One other compound, $4CaO3TiO_2$, melting incongruently at 1755°C has also been reported [8], but its existence has not been confirmed [9].

Electron probe analysis of clinkers has shown that TiO_2 is present in small amounts, presumably in solid solution, in all of the four major compounds of portland cement [10]. Therefore, only any residual amount of titania is available to form the $3CaO2TiO_2$ (C_3T_2), $3CaOTiO_2$ (C_3T), or $CaOTiO_2$ (CT) solid solution [7].

The present work mainly concerns the investigation of the formation of titanium compounds in the system $3CaOSiO_2$-TiO_2 at 1450°C. Its effect on the clinkerisation, stabilization of various polymorphic forms, and the limit of incorporation in C_3S has also been studied.

1. Experimental

1.1. Preparation of specimens

Pure tricalcium silicate and its solid solutions with titania were made by repeated firings of calcium carbonate and quartz in the stoichiometric ratio of 3:1 in the presence of varying amounts of TiO_2 from 0.5–6% by weight at 1450°C. All the materials used were of analytical reagent grade. Calcium carbonate and quartz were ground to a fine powder and homogenized with TiO_2 in anhydrous acetone. The dried mass was pressed into pellets and fired at 1450°C for

---

* Corresponding author. Tel.: 91-129-246174; Fax: 91-129-242100; E-mail: nccbm@giasdl01.vsnl.net.in.

PII: S0008-8846(98)00231-2

Table 1
% TiO_2/C_3S content

	C_3S					
Specimen	Pure	0.5%	1%	2%	5%	6%
% C_3S	20	28	45	30	35	24

Table 2
Crystal size of C_3S/%TiO_2

		Crystal size of alite/C_3S (μm)			
Author	% TiO_2	Min	Max	Average	Specimen
This study	0.0	5	35	14.0	Tricalcium silicate
	0.5	8	50	20.0	
	1.0	10	80	32.0	
	2.0	5	40	16.0	
	5.0	2	25	10.0	
	6.0	2	30	12.0	
Kurdowski [14]	0.0	—	—	17.9	Clinker
	0.2	—	—	19.7	
	0.4	—	—	21.3	
Knofel [4]	0.0	5	50	20.0	Clinker
	1.5	10	100	40.0	

Table 4
% Free lime/% TiO_2

	C_3S					
Specimen	Pure	0.5%	1%	2%	4%	6%
% free lime						
After 3 h	4.5	3.82	2.38	2.95	3.5	3.96
After 6 h	1.98	1.21	0.90	1.25	1.60	1.90

Table 5
% Free lime in final products/% TiO_2

	C_3S						
Specimen	Pure	0.5%	1%	2%	4%	5%	6%
% free lime	0.05	0.04	0.06	0.08	0.10	0.98	1.52

3 h in a platinum dish in an electric furnace. The sintered pellets were ground to pass a 63-μm sieve and reformed into pellets and fired again at 1450°C for 3 h. Samples were cooled at room temperature (~27°C). This process was repeated till free lime reduced to <0.1% in the pure C_3S. The final products were examined using techniques of microscopy, chemical analysis, and X-ray diffraction (XRD).

1.2. Optical microscopy

The polished sections of the samples were etched with hydrofluoric acid (HF) and examined under a Zeiss polarising microscope (Carl Zeiss, Oberkochem, Germany) with ocular micrometer for qualitative and quantitative estimation of phases. Results are presented in Table 1 and Table 2.

1.3. Electron microscopy

Scanning electron microscope (SEM) and energy dispersive analysis of X-rays (EDAX) studies were carried out on a Philips SEM 515 with EDAX PV 9900 (EDAX International, Inc., Prairie View, IL, USA) for the microstructural and morphological features, limit of incorporation of TiO_2 into C_3S, and its distribution.

1.4. X-ray diffraction studies

Samples were powdered to pass a 45-μm sieve and examined using Rigaku Rad Max system (Rigaku International Co., Tokyo, Japan), with Co Kα radiations and wide angle horizontal goniometer and graphite monochromator. Results are presented in Table 3.

