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Scientific paper

Effect of Limestone Powder and Gypsum on the Compressive Strength Mixture Design of Blast Furnace Slag Blended Cement Mortar

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Abstract

This paper investigates the compressive strength development of blast furnace slag (BFS) blended mortar mixtures incorporating various mineral admixtures, namely BFS, limestone powder (LSP), and gypsum (CS). BFS replacement ratios of 15, 20, and 25 wt.%; LSP replacement ratios of 2, 3, 4, and 5 wt.%; and a CS replacement ratio of 2 wt.% are employed to improve the strength of BFS blended mortar mixtures. The hydration reaction and products resulting from the use of cement, BFS, and mineral admixtures are quantitatively examined with respect to the XRD/Rietveld method in order to investigate the relationship between the produced hydrates and the strength. Experimental investigation reveals that the mortar mixture with BFS 15 wt.%, LSP 4 wt.%, and CS 2 wt.% exhibits similar compressive strength to an ordinary Portland cement mortar mixture. In addition, the strength is found to be decreased as the BFS replacement ratio increases. At a BFS replacement ratio above 20 wt.%, LSP affects the strength improvement of BFS cement and CS affects the initial strength improvement of BFS cement.

1. Introduction

Blast furnace slag (BFS) has been widely used as a mineral admixture in cement and concrete in the concrete industry in order to reduce CO₂ emissions (Miyazawa *et al.* 2010; Chen *et al.* 2012; Kumar *et al.* 2008). In Japan, the replacement levels of BFS are categorized into type A (5-30 wt.%), type B (30-60 wt.%), and type C (60-70 wt.%) according to the Japanese Industrial Standard (JIS). However, only type-B BFS blended cement is actually used in construction and is mainly used for building foundations or underground structures and not in main structural elements, owing to its low compressive strength at an early age (Nippon Slag Association 2015). In order to widen the usefulness of BFS blended cement, type-A BFS blended cement is expected to be used in construction and the mechanical properties and

hydration products need to be further discussed.

In the literature (Gu *et al.* 2015; Cetin *et al.* 2016; Rakhimova *et al.* 2014; Rakhimova *et al.* 2015; Gu *et al.* 2014), BFS blended cement is reported to have the advantages of reducing hydration heat, enhancing long-term strength, and providing some resistance to chloride-induced damage and sulfates. At present, to utilize these advantages effectively, studies to resolve the disadvantages of BFS blended cement are actively being pursued. Various studies are being conducted to resolve the issue of initial strength degradation and the temperature dependency of BFS was also investigated (Castellano *et al.* 2016). Rakhimova *et al.* (2014) investigated the compressive strength development of cement pastes by means of alkali activation. Sajedi and Razak (2010) also researched the influence of various kinds of alkali activators on the properties of BFS blended cement. The results revealed that sodium hydroxide, sodium silicate, and potassium hydroxide could be used as activators to increase the compressive strength of BFS cement. In addition, Gu *et al.* (2014) found that the mechanical and hydration properties of BFS blended cement could be increased by adding -MgO-CaO mixtures as a chemical activator.

At present, one promising approach that has been proposed is to incorporate limestone powder (LSP) to improve the early strength of the BFS blended mixture (Bonavetti *et al.* 2001; Menendez *et al.* 2003). When LSP is added, the C₃A reaction in the cement can be accelerated at an early curing age. Such properties are in contrast to the characteristics of BFS cement. When BFS and LSP are used in a mixture, the strength can be increased as a result of LSP hydration at an early age and as a result of the BFS in long-term aging (Ghrici *et al.* 2007; Lothenbach *et al.* 2008; Courard and Michel 2014; Scholer *et al.* 2015). Additionally, some studies

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Table 1 Chemical and physical properties of the materials.

