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COMMUNICATIONS

THE EFFECT OF AUTOCLAVE TEMPERATURE ON THE EXPANSION AND HYDROTHERMAL PRODUCTS OF HIGH-MgO BLENDED CEMENTS

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ABSTRACT

The relations between the expansion and autoclave products for high MgO blended cements are presented. The results show that restraining actions of silica materials on MgO expansion are increased with the order as follows, slag < fly ash < quartz. The autoclave expansion at 10 MPa is less than at 2 MPa when additions of fly ash or quartz are beyond a suitable amount. It is also established that not only the formation and quantities of tobermorite phase but that of xonotlite phase play an important action in the stabilization of high-MgO blended cements by silica materials © *1998 Elsevier Science Ltd*

Introduction

Unsoundness due to high MgO is ascribed to the volume expansion undergone by the cement during MgO hydration to form $Mg(OH)_2$. Rosa (1) first proposed that the excessive autoclave expansion aroused by as much as 15% MgO can be controlled by the addition of suitable quantities of silica materials. The stable mechanisms of silica materials on high-MgO Portland cement have been proposed by many researchers (2–5), which are mainly attributed to four aspects: 1) excess MgO is chemically combined in hydrated silicates both by Mg^{2+} entering the 1.1-nm tobermorite structure and by formation of chrysotile; 2) diluting action by substituting silica materials for high-MgO cement; 3) sealing action, the abundance of gel-like calcium silicate hydrates formed provide a protective coating on anhydrous clinker grains thereby resisting hydration of MgO; and 4) perhaps the most important, A.J. Majumadr et al. (3) suggested that the nature of calcium silicate hydrate or its amount or both may be important because the extra strength of cementitious matrix based on tobermorite formation is sufficient to accommodate the expansion forces.

Nearly all investigations on the stabilization of high MgO by silica materials were carried out under the autoclave condition of the ASTM test (2 MPa and 3 h). It is well known the autoclave products are varied with the temperature and run time. In this paper, the relations

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TABLE 1
Chemical composition of raw materials.

	Loss	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	F-CaO
Cement clinker	0.32	20.67	5.27	5.87	64.74	1.44	0.90
Fly ash	3.51	59.04	4.37	20.25	5.83	2.13	
Quartz		>99.0					
Blastfurnace slag		38.06	0.77	9.36	40.77	8.79	

between the expansion and autoclave products resulted from temperature variations are presented.

Experimental

The high-MgO cement used in this test was prepared by mixing hard-burned magnesia with Portand cement. The method of preparation enabled cements with silica admixtures to contain the same amount of MgO and therefore to be subjected to the same "expansive force." Fly ash, quartz, and slag are chosen as silica materials, whose chemical compositions are listed in Table 1.

MgO/admixture ratios in blended cements are 1:1, 1:3, and 1:6. Additions of MgO are 5% and 10%. Table 2 lists the proportion of high-MgO blended cements. Autoclave temperature is at 217°C for 3 h and at 300°C for 10 h, correspond to saturated water vapor pressure 2 MPa and 10 MPa.

The specific surface area of all samples is 350+ 10 kg/m^2 and the fineness of MgO added is controlled through a 0.08-mm mesh. The autoclave expansion of samples was determined and the size of specimens is 20 × 20 × 80 mm.

The autoclave products are detected by x-ray powder diffraction analysis.

TABLE 2
Proportion of high-MgO blended cements.

MgO/admixture ratios	Proportion (Wt.%)		
	MgO	admixture	Portland cement
1:1	5	5	90
	10	10	80
1:3	5	15	80
	10	30	60
1:6	5	30	65
	10	60	30
1:9	5	45	50
	10	90	0

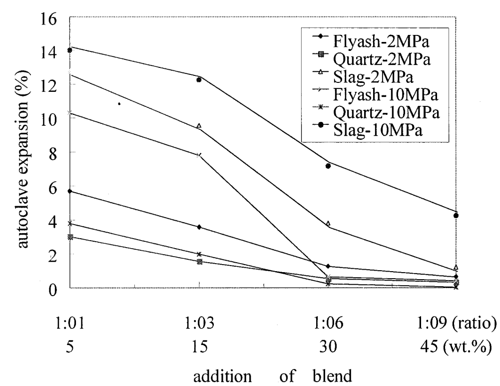

FIG. 1.
Autoclave expansion vs. blended additions (5% MgO).

