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Improvement on sulfate resistance of blended cement with high alumina slag

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ABSTRACT

This paper is focused on the effect of limestone and calcium sulfate content on sulfate resistance of ground granulated blast furnace slag (GGBS) blended cement. Sulfate resistance was evaluated using ASTM C 1012, and a variety of mechanisms of the sulfate resistance of GGBS blended cement were revealed by the analyses of hydration products and sulfate ion ingress. Although GGBS suppresses sulfate ion ingress, it is probable that alumina in GGBS tends to form ettringite with externally supplied sulfate ions. Addition of limestone and increase in calcium sulfate content allow both monocarboaluminate and ettringite to form prior to immersion in sulfate solution. These hydration products remain in the hardened cement matrix and act to suppress further formation of ettringite with external sulfate ions during immersion in sulfate solution. GGBS blended cement with a suitable amount of limestone powder and a controlled content of calcium sulfate exhibits markedly long term sulfate resistance.

1. Introduction

Ground granulated blast furnace slag (GGBS) is a material that can have beneficial effects on concrete. Blending GGBS with Portland cement provides higher fluidity, reduced heat of hydration, decreased water permeability, higher resistance to chloride penetration, mitigation of ASR, and improved chemical resistance as a result of densification due to secondary hydration reactions, together with reduced environmental impact of CO_2 emissions. However, blending GGBS with Portland cement decreases strength development at early age, may decrease carbonation resistance, and increases hydration heat when the GGBS content in blended cement is low or GGBS is activated at elevated temperatures [1–3]. Regarding sulfate resistance, the effect depends on the composition of the GGBS.

It is well known that sulfate resistance is highly influenced by the alumina content of the GGBS used. In 1966, Locher [4] reported sulfate resistance using two types of GGBS with different alumina contents and three Portland cements with different C_3A contents. The results showed that sulfate resistance increased when alumina content of GGBS was 11%, irrespective of the C_3A content of Portland cement, but was adversely affected when high-alumina (17.7%) GGBS was blended at ratios between 20 and 50%. The effect of slag alumina content on sulfate resistance has been studied [1, 5–7], where alumina content of GGBS, replacement level of GGBS in blended cement, and C_3A content of clinker were found to be important factors in determining sulfate resistance. The alumina content of GGBS depends on the type of pig iron plant and the raw materials used. GGBS generated at plants of Japanese steel companies has a stable alumina content of about 15% and is supplied in an enormous quantity for use in Asian countries. Even in the case of using high-alumina GGBS, increasing GGBS content in blended cement to 70% can improve sulfate resistance [5], although other performance such as early strength development and carbonation prevention are degraded. Therefore, it would be very useful if the sulfate resistance of slag blended cement using high-alumina GGBS with moderate levels of cement replacement could be enhanced.

Several approaches to increasing the sulfate resistance of GGBS blended cement have been reported, including the addition of extra materials such as calcium sulfate and limestone powder to control the hydration process of blended cement. Regarding the effect of calcium sulfate, there were studies, including that by Takemoto et al.[6] in 1958 which reported that sulfate attack was significant at lower calcium sulfate contents of GGBS blended cement. In 1996, Gollop et al.[8] found that high resistance of a blend containing 65% of slag was obtained when 5% of gypsum was added above that supplied by the Portland cement. This was attributed in his report to the retention of ettringite which was formed during the early stages of hydration before sulfate attack begun. As for the effect of limestone powder, Chatterji [9] in 1968 suggested that addition of finely ground $CaCO_3$ to Portland cement should result in lower sulfate expansion on subsequent exposure to sulfate solutions because of formation of monocarboaluminate. Recently, Irassar [10] reviewed sulfate resistance where limestone was used as a constituent of cement. The paper concluded that the sulfate resistance of Portland cement with the limestone filler showed a clear dependence on the C_3A content of the parent cement, and that dilution of C_3A

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content or changes in hydration products of the alumina phases did not cause significant changes in long time sulfate performance. However, the sulfate resistance of the slag blended cement with additional limestone filler was uncertain. The hydration products in slag blended cement with limestone filler were investigated by Hoshino et al.[11]. Their results showed that the production of monosulfate increased when slag was blended, and that more carboaluminates were produced when limestone filler was added to the slag blended cement.

These reports suggest that extra addition of limestone filler and calcium sulfate reduces transformation of monosulfate to ettringite by reaction with external sulfate ions, and has the possibility of increasing the sulfate resistance of slag blended cement using high-alumina GGBS even at moderate replacement ratios, along with lower carbonation and improved early strength development.

This paper focused on the effects of limestone and calcium sulfate contents on the sulfate resistance of GGBS blended cement. The sulfate resistance was evaluated by measuring sulfate expansion which represented the formation of expansive ettringite and gypsum.