		OPC	BFS	LSP	CS
Chemical composition (%)	SiO ₂	21.06	34.03	-	-
	Al ₂ O ₃	5.51	14.36	-	-
	Fe ₂ O ₃	2.69	0.83	-	-
	CaO	65.47	43.28	51.67	40.50
	MgO	1.66	6.51	-	-
	K ₂ O	0.40	-	-	-
	Na ₂ O	0.24	-	-	-
Physical properties	SO ₃	1.91	-	-	55.68
	Density (g/cm ³)	3.17	2.91	2.73	2.96
	Blaine fineness (cm ² /g)	3390	3930	4640	3030

have been carried out using gypsum (CS) as an alkali activator (Chang *et al.* 2005), and studies have been conducted to determine the effects of CS on BFS blended cement (Melo Neto *et al.* 2010; Park *et al.* 2016). A disadvantage of replacing BFS cement with CS arises when the replacement ratio of CS exceeds an optimum ratio, after which point the strength is degraded (Melo Neto *et al.* 2010; Park *et al.* 2016).

In addition, in order to quantitatively determine the effect of the replacement binder, the XRD/Rietveld method is used in some studies. This method is widely used for cement binders by quantifying the cement's chemical composition and hydration product. Many researchers have also studied ordinary Portland cement (OPC) and BFS cement using the XRD/Rietveld method (Kondo and Ohsawa 1969; Matsushita *et al.* 2008; Hargis *et al.* 2014; Sagawa *et al.* 2010; Sagawa and Nawa 2014; Sagawa and Nawa 2014). Sagawa and Nawa (2006) quantified BFS hydration using the XRD/Rietveld method with crystallization of the slag at high temperatures in order to investigate the hydration product of BFS blended cement.

This study attempts to improve the strength of BFS cement to a level comparable to that of OPC, with the aim of increasing the amounts of BFS used, such that type-A BFS cement can serve as a replacement for OPC. In addition, LSP and CS are used to enhance the strength of type-A BFS cement. Finally, the XRD/Rietveld method is used to quantify hydration analysis of the BFS blended cement and determine the effect of hydration products on the compressive strength of the BFS blended mixture incorporating various mineral admixtures. Finally, Powers' equation was used to investigate the relationship between compressive strength and the gel/pore ratio.

2. Experimental program

The experimental plan in this study consists of three parts. The first step deals with the development of compressive strength in BFS blended systems incorporating two types of mineral admixture, such as LSP and CS. The second part concerns the hydration degree and hydration products of BFS blended cement paste made with different mineral admixtures with respect to XRD/Rietveld analysis. Finally, the relationship be-

tween the experimental compressive strength results and the gel/pore ratio is investigated using Powers' gel/pore ratio model (1958). Details of the experimental plan and investigated BFS blended cement samples are given below.

2.1 Materials

The cement and BFS were used as per the JIS. The physical properties and chemical compositions of the OPC and BFS are shown in **Table 1**; the two types of mineral admixtures are also presented. The Blaine specific surface areas of the LSP and CS were 4640 cm²/g and 3030 cm²/g, respectively.

2.2 Sample preparation

2.2.1 Preparation of compressive strength test samples

Table 2 shows the experimental design of the mortar used in this study. The water-binder ratio (W/B) was 0.5 and the BFS replacement ratios were 0, 15, 20, and 25%. The mortar was cured using a $\phi 50 \times 100$ mm plastic mold. OPC and BFS were used for the cement types and LSP and CS were also used as mineral materials. The compressive strength levels of all mixtures were measured and curing temperatures were set to 20 °C. The compressive strength was tested after 1, 3, 7, 28, and 91 days under the 20-°C curing conditions.

2.2.2 Preparation of hydration product samples

For the measurement of the hydration product, a paste sample with different mineral materials was fabricated. **Table 3** shows the experimental design of the chemical analysis used in this study. The sample was mixed for two minutes using a hand mixer. To stem material bleeding, it was cured after one hour before commencing curing. Sealed curing was utilized with this sample for six aging conditions (1, 3, 7, 28, 56, and 91 days) at 20 °C.

2.3 Measurement methods

2.3.1 Compressive strength test method

The compressive strength test was conducted in accordance with the JIS A 1108. To test the mortar's compressive strength at an early age, the top surface of the mortar was capped with gypsum after 1 day of curing at 20 °C, owing to the fact that the early age compressive

Table 2 Mixture designations of the BFS blended cement mortar.