Results

Autoclave expansion

5% MgO. Autoclave expansion under different saturated steam pressures as a function of admixture is given in Figures 1 and 2. Figure 1 lists the results of tests containing 5% MgO. For all the samples of blended cements, there is a same downward tendency in the autoclave expansion with the increase of admixtures. Restraining actions of silica materials on MgO expansion are increased with the order as follows, slag < fly ash < quartz, whatever the temperature of test or the amount of silica materials addition. The following conditions must be satisfied for blended cements to pass the ASTM limit of 0.8% expansion: adding more than 30% quartz or 45% fly ash at 2 MPa and adding more than 30% quartz or fly ash at 10 MPa. The expansion of slag samples is far from the ASTM limit of 0.8% when slag addition did not go beyond 45%.

It is also observed for the samples of quartz and fly ash additions that there are the

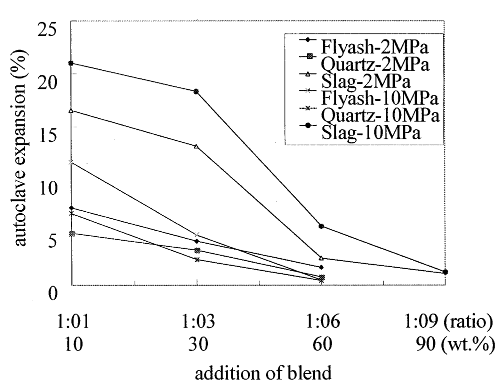

FIG. 2.
Autoclave expansion vs. blended additions (10% MgO).

TABLE 3
Hydrothermal products of fly ash-blended samples.

MgO	MgO/Add. ratio	Pressures (MPa)	Hydrothermal products					
			Tob	MH	$C_2SH(A)$	$C_2SH(C)$	Hydrogarnet	Xo
5	1:6	2	+++	+	++		++	
10	1:1	2	+	++	+++		++	
10	1:3	2	+++	++	++		++	
10	1:6	2	+++	++	++		++	
5	1:6	10				+	++	++
10	1:1	10		++		+++	++	
10	1:3	10	+	+		++	+	+
10	1:6	10	++	+		+		++

Abbreviations: Tob, tobermorite; MH, $Mg(OH)_2$; Xo, xonotlite; +++, quite a few; ++, moderate; +, few.

crosspoints in the Fig. 1 in which the curves of expansion at 2 MPa and 10 MPa are intersected each other. The expansion at 2 MPa is less than at 10 MPa when blended additions are less than the amount at the crosspoint, for example, 23% for quartz sample and 28% for the fly ash sample. Otherwise, the expansion at 10 MPa becomes less than at 2 MPa. It is different that the crosspoint for slag samples did not occur.

10% MgO. From Figure 2, the results of autoclave expansion containing 10% MgO samples are similar to that of 5% MgO in the tendency. The crosspoints lie in 25% for quartz samples and in 35% for fly ash samples. Generally, the expansion values for 10% MgO are larger than for 5% MgO at the same addition of blended materials. For quartz samples to pass the ASTM limit, more than 60% quartz must be added. For fly ash samples, only the case can pass the limit, adding more than 60% fly ash and at 10 MPa simultaneously. The autoclave expansion is greatly improved when slag additions are over 90%, for example, the autoclave value 1.04% at 2 MPa approximate to the ASTM limit.

Hydrothermal products

Hydrothermal products of fly ash blended samples are listed in Table 4. The products of samples containing 5% MgO and more than 30% fly ash at 2 MPa are mainly tobermorite, $C_2SH(A)$, a few of brucite ($Mg(OH)_2$), and hydrogarnet. Tobermorite is changed into xonotlite and brucite disappears when the autoclave pressure is increased to 10 MPa. For 10% MgO samples, tobermorite phases are more and more dominant with the increase of fly ash accompanied with the increase of brucite phases when at 2 MPa; moderate amounts of xonotlite phases coexist with tobermorite, $C_2SH(A)$ phases were substituted by $C_2SH(C)$, and brucite phases decreased with the increase of fly ash additions when at 10 MPa.

As shown in Table 5, autoclave products of quartz-blended samples at 2 MPa are characteristic of xonotlite coexisting with tobermorite. There are some differences in the products at 10 MPa; xonotlite phases are dominant accompanied with the disappearance of tobermorite phases; brucite phases are decreased with the increase of quartz additions, which vanish when additions are more than 60%.