The reaction formulas of external sulfate attack used in this study were as follows:

$$C_3A + 2Ca^{2+} + 2SO_4{}^{2-} + 26H_2O \rightarrow C_6A\overline{S}_3H_{32} \quad (1)$$

$$2C_3A + C_6A\overline{S}_3H_{32} + 4H_2O \rightarrow C_4A\overline{S}H_{12} \quad (2)$$

$$C_4A\overline{S}H_{12} + 2Ca^{2+} + 2SO_4{}^{2-} + 20H_2O \rightarrow C_6A\overline{S}_3H_{32} \quad (3)$$

$$C_3A + 0.5CaCO_3 + 0.5Ca(OH)_2 + 12H_2O \rightarrow C_4A\overline{C}_{0.5}H_{12} \quad (4)$$

Ettringite ($C_6A\overline{S}_3H_{32}$) forms in the cement matrix from the result of reaction between the C_3A in Portland cement and the internal sulfate ions from gypsum, as expressed in formula (1). The next step is shown in formula (2) where remaining C_3A reacts with ettringite to form monosulfate ($C_4A\overline{S}H_{12}$). When sulfate ions are supplied from external sources outside the cement matrix, ettringite is formed as expressed in formula (3) from the result of reaction between the monosulfate and the external sulfate ions, causing the cement to expand. Calcium ions required in this reaction are supplied from $Ca(OH)_2$ (portlandite) which are produced by the hydration of C_3S and C_2S in the cement matrix. In the case of presence of limestone filler in the cement, carbonate hydrates are formed with the consumption of CH [11] as shown in formula (4).

The current experiment was conducted to verify the difference in sulfate resistance due to the alumina content of GGBS, as well as to investigate the effects of addition of limestone powder and control of calcium sulfate content in using high-alumina GGBS. The mechanisms of the increase in sulfate resistance due to the complex effects of limestone powder and calcium sulfate are discussed based on the experimental results.

2. Materials and methods

2.1. Materials

The blended cements evaluated in this study were prepared by mixing Portland cement, GGBS, limestone powder, and calcium sulfate. The chemical compositions of these materials are shown in Table 1. Two types of Portland cement complying with ASTM C 150 were used in this study: Type V (sulfate resistant) with a C_3A content of 4.9%; and ordinary Portland cement (OPC) with a C_3A content of 8.7%. Table 2 shows the values by the Bogue equations. GGBSs were of the following two types: high-alumina type (SL); and low-alumina type (*low*SL). SL was a Japanese commercial GGBS and contained 15.2% of alumina, and *low*SL was a North American commercial one containing 10.7% alumina. Limestone powder was prepared by grinding Japanese limestone that was composed of calcite. Anhydrite or gypsum was added for the control of calcium sulfate content in the blended cements.

Table 1
Chemical composition and Blaine surface area of materials.

	TypeV	OPC	SL	*low*SL	Limestone filler	Anhydrite	Gypsum
Surface area (cm^2/g)	3750	3280	4460	4480	8450	4140	6610
Chemical composition(%)							
SiO_2	21.2	21.9	34.3	35.0	0.3	0.5	1.7
Al_2O_3	4.4	5.2	15.2	10.7	0.1	0.2	0.8
Fe_2O_3	3.9	3.1	0.5	0.5	0.1	0.1	0.2
CaO	65.5	64.4	42.8	35.9	55.6	40.8	32.3
MgO	1.2	1.4	5.9	11.7	0.2	0.0	0.1
SO_3	2.5	1.7	0.1	3.4		57.5	44.0
Na_2O	0.0	0.2	0.2	0.4			0.0
K_2O	0.6	0.4	0.3	0.5			0.2
TiO_2		0.3	0.5	0.7			0.0
P_2O_5		0.3	0.0				0.0
MnO		0.3	0.5				0.0
LOI	1.4	0.7	0.2	1.9	43.7	0.5	20.5
Total (%)	100.8	99.5	100.3	100.6	99.9	99.6	99.9

2.2. Material proportions

Table 3 shows the material proportions of the blended cements used for this study.

In the experiment, Type V or OPC was used as parent cement. Cement replacement level with GGBS including other admixtures was set to 60% for the Type V-based blends, because high resistance to sulfate attack was demonstrated at slag cement proportions of above 50% of the total cementitious material when Type II cement was used [12]. It was assumed that the use of Type V in place of Type II would result in an emphasized effect of GGBS alumina content and, therefore, a reduced effect of C_3A on sulfate resistance.

In the cases of OPC-based blends, high-alumina GGBS proportions were set to about 30 to 40% by mass as shown in Table 3. The reasons for the use of OPC as the base cement and the selection of these replacement levels were as follows. The use of OPC having higher C_3A than Type V cement at lower replacement levels of GGBS, about 30 to 40%, could be assumed to be very severe sulfate attack conditions from the test results shown in Locher's work [4] where sulfate resistance was studied by varying the C_3A content and the replacement level of GGBS. The addition of suitable amounts of limestone and calcium sulfate might be capable of improving the sulfate resistance under such severe conditions. The other reason was that relatively low replacement levels were preferable for the prevention of carbonation and for higher early strength development of concrete. In addition, since OPC and high-alumina GGBS are widely used in Asia, improvement of sulfate resistance by this approach is of practical significance.

Table 2
Bogue composition of Portland cements.

	TypeV	OPC
Mineral composition(%)		
C_3S	59.2	51.2
C_2S	16.3	24.3
C_3A	4.9	8.7
C_4AF	11.9	9.4

Table 3
Material proportions of blended cements.