Mixture designation	W/B (%)	B:S	Unit content (kg/m ³)				
			W	C	BFS	LSP	CS
Control	0.5	1:3	324	515	-	-	-
B15				438	77	-	-
B15-L2				428	77	10	-
B15-L3				423	77	15	-
B15-L4				418	77	21	-
B15-L5				412	77	26	-
B15-C2				428	77	-	10
B15-L2-C2				418	77	10	10
B15-L3-C2				412	77	15	10
B15-L4-C2				407	77	21	10
B15-L5-C2				402	77	26	10
B20				412	103	-	-
B20-L2				402	103	10	-
B20-L3				437	103	15	-
B20-L4				392	103	21	-
B20-L5				387	103	26	-
B20-C2				402	103	-	10
B20-L2-C2				392	103	10	10
B20-L3-C2				387	103	15	10
B20-L4-C2				381	103	21	10
B20-L5-C2				376	103	26	10
B25				387	129	-	-
B25-L2				376	129	10	-
B25-L3				371	129	15	-
B25-L4				366	129	21	-
B25-L5				361	129	26	-
B25-C2				376	129	-	10
B25-L2-C2				366	129	10	10
B25-L3-C2				361	129	15	10
B25-L4-C2				356	129	21	10
B25-L5-C2				351	129	26	10

Note: B: blast furnace slag, L: limestone powder, C: gypsum

B (replacement ratio wt.%) -L (replacement ratio wt.%) -C (replacement ratio wt.%)

Table 3 Experimental design for the chemical analysis.

Mixture designation	W/B	Weight percentage (%)			
		OPC	BFS	LSP	CS
Control	0.5	100	-	-	-
B20		80	20	-	-
B20-C2		78	20	-	2
B20-L4-C2		74	20	4	2

strength is too low to demold. After the gypsum was completely hardened, compressive strength testing of the mortar was conducted.

2.3.2 Reaction rate and hydration product measurement

An analysis of the hydration was conducted using the XRD/Rietveld method. To assess the BFS reaction rate and to check for alite ($3\text{CaO} \cdot \text{SiO}_2$; C_3S), belite ($2\text{CaO} \cdot \text{SiO}_2$; C_2S), an aluminate phase ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$; C_3A), a ferrite phase ($4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$; C_4AF), and various cement hydration products, the XRD/Rietveld method was used to assess the effects of LSP and CS on the hydration of the BFS blended cement mortar samples. The X-ray diffraction and ignition loss characteristics were measured for samples that were 5 mm³ in size after curing for 1, 3, 7, and 28 days. For each aging condition, acetone replacement was carried out to stop the hydration reaction and the samples were dried before the measurements.

The drying procedure involved drying for 24 hours at 40 °C before the sample was measured. Powder was used for the X-ray diffraction and ignition loss measurements, and the samples were made into powder form using a vibration mill. The method for quantification of BFS was proposed by Sagawa and Nawa (2006) based on the heat treatment method, where the nonreactive BFS was crystallized by carrying out heat treatment for 30 minutes at 900 °C, and the heat loss through this was considered as ignition loss. Then XRD/Rietveld analysis was conducted on the sample.

Figure 1(a) shows the XRD results with respect to

different BFS replacement ratios according to Sagawa and Nawa (2006). The peaks of gehlenite and akermanite near 31.4° were increased and the peak of C_3S near 29.4° was decreased as the BFS replacement ratio increased. **Figure 1(b)** shows the BFS content found from Rietveld analysis. The amounts of gehlenite, akermanite, and merwinite determined from Rietveld analysis were calculated to be the BFS content. **Figure 1(b)** (Sagawa and Nawa 2006) shows that the calculated BFS content was highly consistent with the actual BFS content. Therefore, this method is reliable for the analysis results.

Moreover, for the test conditions for the ignition loss of the OPC, heat treatment was performed for 30 minutes at 950°C . For the XRD measurement, a semiconductor-type high-speed detector was used with $\text{CuK}\alpha$ as a target, a tube voltage of 45 kV, a tube current of 40 mA, a 2θ scan range of $5\text{--}70^\circ$, and a step width of 0.02° . For the Rietveld analysis, Siroquant Ver. 3.0 was used to measure the cement minerals, slag reaction rate, and amount of hydration product, with alumina ($\alpha\text{-Al}_2\text{O}_3$) at an average particle size of $3\text{ }\mu\text{m}$, following the standard methods used in the literature (Jansen *et al.* 2011a; Jansen *et al.* 2011b; Jansen *et al.* 2012).

