Pergamon

Cement and Concrete Research 32 (2002) 1125–1129

CEMENT AND CONCRETE RESEARCH

Influence of MgO on the formation of Ca_3SiO_5 and $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ minerals in alite–sulphoaluminate cement

Xiaocun Liu*, Yanjun Li, Ning Zhang

Department of Materials Science and Engineering, Jinan University, Jinan, Shandong 250022, People's Republic of China

Received 30 July 2001; received in revised form 25 January 2002

Abstract

The influence of MgO on the formation of Ca_3SiO_5 and $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ minerals in alite–sulphoaluminate cement is reported in this paper. The results show that adding a suitable amount of MgO can lower the clinkering temperature, promote the formation of Ca_3SiO_5 and $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ minerals, and help in the coexistence of the two minerals in the clinker. MgO may obviously decrease the formation of $Ca_3Al_2O_6$, and increase the SiO_2 content incorporated into the interstitial phase. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: MgO; Ca_3SiO_5; $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$; Alite–sulphoaluminate cement

1. Introduction

Alite–sulphoaluminate cement containing main minerals Ca_3SiO_5, Ca_2SiO_4, and $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ is the new, energy-conserving type and high-properties cement. The cement not only has the properties of Portland cement but also the properties of rapid hydration and hardening, higher early age strength and smaller volume shrinkage of hardening. Since 1978, many investigations have been reported on this cement [1–4].

The key to the production of alite–sulphoaluminate cement is that two minerals Ca_3SiO_5 and $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ can coexist in the clinker. For Portland cement clinker, investigators considered that MgO is beneficial to reactivity of raw meal, the initial temperature of producing liquid may be dropped in scores of degree. A suitable amount of MgO can decrease the viscosity of the liquid, increase the content of the liquid, accelerate the formation of Ca_3SiO_5, prevent the Ca_3SiO_5 mineral phase content decreasing and the hydration activity lowering caused by the combination with SO_4^{2-} and Al^{3+} in the clinker. The reports also indicated that SO_3 can decrease the pernicious effect of MgO when the content of MgO is higher [5–7]. However, for alite–sulphoaluminate cement containing higher amount of SO_3, the influence of MgO on the mineral formation of the cement clinker has not been reported. In this paper, the effect of MgO on the mineral formation of Ca_3SiO_5 and $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ in the clinker has been investigated by separating the phases in the clinker, X-ray diffraction (XRD), and IR analysis methods.

2. Experimental

Analytically pure chemicals such as $CaCO_3$, SiO_2, Al_2O_3, $CaSO_4{\cdot}2H_2O$, Fe_2O_3, $Mg(OH)_2$, and CaF_2 have been used as starting materials. The mineral composition of the test clinker has been chosen: Ca_3SiO_5 45%, Ca_2SiO_4 30%, $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ 15%, C_4AF 5%, $CaSO_4$ 5% (wt.%). This mineral composition corresponds to the following chemical composition: SiO_2 22.30%, Al_2O_3 8.57%, Fe_2O_3 1.64%, CaO 62.58%, SO_3 4.91% (wt.%).

The raw mixtures were prepared by mixing adequate quantities of pure chemicals with the addition of 0.25% CaF_2 and different contents MgO and grinding in a laboratory ball mill. The quantities of MgO added to the samples are shown in Table 1.

The raw mixtures ground were mixed with 8% water and pressed with pressure of 25 MPa into discs using a mould with the size of 30 mm in diameter and 8 mm in thickness.

---

* Corresponding author. Tel.: +86-531-2765305; fax: +86-531-7963127.

E-mail addresses: liu-xcsd@163.com, liu-xcsd@263.net (X. Liu).

PII: S0008-8846(02)00751-2

Table 1
MgO content in the clinker (wt.%)

Sample no.	1#	2#	3#	4#	5#	6#	7#	8#
MgO	0.0	0.5	1.0	2.0	3.0	5.0	8.0	12.0

The discs were burned to clinker in an electric furnace with silicon molybdenum bars heating elements at 1200, 1250, and 1300 °C, respectively for 60 min, then removed from the furnace at 1200 °C and cooled rapidly in air.