Symbol	Proportion by mass, %							Total SO_3, %
	Type V	OPC	SL	*low*SL	Limestone filler	Gypsum	Anhydrite	
V/(2.5)	100.0							2.5
V + SL/(1.0)	40.0		60.0					1.0
V + *low*SL/(3.0)	40.0			60.0				3.0
V + SL + L4/(1.0)	40.0		56.0		4.0			1.0
V + SL/(4.0)	40.0		53.6			6.5		1.0
V + SL + L4/(4.0)	40.0		49.6		4.0	6.5		4.0
OPC/(2.0)		99.4					0.6	2.0
OPC/(2.8)		97.9					2.1	2.8
OPC + L4/(2.0)		95.4			4.0		0.6	2.0
OPC + SL/(2.6)		60.0	37.3				2.7	2.6
OPC + SL + L4/(2.6)		60.0	33.2		4.0		2.8	2.6
OPC + SL + L8/(2.6)		60.0	29.2		8.0		2.8	2.6
OPC + SL/(4.2)		60.0	34.6				5.4	4.2
OPC + SL/(5.8)		60.0	31.9				8.1	5.8
OPC + SL + L4/(4.2)		60.0	30.6		4.0		5.4	4.2

2.3. Sulfate expansion

Sulfate expansion was evaluated using ASTM C 1012. Mortar bar specimens were immersed in 5% Na_2SO_4 solution at 23 °C when the strength of mortar cubes reached 20 MPa, and changes in the length were measured on six replicates per specimen type. To confirm the long term sulfate expansion, immersion was continued for 4 years for the OPC-based blended cement types as severe conditions of sulfate attack.

2.4. EPMA

The sulfate ion ingress into mortar specimens immersed in sulfate solution was evaluated by electron probe micro analysis (EPMA). The specimens were cut, a section was polished and the measurement surface was coated with carbon. By using EPMA, the spacial variation in sulfur concentration can be displayed. The strength of the characteristic X-ray was calibrated to sulfur concentration by comparing to that of a standard anhydrite crystal.

2.5. XRD

The specimens immersed in sulfate solution were characterized by X-ray diffraction (XRD) to evaluate the cement hydrates and the products formed by sulfate ingress. The mortar specimens were roughly ground, immersed in acetone to stop hydration, and then milled into powder for XRD measurement.

3. Results and discussions

3.1. Expansion

Fig. 1 shows the expansion behaviors determined by ASTM C 1012. Table 4 shows the estimated time to failure which was assumed to take place at an expansion of 1.0%.

The plain Type V (labeled “V/(2.5)”) expanded to failure in 8 months, and the plain OPC (labeled “OPC/(2.0)”) expanded more rapidly and reached failure in about 4 months. The expansion behavior of this Type V cement seemed to be earlier, although this was considered to be normal because ASTM C 1012 tests in a previous study on sulfate resistant Portland cement (SRPC) revealed that 0.10% expansion was reached in 7 to 20 months of exposure [13].

The Type V-based GGBS blended cements showed different expansion behaviors depending on the alumina content of GGBS. The blend with low-alumina GGBS, V + *low*SL/(3.0), remained stable with a small expansion of 0.06% in 2 years. In contrast, the blend with high-alumina GGBS, V + SL/(1.0), expanded faster than the plain Type V cement.

These results suggest that, in the case of simple replacement of GGBS for Portland cement, sulfate expansion is prevented when the alumina content of GGBS is low, while it appears to act the opposite

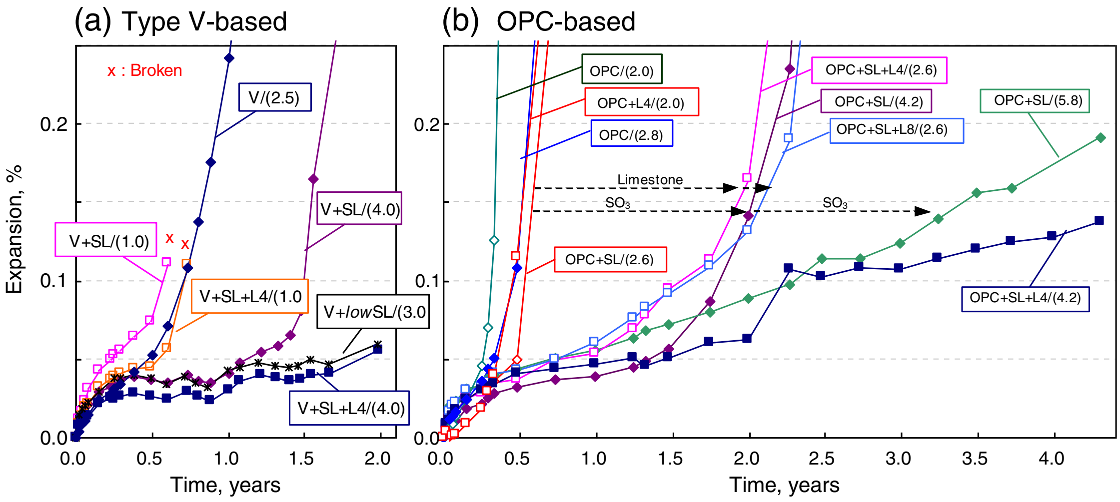

Fig. 1. Expansion behavior of cement specimens by ASTM C 1012.

Table 4
Estimated time to failure which was assumed to occur at 0.1% expansion.