3. Results and Discussion

3.1 Characteristics of compressive strength development

3.1.1 Influence of blast furnace slag on the compressive strength

Figure 2 shows the results for the compressive strength of BFS blended cement mortar samples with replacement ratios of 15%, 20%, and 25% by weight of cement. It can be seen that the compressive strength of the mortar samples tends to decrease with increasing BFS replacement ratio at 1, 3, and 7 days, owing to the fact that the proportion of cement content decreases and the reaction rate of BFS is slow (Çetin *et al.* 2016; Barnett *et al.* 2006; Boukendakdji *et al.* 2012; Miyazawa *et al.* 2014; Özbay *et al.* 2016; Jaya Prithika and Sekar 2016). In fact, it may cause a decrease in the compressive strength at an early curing age. Moreover, the compressive strengths of the mortar samples with 15 and 20 wt.% of BFS at 91 days exceeded that of the OPC sample with no addition of BFS, implying that long-term curing in BFS blended mortar samples is efficient for the development of compressive strength. The above results clarify that curing age can affect the compressive strength development of mortar samples incorporating BFS (Barnett *et al.* 2006; Boukendakdji *et al.* 2012; Özbay *et al.* 2016). In the case of B20, the compressive strength data at 28 days is believed to be due to an experimental error.

3.1.2 Influence of CS on the compressive strength

For the BFS blended cement mortar samples with dif-

ferent BFS replacement ratios and with the same CS contents of 2 wt.% for cement, as shown in **Fig. 3**, the compressive strength in the B20-C2 mortar sample (7.6 MPa) appeared to be similar to that of the reference mortar (7.3 MPa) without BFS, particularly at 1 day, suggesting that the addition of CS in BFS blended ce-

(a) XRD profiles of tempered samples

(b) relationship between actual and measured amounts of BFS in unhydrated cement

Fig. 1 Quantification results for BFS from Sagawa *et al.* (2006)

Fig. 2 Compressive strength of BFS blended mortar.

ment mortar samples would affect the development of compressive strength at an early curing age. It is known that gypsum will generate heat when mixed with water in an exothermic reaction. The particles possess high free energy at high temperature and, as a result, the chemical reaction rate is increased. In addition, the use of CS will provide additional calcium. As described above, high concentrations of CS lead to a higher incidence of C-S-H, which agrees with Chang *et al.* (2005); this is discussed in detail in Section 3.3.

3.1.3 Influence of LSP on the compressive strength

Figure 4 shows the results for the compressive strength of all BFS blended cement mortar samples with different replacement ratios of 0, 2, 3, 4, and 5 wt.% of LSP. Different trends of compressive strength with respect to the BFS replacement ratio can be observed. In the case of a mortar sample incorporating 15 wt.% BFS by weight of cement, the compressive strength was decreased with the increasing LSP replacement ratio, even though the curing ages increased. The compressive strength of mortar at a BFS replacement ratio of 20 wt.% was increased with increasing LSP replacement ratio at all curing ages. However, when the BFS replacement ratio is 25 wt.%, the strength also increased with increasing LSP replacement ratio, except for B25-L5. Previous studies have confirmed that the strength can be improved by using a BFS replacement ratio of 40 wt.% (Sagawa and Nawa 2006), showing a similar trend to that of the BFS replacement ratios of 20% and 25% in this study. However, for a BFS replacement ratio of 15 wt.%, the strength is lowered, indicating a need for further research.

3.1.4 Combined influence of limestone powder and CS on the compressive strength

Figure 5 shows the compressive strength of BFS blended cement mortar with LSP and CS as replacements. It shows that a BFS replacement ratio of 15 wt.% yields almost the same compressive strength value as

OPC mortar. The compressive strength was reduced slightly as the BFS replacement ratio increases from 20 wt.% to 25 wt.%, which shows the same trend as the BFS cement mortar without LSP and CS until a curing age of 91 days. Furthermore, all of the mortar samples prior to 1 day showed the same value of compressive strength as OPC.

