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Effect of MgO on the composition and properties of alite-sulphoaluminate cement

Xiaocun Liu*, Yanjun Li

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

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Abstract

The effect of MgO on the composition and properties of alite-sulphoaluminate cement clinker with commercial-grade raw materials such as limestone, clay, gypsum and fly ash as starting materials has been investigated in order to confirm results previously obtained with pure raw materials. The experiment results confirm that the addition of MgO at about 2–5% can improve the burnability of raw meal, promote the absorption of free lime and the formation of C_3S and $C_4A_3\bar{S}$. In addition, it is shown that this can also increase the strength development of the cement and shorten the setting time. When the content of MgO reaches about 8%, the strength of the cement decreases slightly and the setting time is extended.

Keywords: MgO; Alite-sulphoaluminate cement

1. Introduction

MgO exists in the clinker as minor component because of the natural materials containing some MgO. Different contents of MgO have different effect on the composition and properties of cement clinker. For Portland cement clinker, investigations considered when the content of MgO is less than 2.0–3.0%, is beneficial to the formation of clinker and the properties of cement. However, when the content of MgO is more than 3.0%, it can reduce the burnability of raw meal, increase the content of free lime in clinker and decrease the strength of cement. The higher content of MgO can impair the soundness of cement [1–5]. About the system containing MgO and SO_3 together, previous investigations considered a suitable amount of MgO can accelerate the formation of C_3S, decrease the unfavourable effects of SO_3 on the formation and hydration activity of C_3S. The reports also indicated that SO_3 can decrease the pernicious effect of MgO when content of MgO is higher [6,7]. In a previous paper [8], we studied alite-sulphoaluminate cements containing higher content of SO_3, and reported on the influence of MgO on the mineral formation of this type of cement clinker, when made from pure raw materials. In this paper, the work has been extended towards practical applications by the use of commercial-grade raw materials, and by the inclusion of cement paste tests.

2. Experimental

Natural raw materials such as limestone, clay, gypsum and fly ash from fuel electric plant, and the pure chemicals $Mg(OH)_2$ and CaF_2 were used as test materials. The compositions of the raw materials were determined by chemical analysis and are given in Table 1.

The raw mixture were prepared by mixing adequate quantities of raw materials (Table 1) with the additions of 0.25% CaF_2 and different contents of MgO and grinding in a laboratory ball mill to give a residue of ~5% (wt.%) on the 0.08-mm standard sieve. The practical chemical compositions of the clinker M1 are: SiO_2 21.69, Al_2O_3 8.33, Fe_2O_3 1.45, CaO 60.94, SO_3 4.86, MgO 1.20, TiO_2 0.21, K_2O

* Corresponding author. Tel.: +86 531 2765305; fax: +86 531 7963127.
E-mail address: liu-xcsd@163.com (X. Liu).

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Table 1
Chemical composition of raw materials (wt.%)

	Limestone	Clay	Fly ash	Gypsum
The origin	From Jinan	From Jinan	From Jining fuel electric plant	From Taian
The form	Calcite	Kaolinite	Powder	Fibrillar
L.O.I.	42.70	5.60	13.00	20.62
SiO_2	2.57	67.20	48.93	2.32
Al_2O_3	0.74	12.81	29.34	0.40
Fe_2O_3	0.16	4.39	3.36	0.10
CaO	52.64	3.59	1.83	31.88
MgO	0.75	1.67	0.81	–
K_2O	0.12	2.33	1.20	–
Na_2O	0.04	1.12	0.25	–
TiO_2	–	0.78	0.56	–
SO_3	0.06	0.20	0.32	44.76
Total	99.78	99.69	99.92	100.08

0.59, Na_2O 0.23 (wt.%). The chemical compositions correspond to the mineral compositions are: C_3S 44.4, C_2S 28.8, $C_4A_3\bar{S}$ 14.8, C_4AF 4.4, $CaSO_4$ 5.0 (wt.%). The content of MgO in the clinkers are shown in Table 2.

The ground raw mixtures were burned to clinker in an electric furnace with molybdenum disilicide bars at 1250 and 1300 °C, respectively, for 40 min, then removed from the furnace at 1200 °C and cooled rapidly in air.

In order to investigate the degree of clinker phase formation at different temperatures, the content of free lime was determined chemically after dissolving in ethanol–glycerin. The mineral composition of the clinker was analyzed by XRD and by microscope under reflecting light.

The cement was made by mixing 95% clinker (burned at 1300 °C) and 5% gypsum, and grinding in a laboratory ball mill to a specific surface area of ~320 m^2/kg (Blaine).

Compressive strengths were tested on 2-cm cubes prepared from cement paste with a water/cement ratio of 0.30 at 3, 7 and 28 days after 24-h curing in moist air and subsequently in water at 20 °C. The setting time was tested on paste with a constant water/cement ratio of 0.30 using a cylindrical mould of 4-cm diameter and 4-cm height. Hydration products and the hydration behaviors of the cement were investigated by TG–DTA tests. The hydration was stopped by ethanol.