In order to investigate clinker formation at different temperatures, the content of free lime in the clinkers was determined chemically after dissolving with ethanol–glycerin. Mineral compositions of the clinker burned at 1300 °C for 60 min were analyzed by XRD (Cu, Kα, $\lambda = 0.154$ nm) and by microscope under reflecting light.

A residue rich in $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ phase was obtained by the dissolution of the silicate phase (Ca_3SiO_5 and Ca_2SiO_4) with salicylic acid and methanol, by the dissolution of the free lime and sulphate phase except the $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ with aqueous solution of ammonium chloride [8]. A residue rich in alite and belite was obtained by the dissolution of the interstitial phase ($3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$, C_4AF, and $CaSO_4$) with an aqueous solution of potassium hydroxide and sucrose in clinkers burned at 1300 °C for 60 min [9]. Two residues were analyzed by XRD and IR absorption spectrum, respectively.

In order to investigate the distribution of MgO in the clinkers, MgO in the silicate phase and in the interstitial phase and free MgO were dissolved by aqueous solution of 5% boric acid, ethanol–glycerin–ammonium nitrate solution, and acetic acid–methanol–ammonium chloride solution, respectively [10]. The content of MgO was determined by the chemical analysis method.

3. Results and discussion

3.1. The clinkering properties of the clinkers

Comparing the appearance of clinkers, it can be observed that the firing shrinkage of clinkers increases with an increase of MgO content and that the samples with MgO are more compact than the samples without MgO. This shows that a suitable amount of MgO can promote the clinkering process of the samples.

Free lime contents of clinkers burned at different temperatures are shown in Fig. 1. It can be seen that free lime content of the clinkers with MgO is lower than that without MgO burned at 1200, 1250, 1300 °C. When the MgO contents added range from 0.5% to 3.0%, free lime content decreases obviously. When MgO content is more than 5.0%, free lime content of the clinkers is still lower than 1# (without MgO). This is different from Portland cement. In alite–sulphoaluminate cement, lower free lime content of clinker with MgO may be attributed to the interaction of higher SO_3 and higher MgO [7].

3.2. Effect of MgO on the minerals formation

3.2.1. Effect of MgO on the formation of Ca_3SiO_5

The XRD patterns of the clinkers burned at 1300 °C are shown in Fig. 2. By XRD analysis, the main phases in the clinker are Ca_3SiO_5, Ca_2SiO_4 and $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$. When the MgO content is more than 3.0%, the periclase phase is formed in the clinkers. Comparing the intensity of XRD peaks of various samples, it can be seen that the intensity of diffraction peaks ($d = 0.303$, 0.261, 0.176 nm) of the Ca_3SiO_5 phase in Sample 1# (without MgO) is lower. This shows that the formation of Ca_3SiO_5 is smaller. If the addition of the MgO content is 0.5%, the formation of Ca_3SiO_5 increases substantially. When MgO contents range from 2.0% to 5.0%, the amount of Ca_3SiO_5 in the clinkers is larger. Even when MgO content reaches 8.0% or 12.0%, the content of Ca_3SiO_5 is still larger than Sample 1#. This demonstrates that MgO in the clinker can promote the formation of Ca_3SiO_5. Researches in the past have demonstrated that CaF_2 benefits the coexistence of Ca_3SiO_5 and $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$. In this paper, the studies demonstrate that the MgO also benefits the coexistence of Ca_3SiO_5 and $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$.

The XRD patterns of the residue rich in $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ phase and the residue rich in alite and belite obtained by the selective dissolution are shown in Fig. 3. It more clearly indicates the formation of the minerals in the clinker as the $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$-rich phase and the silicate-rich phase have been separated out. From Fig. 3, it can be seen that the intensity of diffraction peaks of Ca_3SiO_5 in the sample with MgO is higher than Sample 1#