1.5. Chemical analysis

Free lime was estimated using ethylene glycol method [10]. Results are presented in Table 4 and Table 5.

1.6. Separation of titanium compounds

Maleic acid and methanol digestion method [11] was adopted to separate the titanium compounds formed. The nonsilicate residue left behind after the separation could not be digested with hydrochloric acid, hence it was solubilized by fusing with sodium carbonate at 1050°C for 20 min in a furnace. Subsequently it was treated with hydrochloric acid, evaporated to dryness in a beaker, and baked at 110°C to remove any SiO_2 present. Again, it was treated with concentrated hydrochloric acid and distilled water, heated to below boiling, filtered, and prepared up to 500 ml. Calcium was estimated in the solution by titrating with 0.01 M-EDTA, using Patton & Reeders reagent indicator at pH 12 [12]. TiO_2 was estimated by colorimetric method by complexing with hydrogen peroxide [13].

Table 3
Polymorphs of C_3S/% TiO_2

This study (1450°C)	Kondo [15] (1500°C)	VKM [18] (1500°C)	Knofel [16] (1550°C)	Maki [19](1600°C)
C_3S T_1	C_3S T_1	C_3S T_1	—	C_3S T_{11}
C_3S 1% T_1	—	C_3S 1% M_1	—	C_3S 1% M_1
C_3S 2% T_{11}	C_3S up to 1.75% T_{11}	C_3S 2% M_{11}	C_3S up to 3.50% T_1	—
C_3S 4–5% M_1	—	C_3S > 2% R	3.5–4.5% T_{11} above 4.5% M_1	—
C_3S 6% R				

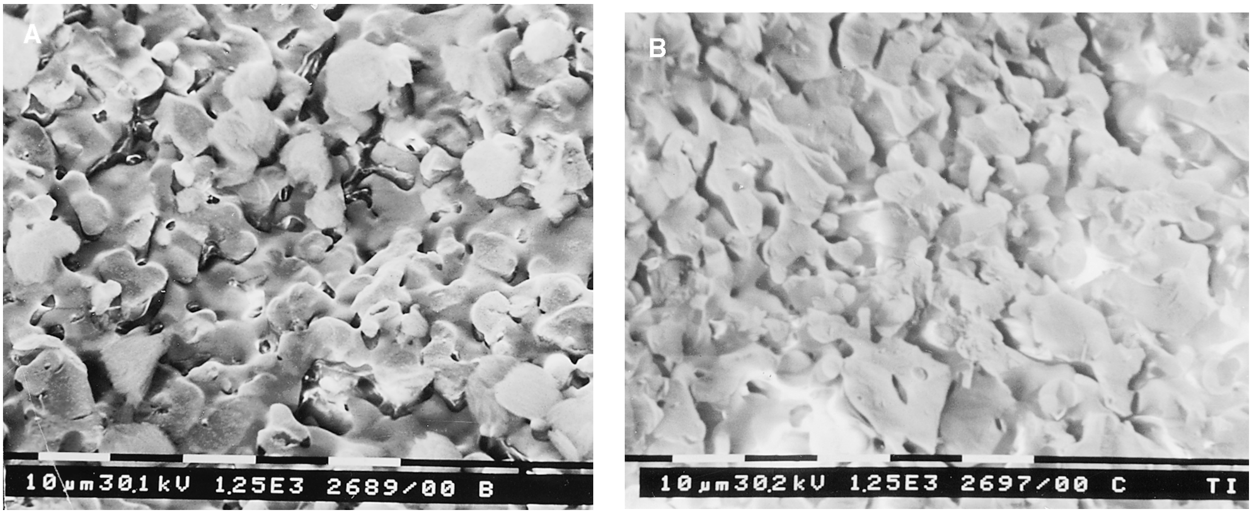

Fig. 1. Crystals of C_3S with varying percent of TiO_2: (*A*) 1%; (*B*) 2%.