Symbol	Time to expansion (0.1%), months
V/(2.5)	8.2
V + SL/(1.0)	6.8
V + *low*SL/(3.0)	>24
V + SL + L4/(1.0)	8.2
V + SL/(4.0)	18.0
V + SL + L4/(4.0)	>24
OPC/(2.0)	3.7
OPC/(2.8)	5.5
OPC + L4/(2.0)	5.4
OPC + SL/(2.6)	6.3
OPC + SL + L4/(2.6)	18.6
OPC + SL + L8/(2.6)	19.2
OPC + SL/(4.2)	21.7
OPC + SL/(5.8)	>24
OPC + SL + L4/(4.2)	>24

when the alumina content is high, irrespective of the low C_3A content of the Portland cement used.

The addition of limestone powder and the increase in calcium sulfate content to the unstable high-alumina GGBS blended cement improved sulfate resistance. Expansion in V + SL + L4/(1.0) containing 4% limestone powder was slightly delayed as compared with V +SL/(1.0) containing no limestone, with the time to 0.1% expansion extended from 7 months to 8 months. On the other hand, the GGBS blended cement with an increased calcium sulfate content of 4.0%, V + SL/(4.0), showed higher sulfate resistance. Expansion at 18 months was less than 0.10%, satisfying the requirements for sulfate resistant class S3 – very severe – in ACI 318-08. Moreover, those with the combination of limestone powder and 4.0% SO_3 content, V + SL + L4/(4.0) and OPC +SL + L4(4.2), showed sufficient sulfate resistance, with similar expansion behavior to the blend of Type V plus low-alumina GGBS.

These results suggest that merely blending GGBS with Type V cement did not improve sulfate resistance when the alumina content of GGBS was high, but adding limestone powder and/or increasing the calcium sulfate content of the blend did improve sulfate resistance of the hardened cement. The combination of limestone and calcium sulfate added to high-alumina GGBS blended cement was found to markedly enhance sulfate resistance, as compared with adding either limestone or calcium sulfate alone. For practical use of these materials, it is necessary that the proportions be investigated. Effects of excessive additions are known as follows. Adding high amounts of limestone results in concerns about other adverse effects on sulfate resistance [14] (described later). Excessively increasing the calcium sulfate content in Portland cement can increase early age expansion, as demonstrated by ASTM C 1038 test.

The combined use of limestone and calcium sulfate in GGBS blended cement will make sulfate resistant cement available in countries and areas where sufficient sulfate resistance cannot be achieved with SRPC due to unavailability of low-alumina GGBS and/or very severe sulfate environments.

Regarding the blended cements composed of OPC, the onset of expansion was retarded by around 2 months compared with the plain OPC, by addition of limestone powder as shown by OPC + L4(2.0) or by increase in calcium sulfate content up to 2.8% as shown by OPC/(2.8), although the expansions did exceed 0.10% within 6 months. Without GGBS, modification of OPC by addition of limestone powder or increase in calcium sulfate content was insufficient to achieve stable sulfate resistance.

As also shown in Fig. 1, OPC blended with high-alumina GGBS, OPC + SL/(2.6), rapidly expanded in 6 months. Simply blending high-alumina GGBS with OPC achieved only a slight improvement in sulfate resistance.

In contrast, in GGBS blended cements with addition of 4% or 8% of limestone powder, OPC + SL + L4/(2.6) and OPC + SL + L8/(2.6), respectively, time to 0.10% expansion was extended to 18 months (Table 4 and arrows in Fig. 1 (b)), meeting high sulfate resistance requirements of Class S3 in ACI 318–08. However, the addition of 8% limestone showed sulfate resistance comparable to that of 4% addition. This result indicates that the excessive amount of limestone powder does not improve sulfate resistance.

González et al.[14] reported that 10% replacement of low C_3A (6%) Portland cements by limestone caused no significant change in the sulfate performance of cements, whereas 20% replacement worsened sulfate performance. They explained this behavior by the changes in the degree of hydration, capillary porosity, and types of hydration products produced by limestone addition. Schmidt et al.[15] reported that the addition of a few percent of limestone in Portland cement (7%) reduced porosity and increased sulfate resistance, but 25% addition increased porosity and lowered sulfate resistance. Considering these previous studies, although there are effects of the base Portland cement, the sulfate expansion depends not only on the C_3A of the parent cement but also on the alumina content of the GGBS. In this study, the addition of limestone improved the sulfate resistance of GGBS blended cement. Also, the limestone contents of 4% and 8% used in this experiment did not result in significant difference in expansion behaviors because these levels of limestone did not greatly influence the porosity and the 4% limestone was chemically sufficient, due to the limited solubility of limestone filler which also limited the effect on the cement hydrates.

When calcium sulfate content of OPC blended with high-alumina GGBS was increased from 2.6% to 4.2% and to 5.8%, expansion determined by ASTM C 1012 was dramatically suppressed (arrows in Fig. 1 (b)).

Moreover, expansion of the OPC + SL + L4/(4.2) mortar containing limestone powder and increased calcium sulfate was only about 0.12% at 4 years. The combined effect of the two provided more stable sulfate resistance than that by either one separately.

Addition of a suitable amount of limestone powder and proper control of calcium sulfate content can improve sulfate resistance of GGBS blended cement, even when OPC is used for the base cement and the GGBS content is only about 30–40%, as used in this experiment. If blended cements with these replacement proportions can be used in sulfate soil or ground water environments, construction will be significantly expedited by the earlier strength development which would not be achieved by GGBS blended cements with high replacement proportions, while providing still many advantages of GGBS which would not be available with the use of OPC alone.