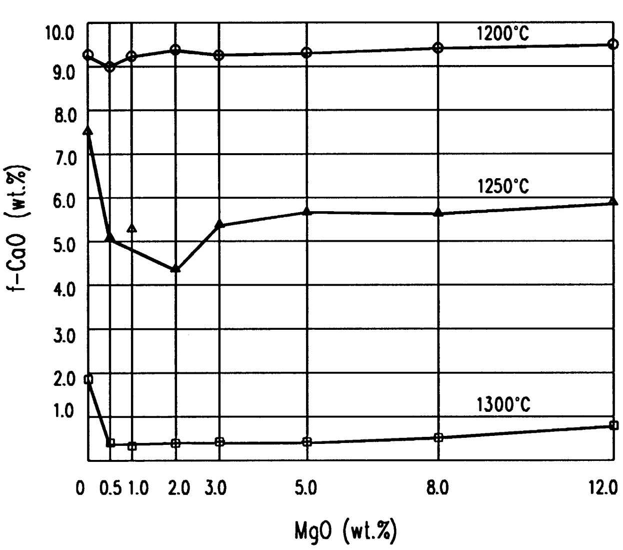


Fig. 1. Free lime content in clinkers as a function of MgO.

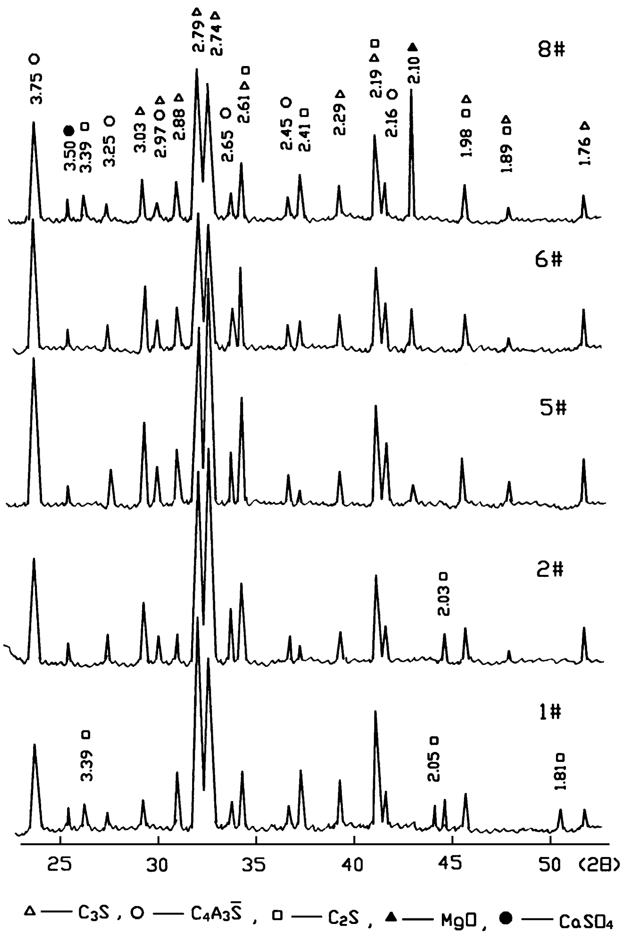


Fig. 2. XRD patterns of clinkers (burned at 1300 °C).

obviously. This is in line with Fig. 2. The results indicate that MgO can promote the formation of the Ca_3SiO_5 mineral and is beneficial to the coexistence of Ca_3SiO_5 and $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ in the clinker.

Chemical analysis results of the residue rich in $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ phase and the residue rich in silicate phase are shown in Table 2. Contents of MgO in the silicate phase and in the interstitial phase and periclase are shown Table 3. From the chemical composition of the residues and the distribution of MgO in Tables 2 and 3, it can be seen that MgO exists mainly in the interstitial phase and is smaller in the silicate phase. When the MgO contents are 3.0%, 5.0%, and 12.0%, respectively, its presence in the silicate phase is 0.49%, 0.51%, and 0.55%, respectively, showing little change in the MgO content; but the contents of MgO in the interstitial phase are 2.01%, 2.39%, and 3.27%, respectively, which show increase with the increase of MgO addition; the amounts of periclase are 0.49%, 2.14%, and 8.20%, respectively, which show increase with the increase of MgO addition.

By microscopic observation, Clinker 1# is less compact than the samples with MgO, the interstitial phase content is smaller, the inclusion is more, the alite crystals are 0.05–0.07 mm in size. The petrographic characteristic of the clinker is caused by containing more SO_3 content. The clinkers containing 1.0–5.0% MgO are more compact, the alite crystals are 0.04–0.05 mm in size, the interstitial phase content increases, and the inclusion content decreases. This shows that the MgO addition can improve alite crystal growth. In previous investigations on Portland cement clinker [5–7], the results indicated that presence of MgO can increase the content of the liquid phase at high temperatures, decrease the temperature of initial liquid phase and liquid viscosity, help the ion to move and the formation of Ca_3SiO_5 mineral. In the system, there is obviously a promoting effect on the formation of Ca_3SiO_5 thanks to the influence of MgO.