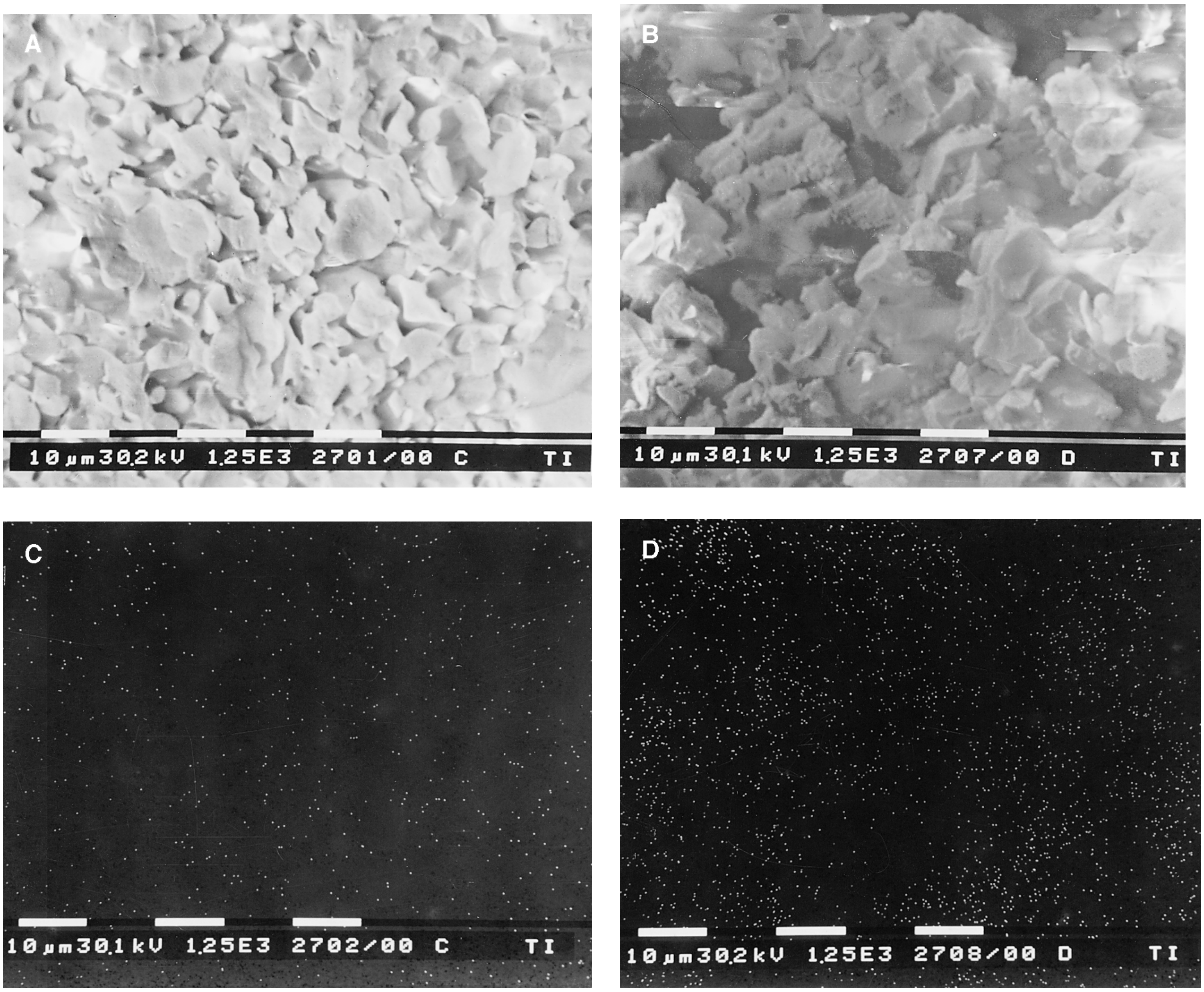

Fig. 2. (*A–D*) Distribution of TiO_2. C_3S with 4% TiO_2 (*A, C*); C_3S with 6% TiO_2 (*B, D*).