3.2. Analyses on ASTM C 1012 specimens

3.2.1. Sulfate ion ingress

Analyses were conducted to investigate the mechanisms of sulfate resistance. A special focus was placed on sulfur distributions in the specimens, assuming the major cause of sulfate expansion in Na_2SO_4 solution to be ettringite formation by reaction of calcium aluminate hydrates with external sulfate ions.

Sulfur concentrations in the sections were measured on transverse slices taken from near the center of the ASTM C 1012 mortar specimens after 2 years of immersion. Fig. 2 shows the distributions of sulfate concentration in the specimens.

Sulfate ion ingress was recognized in all the analyzed specimens, with cracks found on the section of V + SL/(1.0) and disintegration found at the edges of V + SL + L4/(1.0). Sulfur concentration near the surface was higher than that near the center. The depth of penetration of sulfate ions was the largest in V/(2.5), and there was little difference in the distributions of sulfur concentration among the specimens of the GGBS blended cements.

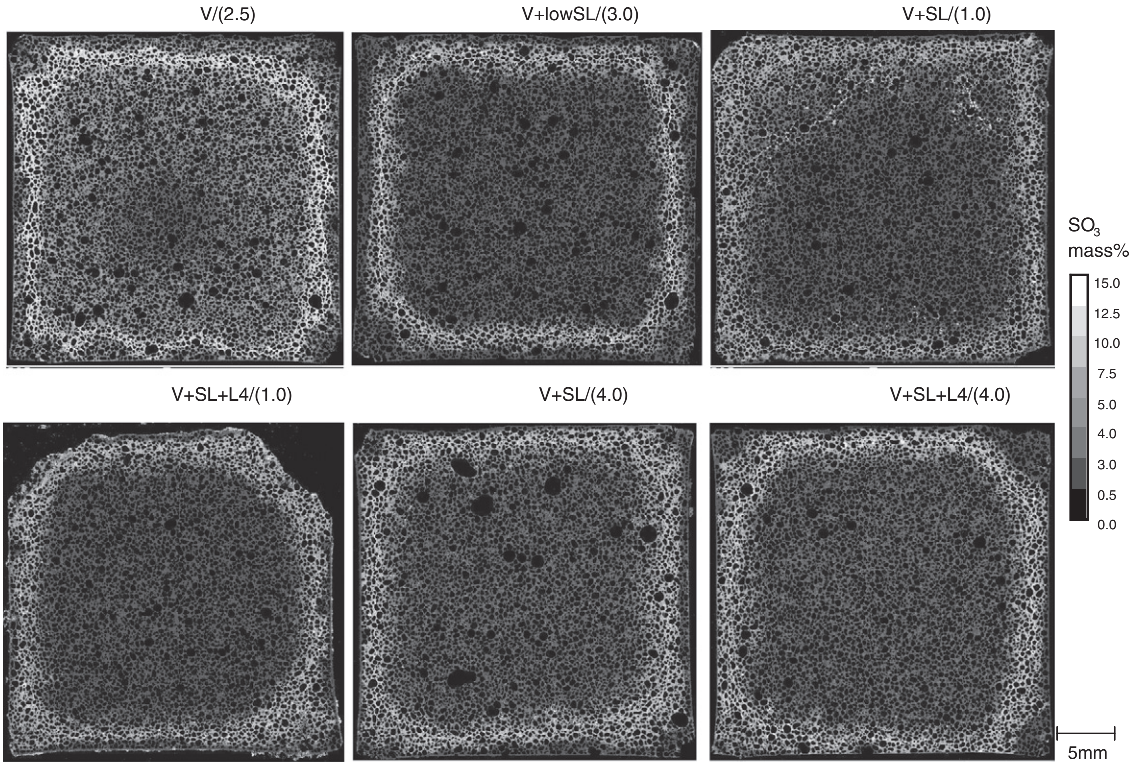

Fig. 2. Distributions of SO_3 concentration in ASTM C 1012 mortar specimens after 2 years of immersion.

SO_3 contents in representative specimens determined by EPMA are shown in Fig. 3. The SO_3 content was expressed as the average of EPMA data in the vertical direction, except for the top and bottom surface layers of 8 mm each as shown in Fig. 2.

In V/(2.5) specimen, sulfur was concentrated near the surface and it reached the center of the specimen. To the contrary, GGBS blended specimens exhibited a flat distribution of sulfur concentration in their insides irrespective of the alumina content of GGBS, suggesting suppression of sulfur penetration into the inside. These results indicate that blending in GGBS retards sulfate ion ingress, and this retardation does not differ according to alumina content of GGBS, added amount of limestone powder or calcium sulfate content. This suggests that sulfate penetration alone does not necessarily produce expansion. Incidentally, SO_3 concentrations in these mortar specimens around the center shown in Figs. 2 and 3 matched the SO_3 contents of the blended cements expressed in Table 3, although the reliability of the quantitative determination of sulfur by EPMA has not been strictly confirmed.

3.2.2. Hydration products in ASTM C 1012 specimens

Fig. 4 shows XRD patterns of the mortar specimens after 2 years of immersion. The specimens were taken from other parts of the same specimens used for EPMA.

Peak intensities of ettringite and portlandite in the Type V cement mortar were the highest of all the cements. Blending in GGBS reduced the intensity of the portlandite peak, irrespective of the alumina content of GGBS. The mechanism of the consumption of portlandite was described in previous reviews including that by Uchikawa [16].