In the above strength test results, with regard to the effects of using CS as a replacement material, the strength at an early curing age (1 day) was identical to that of OPC, and it was determined that the low initial

Fig. 3 Compressive strength of BFS blended mortar incorporating CS.

Fig. 4 Compressive strength of BFS blended mortar incorporating LSP.

strength stemming from the use of BFS as a replacement material can be improved. Regarding the effect of LSP, it was found that the strength was increased at BFS replacement ratios of 25 wt.% as the LSP replacement ratio increased. In addition, the compressive strength was greater than that of OPC at both an early curing age and after long-term curing. When using a combination of LSP and CS, a trend similar to that of BFS replacement was observed, where the strength decreased slightly as the amount of binder increased, except for the use of OPC. However, for all mixtures, it was ob-

served that the strength at the early curing age (1 day) was similar to that of OPC.

3.2 Compressive strength of BFS blended paste samples incorporating various mineral admixtures

Figure 6 shows the compressive strengths of BFS blended paste samples with mineral admixtures at curing ages of 1, 3, 7, 28, and 91 days. The compressive strength at 1 day was measured to be 7.3 MPa, 5.4 MPa, 7.6 MPa, and 7.9 MPa for OPC, B20, B20-C2, and B20-L4-C2 mortar samples. In the case of the B20 mortar sample, with a BFS replacement ratio of 20 wt.%, the compressive strength at 1 day showed an initial strength lower than that of the OPC mortar sample, but after 91 days its compressive strength was recorded to be 50 MPa, exceeding that of the OPC sample. This finding is in good agreement with the results obtained in the mortar strength tests in Section 3.1. For the B20-C2 sample, with a CS replacement ratio 2 wt.%, the compressive strength at 1 day was measured to be 7.6 MPa and similar to that of OPC, while the same compressive strength development as for the B20 sample was observed after 3 to 91 days, suggesting that the use of CS in BFS blended mortar can help to accelerate the hydration reaction of BFS. The obtained results agree with those in previous studies reported in the literature (Chang *et al.* 2005).

In addition, the B20-L4-C2 mortar sample exhibited the same compressive strength as the B20-C2 samples for curing ages of 1, 3, 7, and 28 days, but not 91 days.

3.3 Hydration reaction analysis of paste samples

3.3.1 Hydration degree of cement

Figure 7 shows the hydration degree calculated by XRD/Rietveld analysis for the four types of BFS blended pastes incorporating LSP, CS, and OPC. It can

Fig. 5 Compressive strength of BFS blended mortar incorporating CS and LSP.

Fig. 6 Compressive strength of BFS blended cement paste.

be seen that by incorporating CS and LSP the hydration degree of the cement minerals in the BFS blended paste after 1 day of curing was higher than that of the reference pastes, suggesting that CS and LSP can accelerate the hydration of cement minerals at an early curing age of 1 day. The change of hydration degree for each cement mineral will be described in following sections.

Figure 8 presents the hydration degree of BFS in the investigated paste samples. It shows that the hydration degree of the paste was approximately 63.7% after 91 days of curing. It was reported by Sagawa *et al.* (2006) that the hydration degree of cement is increased when the BFS replacement ratio is decreased. In this research, a BFS replacement ratio of 20 wt.% was used, in Sagawa *et al.* (2006) studies the results of paste produced with a BFS replacement ratio of 40 wt.%, the hydration degree of the slag was recorded for 40 wt.% to 50 wt.%. Moreover, for pastes made with LSP and CS, the hydration degree was high until a curing age of 7 days, and then low for curing ages from 28 to 91 days, as compared to the B20 paste.

Fig. 7 Hydration degree of cement.

Fig. 8 Hydration degree of BFS.

3.3.2 Hydration degree of C_3S , C_2S , C_3A , and C_4AF

Figures 9(a) and (b) show the results for the hydration degree of C_3S and C_2S for the investigated BFS blended paste samples. It has previously been reported that the addition of BFS to cement accelerates the hydration of C_3S and slows the hydration of C_2S , and thus the BFS can affect the hydration reaction of cement minerals (Sagawa and Nawa 2006; Hoshino *et al.* 2006b). Similar results were obtained in this paper. In the case of the B20 sample incorporating 20% by weight of BFS for cement, the hydration degree of C_3S in the paste sample did not change and was slightly increased in comparison to OPC without BFS, implying that the hydration of C_3S tends to accelerate, owing to the addition of the slag, which agrees with earlier studies as described above (Sagawa and Nawa 2006; Hoshino *et al.* 2006b).