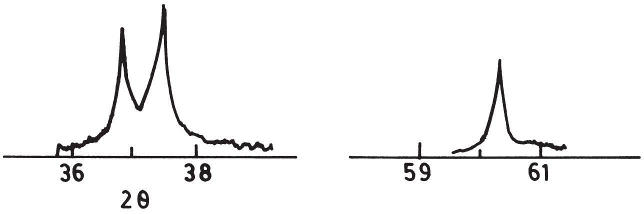

Fig. 3. C_3S (6% TiO_2), rhombohedral form.

2. Results and discussion

2.1. Optical microscopy

After first firing of the pure C_3S and TiO_2 doped specimens at 1450°C for 3 h, the quantitative estimation of the C_3S content was done by point count method. Results are given in Table 1. The crystal size of C_3S formed in the final products was also estimated with optical microscopy (OM). Results are presented in Table 2, along with data reported by other workers. Results prove that the crystal size is increased with the introduction of TiO_2 and is maximum when TiO_2 is 1%. Size begins diminishing with TiO_2 >1%.

2.2. Electron microscopy

The microstructural and morphological features of the tricalcium silicate samples doped with various concentrations of TiO_2 (0.5, 1, 2–6%) were analyzed under scanning electron microscope and EDAX including electron probe X-ray mapping to determine the distribution of Ti. Samples with 0.5% and 1% TiO_2 show well-formed larger size hexagonal C_3S crystals as compared to pure undoped C_3S phase. Specimens with higher content of TiO_2 show distorted crystals. Micrographs are presented in Fig. 1.

The elemental distribution for Ti X-ray mapping indicate an even distribution of Ti in the tricalcium silicate up to 4%. Beyond 4% it is mainly located in the interstitial. Micrographs are presented in Fig. 2. EDAX analysis showed C_3S to contain up to 4.5% TiO_2, indicating the limit of incorporation of TiO_2 to be 4.5% at 1450°C (average of six samples and five point analysis on each sample). Kondo and Yoshida [15] reported this limit to be 0.13 mole of $3CaOTiO_2$ (TiO_2 = 4.6% by weight) at 1500°C and 0.14 mole $3CaOTiO_2$ (TiO_2 = 4.9% by wt.) at 1600°C respectively. Knofel [16] reported the limit of incorporation of TiO_2 in C_3S to be 5 + 0.3% at 1500°C.

The formation of any titanium compounds could not be detected, probably because of the small amount of these compounds, although these compounds have been detected by XRD and chemical analysis. Knofel [16] detected $Ca_3Ti_2O_7$ (C_3T_2) in the sample of C_3S containing 6% TiO_2 fired at 1500°C for 12 h using electron beam microanalysis. In addition to C_3T_2, another compound having formula $14CaO5SiO_22TiO_2$ ($C_{14}S_5T_2$, calculated from its composition as analyzed by electron beam microanalysis) was also detected.

2.3. XRD analysis

There are basically seven polymorphic forms in which C_3S exists. TiO_2 if present in the lattice of C_3S leads to the formation of monoclinic or rhombohedral form of C_3S [17]. The various polymorphs with different concentrations of TiO_2 as detected by XRD are given in Table 3, in comparison to the findings of the other researchers. Fig. 3 shows the rhombohedral form of C_3S containing 6% TiO_2.

XRD studies of the specimens do not reveal any titanium compound up to 2% TiO_2. In the specimens containing 5 and 6% TiO_2, C_2S and calcium titanium oxide $CaOTiO_2$ have been identified. The two peaks obtained at $2\theta = 27.02$ (d = 3.824 Å) and $2\theta = 38.62$ (d = 2.701) (CoKα) show the presence of $CaOTiO_2$ (Fig. 4).