The reduction in portlandite which could act as a source component in the ettringite formation as expressed by formula (3) was considered to be one of the reasons for improved sulfate resistance.

Regarding the ettringite content of the GGBS blended cements, V + *low*SL/(3.0) showed lower intensities of the ettringite peaks, and showed no peak of other known aluminate hydrates. Moreover, in all the high-alumina GGBS blended cement mortars, the intensity of the ettringite peak was comparable to that in the Type V cement mortar in spite of the lower content of cement. Addition of limestone

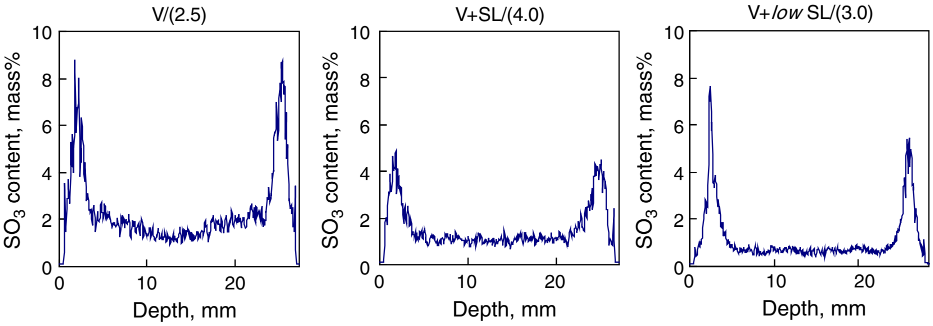

Fig. 3. Calculated SO_3 contents in the mortars.

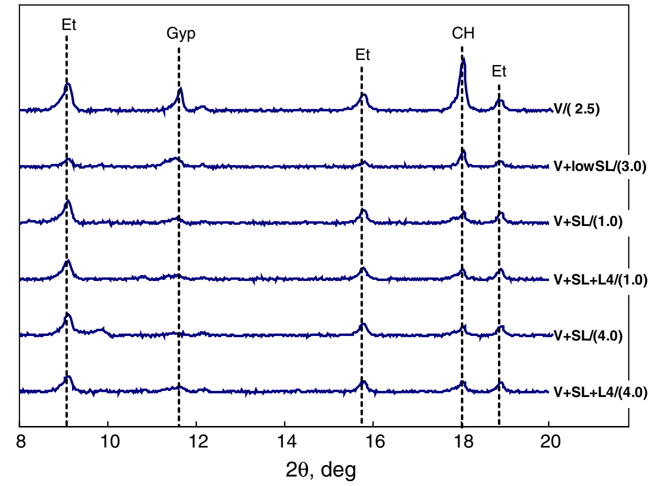

Fig. 4. XRD patterns of ASTM C 1012 mortar specimens after 2 years of immersion. Et: ettringite, Gyp: gypsum, CH: portlandite.

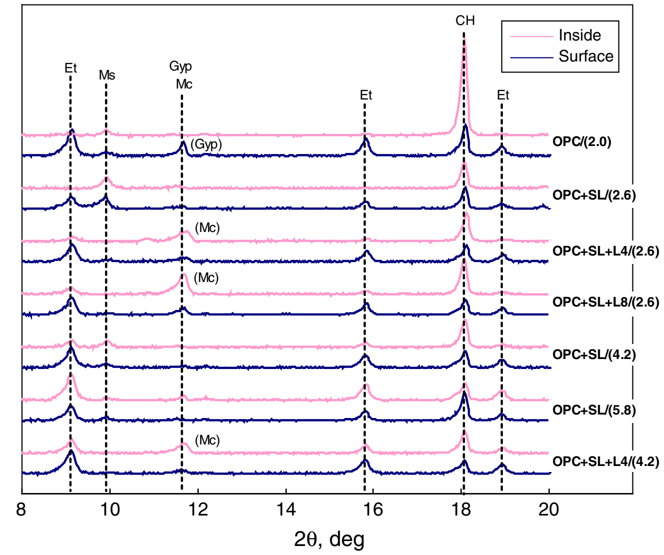

Fig. 5. XRD patterns of mortar cubes after 6 months exposure to sodium sulfate. Et: ettringite, Ms: monosulfate, Gyp: gypsum, Mc: monocarboaluminate, CH: portlandite.

and increase in calcium sulfate in high-alumina GGBS blended cement clearly did not affect the intensity of the ettringite peaks.

For the XRD analyses, whole cross-sections of the mortar samples were ground without distinction between the surface where sulfur penetrated and the inner core. Therefore, the XRD peak heights obtained were the averages. The total sulfur content of the V + SL/(1.0) specimen after immersion in Na_2SO_4 solution was considered to be lower than that of the V + *low*SL/(3.0) mortar, because sulfur penetrations in these two samples were not significantly different by EPMA (Fig. 2), while the initial SO_3 content of V + SL/(1.0) was lower than that of V + *low*SL/(3.0) as shown in Table 3. Assuming that there were sufficient aluminates that could convert to ettringite in the specimens, the ettringite peak of V + SL/(1.0) should be lower than that of V + *low*SL/(3.0). However, the results were counter to this assumption. Therefore, V + SL/(1.0) had more aluminates, which could convert to ettringite, than V + *low*SL/(3.0). In addition, since these two types contained the same amount of replacement GGBS, alumina in GGBS was likely to have acted as a source of ettringite, and which led to expansion by external sulfate. These are consistent with the phenomenon that V + SL/(1.0) expanded more quickly than the plain Type V (shown in Fig. 1 (a)), and also with a previous report that the high-alumina GGBS adversely affected the sulfate resistance [4].