3. Results and discussion

3.1. The clinkering properties

Comparing the appearance of the clinkers, it can be observed that the clinkers become more compact and volume shrinkage is aggravated with the increase of MgO content. This shows that a suitable amount of MgO can promote the clinkering process.

Free lime content of the clinkers burned at different temperatures is given in Table 2. It can be seen that the addition of MgO at a proper amount can promote the absorption of free lime in the clinkers especially at 1250 °C. When containing MgO, content of the clinkers is in a range from 2.0% to 3.0%, free lime content decreases obviously. This is attributed to better fluxing effect of MgO, because a suitable amount of MgO can decrease the viscosity of the liquid phase and increase the content of the liquid phase and accelerate the formation of C_3S [3,4]. From Table 2, it can be also seen that free lime content of clinkers M5 and M6 with 5.0–8.0% MgO is still lower than clinker M1. This is different from Portland cement. Previous investigations considered that higher content of MgO or SO_3 has unfavourable effect for the clinkering and the properties of Portland cement clinker. However, the interaction of MgO and SO_3 can decrease the unfavourable effect [6,7]. In alite-sulphoaluminate clinker, lower free lime content of the clinkers may be attributed to the interaction of higher SO_3 and higher MgO.

3.2. The mineral formation

XRD analyses of the clinkers burned at 1300 °C gave results similar to those obtained with pure raw materials

Table 2
Properties of the clinkers

Sample no.		M1	M2	M3	M4	M5	M6
MgO (wt.%)		1.2	2.0	2.5	3.0	5.0	8.0
f-CaO (wt.%)	1250 °C	3.98	3.22	2.89	2.91	3.01	3.40
	1300 °C	0.68	0.53	0.40	0.46	0.49	0.55
Cement made from 1300 °C clinker, paste tests at w/c=0.30							
Compressive strength (MPa)	3d	71.3	72.8	73.9	74.1	72.3	68.5
	7d	82.6	86.7	88.4	89.3	84.7	82.2
	28d	107.9	111.5	117.2	119.5	110.8	106.3
Setting time (min)	initial set	79	70	68	69	77	87
	final set	130	118	112	117	135	145
TG analysis of cement pastes after 3 days moist curing at 20 °C							
Weight loss, %	at ~116 °C	8.56	–	–	9.66	9.23	8.24
	at ~460 °C	2.23	–	–	3.18	2.29	1.86

[8].The amounts of C_3S and $C_4A_3\bar{S}$ in the clinker M1 are less than in the clinkers M4 and M5 containing higher content MgO, and a little more than in the clinker M6 with 8.0% MgO. By microscope observation, clinker M1 is looser, the interstitial phase content is smaller, the size of alite crystal is larger and the inclusion content is more. But the clinkers containing 2.0–5.0% MgO are more compact, the size of alite decreases, interstitial phase content increases and inclusion content decreases. The results indicate that a suitable amount of MgO can promote the formation of C_3S and $C_4A_3\bar{S}$. However, when the MgO content is too high, the content of C_3S and $C_4A_3\bar{S}$ in the clinkers decreases. This may be because the viscosity of the liquid phase increases [3,4,8]. The higher content of MgO in clinker M6 should also make the relative content of the C_3S and $C_4A_3\bar{S}$ lower, assuming that MgO does not enter significantly into these phases.

3.3. The physical and mechanical properties

The strength development of the cement pastes is shown in Table 2. It can be seen that the strength of cements containing 2.0–5.0% MgO is higher than cement M1 at various hydration ages, and the strength of cement M6 containing 8.0% MgO is a little lower than cement M1. The TG–DTA data of the cement after 3 days hydration are given in Table 2. The weight losses at about 116 and 460 °C can be attributable to dehydration of ettringite and $Ca(OH)_2$ in samples. The results demonstrate that the cements containing 2.0–5.0% MgO contain more bound water than cement M1. This is in consistent with the higher content of the main minerals C_3S and $C_4A_3\bar{S}$ in these clinkers. From the analyses above, it can be concluded that a suitable amount of MgO can increase the strength development of the cement. For the cement M6, decrease of the strength is attributed to the decrease of the minerals C_3S and $C_4A_3\bar{S}$ content in the clinker. Besides, considering the soundness of the cement, the content of MgO in the clinkers must be limited. The setting behavior of the cements is also given in Table 2. It can be seen that a suitable amount of MgO can shorten the setting time. When the content of MgO reaches 8.0%, the setting time of the cement is extended. This corresponds to the change in the phase composition of the clinker.

4. Conclusions

Our results confirm that commercial-grade raw materials behave similarly to pure raw materials, i.e. that:

1. A suitable amount of MgO (2–5%) can improve the burnability of raw meal, promote the absorption of free lime and the formation of C_3S and $C_4A_3\bar{S}$.
2. When the content of MgO in the clinker is in a range from 2.0% to 5.0%, the strengths development of the cement is improved and the setting time is shortened. If the MgO content reaches about 8.0%, strength of the cement decreases slightly and the setting time is extended.
3. A higher content of MgO can be permitted in alite-sulphoaluminate clinker than in OPC clinkers.

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