As the peaks representing $CaOTiO_2$ were not very sharp, it was difficult to ascertain the formation of the $CaOTiO_2$ phase. The sample containing 6% TiO_2 was digested with maleic acid and methanol [11] to remove all the silicate phases and free lime. The residue obtained was examined by XRD. The presence of $CaOTiO_2$ was confirmed (Fig. 5). Peaks representing $CaOTiO_2$ are 2θ = 27.02 (d = 3.824 Å), 2θ = 38.62 (d = 2.701 Å), 2θ = 45.740 (d = 2.303 Å) and 2θ = 47.64 (d = 2.217 Å).

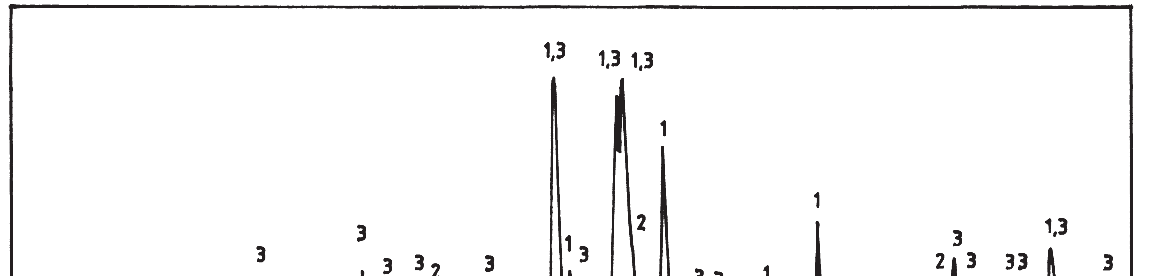

Fig. 4. XRD of C_3S with 6% TiO_2 (1 C_3S; 2 $CaOTiO_2$; 3 C_2S).

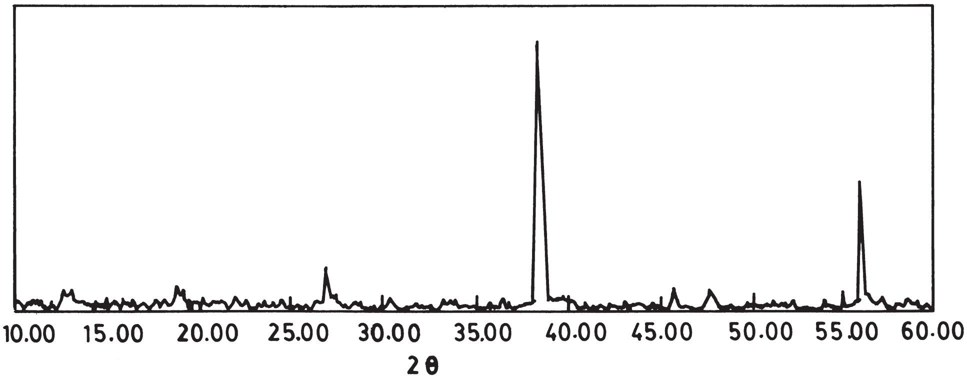

Fig. 5. XRD of chemically separated nonsilicate residue.

Knofel [4] studied the effect of TiO_2 on a laboratory clinker. TiO_2 in graduated quantities of up to 3.9% was mixed with the raw materials for this clinker. The specimens were burned at 1450°C. The XRD investigation of the fired specimens confirmed the decrease in alite with increasing TiO_2 content. Titanium phases [titanite (CaO-TiO_2SiO_2), pervoskite (CaOTiO_2), etc.] were not detected by X-ray examinations in any specimen.

2.4. Chemical analysis

Free lime content of the specimens fired repeatedly for 3 h at 1450°C (results of two firings) is as presented in Table 4. With up to 1% TiO_2 there is a decrease in the free lime and beyond this there is an increasing trend. Addition of 1% TiO_2 reduces the free lime in one firing to almost same level as obtained by two firings in the case of pure C_3S.