In the case of the low-alumina GGBS blended cement, it is probable that the decrease in the amount of ettringite improved sulfate resistance. However, some high-alumina GGBS blended cements showed stable sulfate resistance as compared with other cements, without any decrease in the amount of ettringite as determined by XRD.

Therefore, to understand the mechanism of sulfate resistance influenced by limestone fillers and calcium sulfate added to high-alumina GGBS, the amount of expansive ettringite should be evaluated together with other aluminate hydrates, and considering the locations of external sulfate penetration. The ASTM C 1012 mortar specimens may not be appropriate for use in the analysis of hydrates by dividing them into different portions, because of their small cross section areas and deterioration by sulfate attack in some cases.

3.3. Mechanisms of improvement in sulfate resistance

In order to clarify the mechanisms of improvement in sulfate resistance, another immersion test was conducted focusing on transformation of calcium aluminate hydrates by a supply of external sulfate ions and its effects on sulfate expansion. Mortar cube specimens of OPC-based blends were prepared using the same mix proportions as those used in the expansion test in Table 3, and they were immersed in 5% Na_2SO_4 solution for 6 months. The specimens were then cut at 5 mm from each outer surface to separate the “inside portion” and “surface portion”. Although not shown here, distribution of SO_3 concentration was measured in all the specimens by EPMA, where depths of sulfate ion penetration were confirmed to be less than 5 mm.

In the inside portion, ettringite and other hydration products that varied depending on the composition of each blended cement were observed as the original products, and, in the surface portion, ettringite and other hydration products that were produced or reduced by the penetration of external sulfur were observed in addition to the original products. Therefore, it was possible to estimate new ettringite formation and change in other hydration products by subtracting the XRD peaks in the inside portion from those in the surface portion.

Fig. 5 shows XRD patterns of the surface and inside portions. In these patterns, it was difficult to distinguish between the two peaks at 11.6° and 11.7°: monocarboaluminate (Mc) at 11.6° and gypsum (Gyp) at 11.7°. However, the peak in the surface portion of OPC/(2.0) in this angle range was considered to be due to gypsum because there was no limestone. On the contrary, the peaks in OPC + SL + L4/(2.6) and OPC + SL + L8/(2.6) in this angle range were considered to be mainly due to monocarboaluminate, because they contained limestone powder and clearer peaks were detected in the inside samples where sulfate ions had not penetrated.

From the point of view of hydration products, mechanisms of preventingsulfate expansion in individual blended cements are discussed as follows:

3.3.1. OPC without GGBS

In the inside portion of OPC/(2.0), a strong portlandite peak and a monosulfate peak were detected. In contrast, in the surface portion, both the monosulfate and portlandite peaks were lower, and, instead, a clear peak of ettringite was detected. This result suggests that the monosulfate near the surface converted into expansive ettringite by the reaction with external sulfate ions and internal portlandite, and as a result, rapid expansion occurred.

Without GGBS, modification of OPC by addition of limestone powder or increase in calcium sulfate content was insufficient to achieve stable sulfate resistance as shown in Fig. 1. Although the reason was not identified, external sulfate ions were expected to penetrate more easily without GGBS, and any gypsum formation from the penetrating sulfate would be less likely to be involved in expansion if the formation of expansive ettringite was suppressed by adding limestone powder or additional calcium sulfate to cement.

3.3.2. Simple blend of OPC with GGBS

In the inside of OPC + SL/(2.6), the intensity of the monosulfate peak was higher than that of the plain OPC, and ettringite and monosulfate peaks were found in the surface portion. This result suggests that expansive ettringite formation by the reaction of monosulfate with external sulfate ions cause rapid expansion in the same way as OPC/(2.0). However, the rapid expansion was slightly retarded compared with the plain OPC. This is because of secondary hydration reactions of GGBS consuming $Ca(OH)_2$ which is one of the reactants for ettringite formation, and the densified hydrated matrix provided by the GGBS reaction helps prevent sulfate ion ingress.

3.3.3. Effect of limestone powder

Hydration products in GGBS blended cement containing limestone powder such as OPC + SL + L4/(2.6) and OPC + SL + L8/(2.6) were different from those in the other cements mentioned above. In the inside portion, ettringite and monocarboaluminate were found, and no monosulfate was detected. Hydration reactions of calcium aluminate phases in slag cement containing limestone have been reported by Hoshino et al.[11], where ettringite generated at early ages did not transform into monosulfate and remained at constant amounts even in later ages, while monocarboaluminate and hemicarboaluminate were generated. The results obtained in this study are consistent with this former study.

In the inside portion, where sulfate ions had not penetrated, ettringite formed at early ages transformed to monosulfate, and additional ettringite transformed to monocarboaluminate and hemicarboaluminate due to reaction with the limestone. These calcium aluminate hydrates may reduce or delay the formation of expansive ettringite when exposed to external sulfate ions.