In addition, when the B20-C2 samples were replaced by combinations of 20-wt.% BFS with 2-wt.% CS, the hydration degree of C_3S was increased above 10% compared to the OPC and B20-C2 samples at curing ages of 1 and 3 days, which justifies the result of **Fig. 6**. Therefore, it is considered that the addition of BFS and CS can affect the development of compressive strength.

It is also observed that, in the case of the B20-L4-C2 samples made with LSP, CS, and BFS, the hydration degree of C_3S did not differ from that of the B20-C2 sample. According to Hoshino *et al.* (2006b), when comparing OPC and OPC-LSP samples, the hydration degree of C_3S in cement did not change. However, in the case of the OPC-BFS-LSP sample, the hydration degree of C_3S was higher than that of OPC, suggesting that the addition of LSP for binder had a negligible effect on the hydration of C_3S . **Figure 9(b)** presents the hydration degree of C_2S for the investigated paste samples. It is concluded that, except for the B20-C2 paste sample, the same results for the hydration degree of C_3S were also observed in these pastes. **Figure 9(b)** shows that incorporating BFS and LSP for cement had an insignificant effect on the hydration of C_2S .

It is well known that, as mentioned above, a BFS replacement ratio of 40 wt.% in the cement would delay the hydration of C_2S , but, in this research, different results were obtained. From **Fig. 9(b)**, in comparison to the OPC paste, the hydration degree of C_2S in B20 cement paste slightly increases up to 28 days, which implies that BFS would accelerate the hydration of C_2S .

In addition to this observation, in the cases of addition of CS and LSP, the hydration of C_2S is low compared to the B20 cement paste. This suggests that C_2S would delay hydration.

Figures 9(c) and (d) show the hydration degree of C_3A and C_4AF for the investigated BFS blended paste samples. Previous studies on the hydration reaction of C_3A and C_4AF in cement (Sagawa and Nawa 2006) have reported that it was accelerated when BFS was used. It can be seen that the hydration degree of C_3A and C_4AF for the BFS cement paste sample was accel-

erated and similar to that of OPC cement paste (Hoshino *et al.* 2006a; Hoshino *et al.* 2006b). However, for samples using LSP and CS, the hydration reaction of C_4AF is slightly low in comparison to both OPC and B20 paste samples.

3.3.3 Hydration products

Figure 10 shows the amounts of hydration products of ettringite (AFt), mono-sulfate (AFm), katoite, monocarbonate (MC), and hemicarbonate (HC) for the investigated BFS blended paste samples. **Figure 10(a)** shows the results for the amount of AFt produced. It can be observed that the amount of AFt tends to gradually decrease with curing age. On the other hand, in the case of the B20-L4-C2 samples at a curing age of 3 days, the amount produced is higher than for the other samples.

Figure 10(b) shows the produced amounts of AFm in the OPC, B20, and B20-C2 samples. For the B20-L4-C2 sample mixed with LSP mineral, AFm was not identified during the hydration process. In contrast to the AFt

trends, the amount of AFm displayed a trend of increasing with curing age, which agrees with previous studies. It is considered that for the sample without LSP, the AFm hydration product is generated by AFt reacting with C_3A from an early curing age. However, if the sample is replaced with LSP, then C_3A preferentially reacts with the LSP mineral, which causes it to generate carbonate hydrates (MC, HC), as shown in **Fig. 10(d)** (Hoshino *et al.* 2006b). **Figure 10(c)** shows the produced amounts of katoite. It is concluded that the OPC sample yields the greatest amount of katoite, which decreases as the cement is replaced by the minerals.