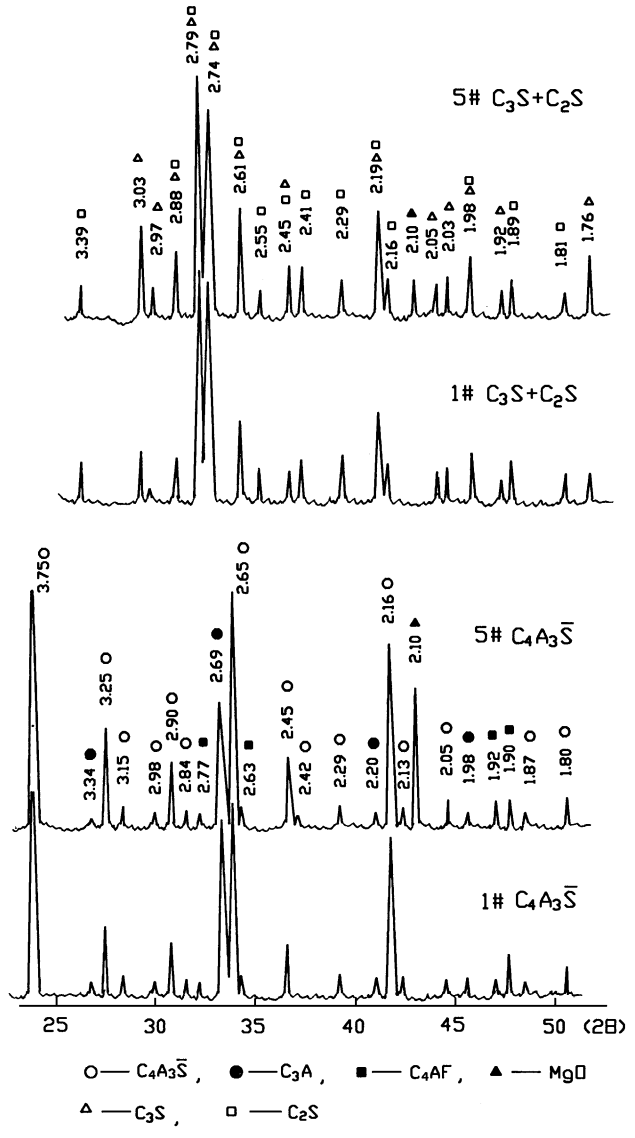


Fig. 3. XRD patterns of the residue rich in $C_4A_3\bar{S}$, and in silicate phase (burned at 1300 °C).

Table 2
Chemical composition of the residue rich in $3CaO·3Al_2O_3·CaSO_4$ phase and the residue rich in silicate phase (burned at 1300 °C)

	No.	Weight of the residues (g)	Chemical composition (wt.%)						Calculating mineral weight (g)
			SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	
The residue rich in silicate phase (9 g cement)	1#	6.2636	27.04	2.88	1.58	64.65	–	3.01	
	5#	6.4686	26.95	3.26	0.99	60.63	4.02	2.60	
	6#	6.6291	25.87	3.07	0.92	59.66	6.32	2.51	
	8#	6.9357	22.16	2.55	0.80	55.43	14.40	2.26	
The residue rich in $3CaO·3Al_2O_3·CaSO_4$ phase (10 g cement)	1#	1.1150	4.75	38.34	4.13	38.32	–	8.20	0.69
	5#	1.4636	7.26	33.98	5.31	33.95	11.67	7.42	0.83
	6#	1.6142	8.13	31.02	4.96	30.97	17.83	6.67	0.81
	8#	2.2109	11.27	20.49	3.72	19.18	39.72	3.93	0.66