TABLE 4
Hydrothermal products of quartz-blended samples.

MgO	MgO/Add. ratio	Pressures (MPa)	Hydrothermal products					
			Tob	MH	$C_2SH(A)$	$C_2SH(C)$	Hydrogarnet	Xo
5	1:6	2	++				+	+
10	1:1	2		++	+++		+	
10	1:3	2	+++	++			+	+
10	1:6	2	+++	+			+	++
5	1:6	10						+++
10	1:1	10		++		+++	++	
10	1:3	10		+			+	++
10	1:6	10					+	+++

Abbreviations: Tob, tobermorite; MH, $Mg(OH)_2$; Xo, xonotlite; +++, quite a few; ++, moderate; +, few.

The autoclave products of slag-blended samples are quite different from both fly ash- and quartz-blended samples whatever the autoclave pressures of test are. Brucite phases and $C_2SH(A)$ are main products at 2 MPa. $C_2SH(C)$ phases are substituted for $C_2SH(A)$, at the same time, brucite exists in large quantities at 10 MPa. It is noticed that tobermorite phase is not formed until slag additions are more than 90% following in the train of brucite decrease.

Discussion

There are close relations between the autoclave expansion and hydrothermal products. According to the above results, two factors play an important action in the stabilization of high-MgO blended cements by silica materials. The first is both formation and quantities of tobermorite phase. A.J. Majumdar et al. suggested that the development of high strength in the autoclave mixtures is consequent upon the formation of tobermorite phase, and that the extra strength produced from the formation of tobermorite is perhaps sufficient to accommodate the expansive forces resulted from the $Mg(OH)_2$. Our results show that the expansion is decreased with the increase of silica materials corresponding to the formation of tobermorite. For quartz-blended samples containing 5% MgO, the autoclave expansion can pass

TABLE 5
Hydrothermal products of slag-blended samples.

MgO	MgO/Add. ratio	Pressures (MPa)	Hydrothermal products				
			Tob	MH	$C_2SH(A)$	$C_2SH(C)$	Hydrogarnet
5	1:6	2		+	+++		++
5	1:6	10		+		+++	++
10	1:6	10		+++		+++	++
10	1:9	2	+++	++	++		++

Abbreviations: Tob, tobermorite; MH, $Mg(OH)_2$; +++, quite a few; ++, moderate; +, few.

ASTM limit when quartz additions get up to 30%. However, there exist quite a few $Mg(OH)_2$ in the samples containing 10% MgO so that a large amount of tobermorite products do not absorb all the expansive forces from the $Mg(OH)_2$. Therefore, we suggest that there exists a dynamic balance between the strength of cement matrix and expansive force.

Both the formation and quantities of xonotlite phase is the second factor in the stabilization of high-MgO blended cements. It has been established (6–7) that the amount of Mg^{2+} that enters the tobermorite structure is rather small. Our results (8) showed that only less than 4% MgO may corporate into tobermorite lattice, but that the corporation in xonotlite phase can be as high as 14–15% MgO. Therefore, it is considered that the coexistence of tobermorite with xonotlite can improve the soundness of high-MgO cements, such as 10% MgO sample adding 60% quartz at 2 MPa; Moreover, the stabilization of high-MgO blended cements at 10 MPa is attributed to the formation of xonotlite phases. The more the additions of silica materials, the more the xonotlite phase. As above described, brucite phase is decreased with the increase of quartz addition at 10 MPa, which vanished when adding more than 60%, although there exists 10% MgO in quartz-blended samples. It may be related with the formation of xonotlite phase and with combining Mg^{2+} into xonotlite phase. No doubt, it is the formation of xonotlite that makes quartz-blended samples containing 10% MgO pass the ASTM limit when at 10 MPa and additions more than 60%.

Conclusion

1) The restraining actions of silica materials on MgO expansion are increased with the order as follows, slag $<$ fly ash $<$ quartz. The autoclave expansion for high-MgO blended cements at 10 MPa is less than at 2 MPa when a suitable amount of fly ash or quartz is added.
2) Both formation and quantities of tobermorite phase play an important action in the stabilization of high-MgO blended cements by silica materials. Meanwhile, there exists a dynamic balance between the strength of cement matrix and expansive force.
3) Both the formation and quantities of xonotlite phase greatly improve the stabilization of high-MgO blended cements when at higher autoclave pressure.

Acknowledgments

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