Free lime content in the final products (when % free lime in pure C_3S is reduced $<0.1\%$) is as reported in Table 5. The free lime content is found to be $<0.1\%$ when the amounts of TiO_2 were in the range of 0–4%. Presence of free lime is observed only when TiO_2 is 5.0%. This shows that TiO_2 is substituted for SiO_2 up to approximately 4–5%.

Knofel [16] reported that TiO_2 is substituted for SiO_2 up to approximately 4.5–5.0% in tricalcium silicate at 1550°C. Volkonskii et al. [2] reported that the maximum content of TiO_2 in tricalcium silicate in the form of solid solution may reach 2–3%. The nonincorporated TiO_2 combines with CaO to form the crystalline product CaOTiO_2.

CaO as determined by EDTA titration in the solution of the residue obtained by maleic acid-methanol treatment gave a value of 41.01%. TiO_2 in the same residue was found to be 58.43%. The molar ratio of CaO to TiO_2 from these results equals one, which confirms the presence of CaOTiO_2 compound.

3. Conclusions

Titanium dioxide has a positive effect on the formation of tricalcium silicate up to 1% only. Crystal size of C_3S is increased. Higher concentrations have a deleterious effect on its formation. C_3S up to 2% TiO_2 adopts triclinic form, 4–5% adopts monoclinic form, and 6% adopts rhombohedral form at 1450°C.

TiO_2 is incorporated in C_3S up to 4.5% at 1450°C. Beyond this limit, a compound CaOTiO_2 is formed at 1450°C.

Acknowledgments

The work reported here is a part of PhD work of one of the authors (N.K. Katyal), carried out at National Council for Cement & Building Materials. This paper is being published with the permission of Dr. S.P. Ghosh, Director General of the Council.

References

[1] I. Teoreanu, M. Muntean, H. Balusoiu, Il Cemento, 4 (1987) 397–404.
[2] B.V. Volkonskii, S.D. Makashev, N.P. Shtejert, Tsement 6 (1974) 17–19.
[3] I.L. Luginina, R.G. Nigmadilova, Int. Symp. Cem. Chem., Brasil, vol. 6, 1986, p. 510.
[4] Von D. Knofel, Siegen ZKG, 4 (1977) 191–196.
[5] M. Georgescu, A. Puri, Mater Constr (Bucharest) 12 (1982) 177–82.
[6] W. Eitel, Silicate Science, vol. V, Academic Press, New York, 1966, pp. 334–335.
[7] Kuhl, F.M. Lea, The Chemistry of Cement & Concrete, Edward Arnold Publishers, London, 1976, pp. 75–76.
[8] R.S. Roth, J. Res. Natn Bur Stand, 61 (1958) 437.
[9] J.A. Imlach, F.P. Glasser, Trans Br Ceram Soc 67 (1968) 581.
[10] Bureau of Indian Standards, 4032-1985 India.
[11] J.E. Mander, L.D. Adams, E.E. Larkin, Cem Concr Res 4 (1974) 533–544.
[12] A.I. Vogel, Quantitative Inorganic Analysis, 3rd edition, The English Language Book Society and Longman, London, 1971, p. 439.
[13] A.I. Vogel, Quantitative Inorganic Analysis, 3rd edition, The English Language Book Society and Longman, London, 1971, p. 788.
[14] W. Kurdowski, I-4 VI Int. Cong. on Chem. Cem., Moscow, 1974.
[15] R. Kondo, K. Yoshida, 5th Int. Symp. on the Chem. Cement, Tokyo, I-262, 1968, pp. 262–274.
[16] Von D. Knofel, Siegen ZKG, 1 (1979) 35–40.
[17] I. Maki, K. Kato, Cem Concr Res 12 (1982) 93–100.
[18] V.K. Mathur, R.K. Goswamy, K.M. Sharma, NCB Int. Seminar on Cem. & Building Mat., New Delhi, India, VIII-37, 1991.
[19] I. Maki, M. Hattori, Il Cemento 2 (1989) 131–140.