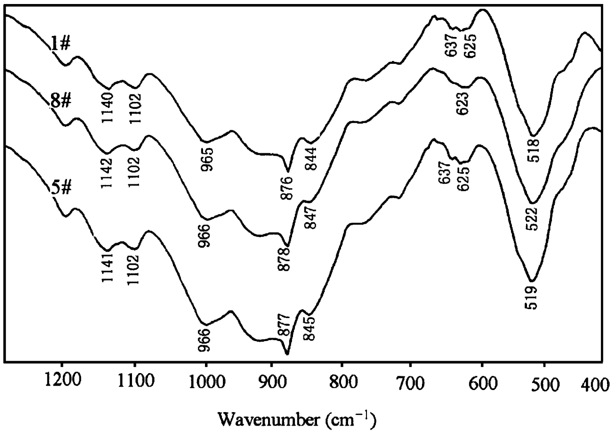
The IR absorption spectrum of the residue rich in alite and belite is shown in Fig. 4(a). From Fig. 4(a), it can be seen that the absorption bands (520, 845, 880, 994 cm^{-1}) of $[SiO_4]$ in the silicate phase of the sample with MgO shift to high wavenumber as compared with that of Sample 1#, and the shape of the absorption bands change a little. This is because some Mg^{2+} replaces Ca^{2+} causing an effect on the crystal structure of the silicate phase.

3.2.2. *Effect of MgO on formation of $3CaO·3Al_2O_3·CaSO_4$*

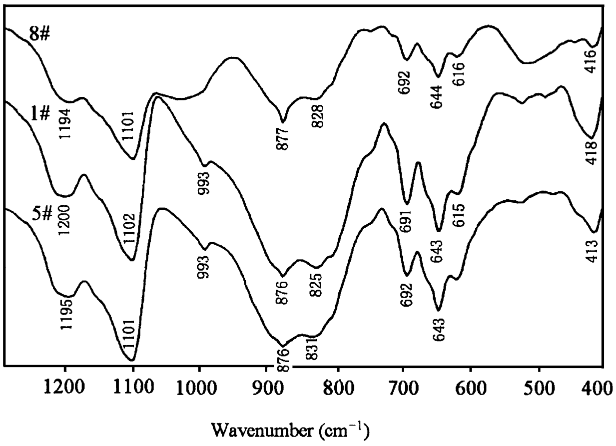
From XRD analysis in Fig. 2, it can be seen that the intensity of diffraction peaks of $3CaO·3Al_2O_3·CaSO_4$ in the samples with MgO is obviously higher than Sample 1#. This indicates that MgO can increase the formation of $3CaO·3Al_2O_3·CaSO_4$ mineral in the clinkers. The results are also demonstrated by the XRD patterns of the residue rich in $3CaO·3Al_2O_3·CaSO_4$ phase in Fig. 3. On the other hand, the content of $3CaO·3Al_2O_3·CaSO_4$ in Sample 5# calculated according to the content of SO_3 in chemical composition of the residue rich in $3CaO·3Al_2O_3·CaSO_4$ phase is higher than Sample 1#, but Sample 8# is lower than Sample 1#. From Fig. 3, it can be also seen that the intensity of diffraction peaks of $Ca_3Al_2O_6$ in Sample 1# is obviously higher than Samples 5# and 8#. This also indicates that MgO can promote the formation of $3CaO·3Al_2O_3·CaSO_4$ mineral in the clinkers. From the XRD analysis of the clinkers burned at 1200 and 1250 °C, it is also seen that the formation content of the $3CaO·3Al_2O_3·CaSO_4$ in the samples with MgO is more than Sample 1#. This is in agreement with the investigation results on the influence of MgO on the formation of $3CaO·3Al_2O_3·CaSO_4$ single-phase mineral [11]. In the

Table 3
Distribution of MgO in the clinkers (burned at 1300 °C)

	Content of adding MgO (wt.%)	Distribution of MgO in the clinkers (wt.%)		
		In silicate phase	In interstitial phase	Periclase
5#	3.0	0.49	2.01	0.49
6#	5.0	0.51	2.39	2.14
8#	12.0	0.55	3.27	8.20



(a) C_3S+C_2S



(b) $C_4A_3\bar{S}$

Fig. 4. IR absorption spectrum of the residue rich in $C_4A_3\bar{S}$ and in silicate phase.