The effects of CS and LSP on the compressive strength development of type-A BFS blended cement can be analyzed from the above reaction rates and amounts of hydration products. The conclusions are as follows. The compressive strength at a curing age of 1 day can be increased by the promotion of the reaction of C_3S and BFS. The compressive strength development of samples with LSP of at a curing age of 91 days is found

Fig. 9 Degree of hydration of the BFS blended cement minerals.

to stagnate, owing to the suppression of the reaction of the BFS. In addition, in order to examine the relationship between the void volume and strength, the porosity can be calculated by assuming a density of C-S-H.

3.4 Relationship between porosity and compressive strength

It is well known that the compressive strength of a cement-based composite depends on the porosity, which can be experimentally evaluated using mercury intrusion porosimetry, drying methods, and so on. However, a different approach considering the hydration mechanism was adopted in this study in order to investigate the porosity and compressive strength in the investigated paste samples. Powers suggested the gel/pore equation, in which the porosity can be calculated from the hydration degree of cement minerals, the contents of hydration products, and the density of the C-S-H gel with respect to the results of XRD/Rietveld analysis:

$$X(t) = \frac{V_{hydrates}(t)}{V_{hydrates}(t) + V_{pore}(t)} \quad (1)$$

and:

$$S(t) = S_0 X(t)^N \quad (2)$$

where $X(t)$: gel/pore ratio (vol./vol.), $V_{hydrates}(t)$: hydration amount (vol.), $V_{pore}(t)$: pore volume (vol.), $S(t)$: strength (MPa), and S_0, N : integers.

When the gel/pore ratio is considered to be a function of the hydrate, S_0 denotes the strength when the capillary pores of the hydrate are completely filled. This is normally known as the ultimate strength or the highest strength. Moreover, the value of N represents the pore dependency of the strength. However, the relationship between gel/pore ratio and strength is identical regardless of the type of Portland cement used (Maruyama and Igarashi 2012). In this study, the relationship between gel/pore ratio and strength can be expressed in the same way regardless of the binder type.

Fig. 10 Amounts of hydration products of the BFS blended cement minerals.

The volumes of unreacted cement mineral (V_{un}) and hydration products (V_{hyd}) can be calculated using the quantitative value of density of each compound obtained from XRD/Rietveld analysis. In addition, the volume of the C-S-H can be estimated by considering the amount of C-S-H gel that is found to be amorphous via XRD/Rietveld analysis. The pore amount is calculated by subtracting V_{un} , V_{hyd} , and V_{CSH} from the unit cement paste volume. In other words, the volume and the pore volume of the C-S-H the density as the unknown C-S-H is calculated, and it is possible to calculate the gel/pore ratio from this value.

Figures 11(a) and (b) show the relationship between the calculated gel/pore ratio and the compressive strength and the relationship between the calculated density of C-S-H and curing age, respectively. Table 4 summarizes the values of the densities of the produced hydrates taken from the literature. It can be seen that, regardless of the types of materials used, the relationship between gel/pore ratio and strength is similar to the calculated values and these values of S_0 and N are almost the same as those found in previous studies. Moreover, in the literature, the CaO/SiO₂ molar ratio in C-S-H (hereafter denoted the C/S ratio) has been reported to exhibit a correlation with the density of the C-S-H (Sagawa *et al.* 2010).

Figure 12 presents the relationship between the C/S ratio and the density of C-S-H, comparing the results of this study to those reported by Sagawa *et al.* (2010). The C/S ratio is calculated from the mass balance of SiO₂ and CaO, including the amount of CH remaining in the cement paste after hydration. For a BFS blended cement paste, the calculation of the C/S ratio was carried out in the same manner as previously reported by Taylor (1997) for the phase composition model of BFS blended cement. It is confirmed that the density of C-S-H obtained in this study is slightly different from that previously recorded at 1 day but, after 3 days, the values are roughly equal to the values from the previous study.

Table 4 Densities of the hydrates.

Hydrate	Density (g/cm ³)
Calcite	2.71
CH	2.24
AFt	1.79
AFm	2.02
Hc	1.83
Mc	2.18
Katoite	2.53
HT	2.13

Moreover, Fig. 12 implies that the density of C-S-H decreases with increasing curing age and that the density of the BFS blended cement paste tends to be low compared to that of OPC paste, which agrees with the findings of Sagawa *et al.* (2010) and Suda (2013).