In the surface portion of these mortars, the intensity of the monocarboaluminate peak was lower than that in the inside portion, and the ettringite peak was higher. This phenomenon suggests that monocarboaluminate can slowly convert to ettringite with the supply of external sulfate ions. Irasser [10] described in his review that monocarboaluminate, monosulfoaluminate, hemicarboaluminate and hydrogarnets were unstable phases and would be transformed into ettringite in a blend using high C_3A content parent cement, leading to extended deterioration. Besides, Matschei et al.[17] presented phase assemblages by thermodynamic calculations of a hydrated mixture consisting of C_3A and portlandite together with sulfate and carbonate. Their results showed that at a high initial sulfate ratio (SO_3/Al_2O_3), monocarboaluminate and/or hemicarboaluminate would not be detected and ettringite and gypsum would be observed. Their results did not directly show the possibility of conversion, although, considering thermodynamic stability, monocarboaluminate would be converted to ettringite in the presence of excessive sulfate. This idea provides a reason for the limited improvement of sulfate resistance.

3.3.4. Effect of calcium sulfate

With calcium sulfate content in GGBS blended cements increased from 2.6% to 4.2% and to 5.8%, the intensity of monosulfate peak decreased and that of ettringite peak increased in the inside portion. At the same time, sulfate resistance improved, responding to the increase in calcium sulfate content. If it is assumed that ettringite expansion is caused by additional ettringite formation due to exposure to external sulfate ions, the key is the amount of calcium aluminates available for transformation to ettringite during immersion in sulfate solution. When more calcium sulfate is contained in GGBS blended cement, the initial amount of ettringite formed will be higher, while that of monosulfate will be smaller. This results in a lower possibility of additional ettringite formation due to external sulfate ions.

3.3.5. Complex effect of limestone and calcium sulfate

In the inside portion of OPC + SL + L4/(4.2) containing limestone powder and increased calcium sulfate, ettringite and monocarboaluminate but no monosulfate were detected, which was similar to OPC + SL + L4/(2.6) and OPC + SL + L8/(2.6). Moreover, compared with these cements, OPC + SL + L4/(4.2) showed a smaller difference in the intensities of the ettringite peak between the inside and surface portions, which was due to the increased calcium sulfate. The combination of limestone addition and increase in calcium sulfate provides a complex effect on sulfate resistance. With calcium sulfate increased, ettringite increases but monosulfate still remains. However, when calcium sulfate is increased together with addition of limestone powder, no monosulfate is formed. As a result, this complex effect provides stable sulfate resistance for 4 years of immersion, without requiring substantial increase in calcium sulfate content.

From the analyses of hydration products and from the expansion tests, alumina in GGBS was considered to be a source for expansive ettringite formation, for the following reasons: 1) in the case of plain OPC with no GGBS, addition of limestone powder and increase in calcium sulfate content provided limited improvement of sulfate resistance; 2) OPC blended with 30 to 40% by mass of high-alumina GGBS (about 15% Al_2O_3), OPC + SL/(2.6), produced more monosulfate than the plain OPC; and 3) high-alumina GGBS produced more ettringite than a low-alumina slag (shown in Fig. 4). Unstable sulfate resistance of high-alumina GGBS blended cement is explained in that alumina in the GGBS acts as a source for ettringite formation by the reaction with external sulfate ions. Improvement of sulfate resistance is considered to be due to a decrease in this ettringite formation.

4. Conclusions

In order to understand the mechanisms of sulfate resistance of GGBS blended cement, ASTM C 1012 expansion tests and analyses of sulfate ingress and hydration products were conducted using both low-alumina and high-alumina GGBS, and varying limestone powder and calcium sulfate contents. The following conclusions can be drawn.

- The GGBS blended cement composed of Type V (5% C_3A) cement and low-alumina GGBS (11% Al_2O_3, and 60% replacement) exhibited stable sulfate resistance. However, the use of high-alumina GGBS (15% Al_2O_3, and 60% replacement) did not effectively improve sulfate resistance without sufficient calcium sulfate content and limestone addition (4%) in the cement.
- Irrespective of the alumina contents of GGBS, blending GGBS with Type V retarded sulfate ingress, and reduced $Ca(OH)_2$ content in the hydrated cement matrix. On the contrary, alumina in GGBS acted as a source of expansive ettringite by reacting with external sulfate ions. Unstable sulfate resistance by blending in high-alumina GGBS was considered to be due to this reaction.
- Addition of limestone powder (4% or 8%) in GGBS blended cement (OPC, 30 to 40% replacement) improved sulfate resistance, because of formation of monocarboaluminate and decrease in monosulfate that tended to form expansive ettringite with external sulfate ions. However, improvement of sulfate resistance by limestone addition through this mechanism was limited, because it was possible that monocarboaluminate transformed slowly to ettringite with the supply of external sulfate ions.
- Increase in calcium sulfate content of GGBS blended cement improved sulfate resistance, because sufficient calcium sulfate increased retention of initially formed ettringite, decreasing the potential for monosulfate reaction with external sulfate ions.
- GGBS blended cement containing suitable amounts of limestone powder and calcium sulfate exhibited highly stable sulfate resistance for 4 years in an accelerated test exposure due to the complex effects of the added materials. This was achieved even with a blend comprised of 60% OPC and high-alumina GGBS (15% Al_2O_3) which was considered as resistant to very severe sulfate attack conditions.

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