formation process of $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$, the following equations are considered (Eqs. (1) and (2)):

$$CaO \cdot Al_2O_3 + 2CaO \rightarrow 3CaO \cdot Al_2O_3 \quad (1)$$

$$3(CaO \cdot Al_2O_3) + CaSO_4 \rightarrow 3CaO \cdot 3Al_2O_3 \cdot CaSO_4 \quad (2)$$

It can be considered that adding MgO can promote the formation of $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ at lower temperatures. When the addition of MgO content reaches 12%, the content of $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ formed in Sample 8# is a little less than Sample 1#. This is because the higher content of MgO in Sample 8# makes the relative content of $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ lower. From the IR absorption spectrum analysis of the residue rich in $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ phase in Fig. 4(b), it shows that MgO has an effect on the wavenumber and shape of the absorption bands (414, 616, 645, 692, 828, 879, 1100, 1193 cm^{-1}) of $[AlO_4]$ and $[SO_4]$ in the $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ phase. This indicates that some of Mg^{2+} goes into the crystal lattice of $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ and the lattice is distorted.

In addition, from the results of the chemical analysis for the residue rich in $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ phase, it can be seen that content of the SiO_2 in the residue increases with increase of MgO content. However, three minerals, $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$, C_4AF, and $Ca_3Al_2O_6$ are only determined in the XRD patterns (Fig. 3) of the residue rich in $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ phase, but there is no silicate phase in the XRD patterns. The results show that MgO can help SiO_2 incorporate into the interstitial phase in the clinkers. This is in agreement with the results of the Ref. [12].

4. Conclusions

1. A suitable amount of MgO (0.5–3.0%) may improve the burnability of alite–sulphoaluminate cement clinker, to lower the clinkering temperature.
2. MgO can promote the formation of Ca_3SiO_5 and $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$, and is beneficial to the coexistence of them in the clinker.
3. MgO can decrease the formation of $Ca_3Al_2O_6$ mineral and help SiO_2 to be incorporated into the interstitial phase.
4. When the content of MgO added range from 5.0% to 8.0%, there is still a beneficial effect for clinkering; this is attributed to the interaction of higher SO_3 and higher MgO in the system.

References

[1] I.V. Kravchenko, T.V. Kuzhecova, V.B. Khlusov, Alite–sulphoaluminate clinker and its cement, Cement (Russian) 8 (1978) 7–8.

[2] V.B. Khlusov, Manufacture and properties of alite–sulphoaluminate clinker, Int. Congr. Chem. Cem., 8th 2 (1987) 181–183 (in Chinese).

[3] T.V. Kuzhecova, N.G. Zealishvili, D.L. Mendeleeva, Manufacture and study of modified alite–sulphoaluminate clinker, Cement (Russian) 5–6 (1991) 39–43.

[4] X. Liu, Y. Li, H. Zhu, Manufacture of alite–sulphoaluminate clinker with fly ash, Cem. Lime (China) 2 (1993) 2–7.

[5] R. Bucchi, Influence of the nature and preparation of raw materials on the reactivity of raw mix, Int. Congr. Chem. Cem., 7th 1 (1980) 3–43.

[6] I. Maki, Relationship of processing parameters to clinker properties; influence of minor components, Int. Congr. Chem. Cem., 8th 1 (1986) 34–37.

[7] C. Schmitt-Henco, Magnesium oxide content of clinker, autoclave test and soundness, Int. Congr. Chem. Cem., 6th 1 (1976) 110–112.

[8] L. Shan, X. Li, A method of determining $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ content in clinker containing sulphate, Congr. Chem. Cem., 4th, Beijing, China 1 (1992) 662–666.

[9] W.A. Gutteridge, On the dissolution of interstitial phase in Portland cement, Cem. Concr. Res. 9 (1979) 319–324.

[10] China Building Materials Academy, Chemical Analysis of Cement, Chinese Building Industrial Press, Beijing, 1986, pp. 740–742.

[11] X. Liu, Y. Li, N. Chen, Influence of Cr_2O_3, MgO on the formation and hydration properties of $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$, J. Chin. Ceram. Soc. 26 (1998) 702–707.

[12] Y. Xi, Minor MgO and Cr_2O_3 in Portland cement, J. Chin. Ceram. Soc. 19 (1991) 305–311.