The hydration product of calcium aluminate (CA) are presented in Figs. 13 and 14. The hydration products are calculated from the volume of the cement paste, considering the density of C-S-H. It is obvious that for LSP, even though the hydration product of CA would increase, the volume of the C-S-H was found to be small

Fig. 12 Relationship between the C/S ratio and the density of C-S-H.

Fig. 11 Compressive strength versus gel/space ratio and density of C-S-H versus curing age.

in comparison to other samples, which justifies the compressive strength result shown in Fig. 6.

Figure 15 shows the results for capillary pore volume calculated using the amounts of hydration products. It is possible to estimate the change in pore ratio of each formulation from the change in C-S-H density. Figure 15 shows that, although the hydration content of B20 and B20-C2 paste samples at 91 days may decrease compared to that of an OPC sample, almost the same compressive strength was obtained as that reported in the results above, implying that low-density C-S-H is produced by the slag and thus fills the pore in the paste matrices. The reaction rate of the compound in each binder and the transition of the hydration product can be shown as a phase change in the composition in the paste with respect to curing age until 91 days, as shown in Fig. 16. The figures imply that a) the volume of C-S-H is high in the paste samples, even though the materials are different; b) the addition of slag to the mixture leads to small amount of CH hydration product; and c) the addition of LSP increases the amount of CA hydration product, but the hydration product of C-S-H decreases throughout the curing period in comparison to other paste samples with respect to the paste variation model.

The reactivity behavior of each compound was obtained through XRD/Rietveld analysis. The amount of hydration product is used to calculate the pore volume by assuming the density of C-S-H. As a result, the relationship between the compressive strength and the pore volume proposed by Powers can be examined with the gel/pore ratio. The compressive strength at a curing age of 91 days of the B20 and B20-C2 samples is the same for OPC, which is considered to be the influence of the low C-S-H density generated by the BFS.

4. Conclusion

In this study, in an effort to develop a type-A of blast furnace slag (BFS) blended cement that can replace ordinary Portland cement (OPC), its strength development was investigated by varying the limestone powder (LSP) and gypsum (CS) replacement ratios. Furthermore, the correlation between the amounts of minerals produced in the cement and the compressive strength was examined through chemical analyses of test samples and by investigating the relationship between porosity and strength. A summary of the results obtained in this study is given below.

- 1) A mortar with BFS replacement exhibited a low early-age strength, which is thought to be due to the dependency of the initial strength of the slag cement on the OPC amount. For long-term aging, the strength obtained was high, in agreement with the literature.
- 2) When using CS as a replacement, the initial strength at a curing age of 1 day was equal to that of OPC. When CS was used as a replacement, significant heat was observed initially; this was determined to be an

Fig. 13 Calcium aluminate hydrate.

Fig. 14 C-S-H volume.

Fig. 15 The calculated capillary pore volume.

Fig. 16 Calculation results for composition of each mixture.

effect of the addition of calcium.

- 3) When using LSP as a replacement, the strength increased at replacement ratios of 20 and 25 wt.%. However, at a BFS replacement ratio of 15 wt.%, the strength decreased slightly. In comparison to findings in the literature (at 40 wt.% BFS), this result was thought to be due to the effect of LSP on the strength enhancement for BFS replacement ratios above a certain value.
- 4) No consistent trends were observed for the results of LSP and CS replacement. However, the initial strength at a curing age of 1 day was equal to that of OPC. The mixture that exhibited a compressive strength similar to that of OPC was BFS 15 wt.% + LSP 4 wt.% + CS 2 wt.%.
- 5) From the results for the measured cement mineral reaction rate, the C_3S reaction amount increased for the case of CS replacement. This increase was thought to have affected the strength enhancement of the CS replacement mixture.
- 6) From the results for the measured hydration product,

AFt was not converted to AFm as a result of LSP replacement. This is thought to be due to the contribution of AFt to the initial production of MC or HC in the LSP replacement case.

- 7) With regard to the relationship between porosity and strength, while the amount of capillary pores decreased with additional aging, the strength increased. Therefore, it was determined that, as the degree of hydration increased, the amounts of capillary pores decreased with aging and the strength increased accordingly.

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