Experimental Study for Effects of Hydrate Products on Shrinkage Behaviour in Low Volume Blast Furnace Slag Cement Concrete

T Kanda¹, H Momose¹, K Ishizeki¹ and T Sagawa²

¹ Kajima Technical Research Institute, 2-19-1 Tobitakyu, Chofu, Tokyo 182-0036, Japan
² Department of Civil and Environmental Engineering, Faculty of Engineering, Maebashi Institute of Technology, Kamisatori, Maehashi, Gunma 371-0816, Japan

Abstract. Blast furnace slag (BFS) cement concrete is reported to be prone to shrinkage cracking at high temperature in tropical climate. To solve this problem is important to extend BFS cement concrete which is known as a key to reduce carbon footprint in concrete production. This study focuses shrinkage reducing effects to increase gypsum and calcium carbonate in low volume BSF cement concrete as trace additives. Free shrinkage experiment and hydration analysis experiment are conducted to clarify the focused issues. These two experiments clarified that: i) increasing gypsum amount up to 4.5% of binder mass effectively reduced free shrinkage strain subjected to 30 degree of ambient temperature, ii) this free shrinkage reduction is considered due to restraining transformation of Ettringite to Monosulfate, which is known to lead serious volume reduction in hydrate products, iii) increased gypsum amount up to 4.5% appeared not a source of Delayed Ettringite Formation.

1. Introduction

Blast furnace slag cement concrete (hereinafter, "BFS concrete") is the subject of high expectations for the reduction of environmental impacts, yet concern about increased shrinkage especially in higher summer temperatures and propensity to shrinkage cracking constitutes a barrier to its popularization[1][2]. The authors have studied in detail the shrinkage and cracking behaviour of medium volume blast furnace slag cement (Class B in Japanese Industrial Standard R 5211) concrete under such higher temperatures and have proposed countermeasures for suppressing the above-mentioned unwanted behaviours through the addition of trace additives such as anhydrite gypsum. However, such measures did not necessarily reach the required level in terms of cost and effect to warrant their broad application for general purposes [3].

The use of low volume blast furnace slag cement Class A in JIS R 5211 (BA), which uses a lesser proportion of blast furnace slag, instead of blast furnace slag cement Class B (BB), allows the attainment of properties that more closely approximate those of ordinary Portland cement (N) concrete, allowing universal use of BFS concrete and making the aforementioned measures more practical and economical, opening the possibility of achieving BFS concrete with crack resistance superior to that of N concrete[4].

Based on the above, in this study the authors focused on BA concrete, conducting experiments to determine the effect of adding trace additives and the type of hydrate product generated during hardening in an environment that simulates high summer/tropical temperatures in order to achieve low-shrinkage concrete having small shrinkage and excellent crack resistance.
2. Experimental design

2.1. Free shrinkage experiment

In this study, we conducted a free shrinkage experiment and hydration analysis experiment (Table 1). The free shrinkage experiment, whose aim was to shed light on the effect of the SO$_3$ usage rate and CaCO$_3$ usage rate as trace additives on the free shrinkage strain behaviour of BA concrete, as shown in Table 1. The three experimental factors of BFS dosage ratio, SO$_3$ dosage ratio, and CaCO$_3$ dosage ratio are selected in the experiments. In addition to the SO$_3$ dosage ratio of 2.5%, which is a level close to that of commercial BA concrete, the dosage ratios of 3.5% and 4.5% were also investigated. The resulting concretes were called low-shrinkage blast furnace type A (hereinafter, "BLS(A)"), and these concretes were compared with commercially available BA, BB, and N. Three CaCO$_3$ dosage ratio levels, from 0% (no addition) to 7%, were used.

In the free shrinkage experiment, a free shrinkage test and a compressive strength test were carried out. For the free shrinkage test, cylindrical specimens measuring $\phi$ 100 \times 200 mm, shown in Figure 1, were used to measure the history of free strain after concrete placing. Two specimens were prepared for each level. The samples were cast in two layers, and immediately after casting, they were subjected to sealed curing at 30°C. After sealed curing at 30°C for 7 days, the samples underwent dry curing at 30°C and RH60%. Strain measurement was carried out before concrete casting until 189 days (dry material age of 182 days). The setting end time was used as the start of strain measurement. The specimens for the compressive strength test were cured according to the curing conditions of the free shrinkage test from immediately after casting. After sealed curing at 30°C for 7 days, the specimens underwent dry curing at 30°C and RH60%, and at the age of 28 days, they were subjected to the compressive strength test and Young's modulus test.

| Table 1. Overview of experiments. | Table 2. Combination of experimental parameters in free shrinkage experiment. |
|---|---|
| Experiment | Exper. parameter | Level |
| Shrinkage experiment | BFS additive dosage ratio (%) | 0, 20, 42 |
| | SO$_3$ dosage ratio (%) | 2.5, 3.5, 4.5 |
| | CaCO$_3$ dosage ratio (%) | 0, 3, 5, 7, 10 |
| Hydration experiment | Binder type | BLS(A), BA, OPC |
| | Ambient temperature (°C) | 30, 20, 10 |
| Concrete | Constitutive material combination in BFS | |
| BFS dosage ratio (%) | SO$_3$ dosage ratio (%) | CaCO$_3$ dosage ratio (%) |
| BLS(A)-2.5-3 | 20 | 2.5 | 3 |
| BLS(A)-2.5-5 | 20 | 2.5 | 5 |
| BLS(A)-2.5-7 | 20 | 2.5 | 7 |
| BLS(A)-3.5-3 | 20 | 3.5 | 3 |
| BLS(A)-3.5-5 | 20 | 3.5 | 5 |
| BLS(A)-3.5-7 | 20 | 3.5 | 7 |
| BLS(A)-4.5-3 | 20 | 4.5 | 3 |
| BLS(A)-4.5-5 | 20 | 4.5 | 5 |
| BLS(A)-4.5-7 | 20 | 4.5 | 7 |
| BA | 20 | 2.2 | - |
| BB | 42 | 2.2 | - |
| N | - | 2.2 | - |
Table 2 shows combination of additives in binder of concretes used for the free shrinkage experiment. According to the levels listed in Table 1, for BLS(A), a total of 9 different mix proportions were used by varying the SO₃ dosage ratio and the CaCO₃ dosage ratio among 3 levels, respectively. The water to binder ratio and unit water content of all BLS(A) concretes were 50% and 175 kg/m³, respectively, and the same values were adopted also for the BA, BB and N concretes used for comparison purposes. Table 3 lists the materials used. Cement OPC1 used for the free shrinkage experiment was admixed with 2.0% of SO₃ and 5% of blast furnace slag by mass ratio as trace additives during production. Ground granulated blast furnace slag BFS1 with negligible SO₃ content was used. With specific surface area of 4200 cm², which falls within the commonly used range, it meets the 4000 class requirement specified in JIS A 6206. The number of 4000 means nominal specific surface area in BFS powder. The BFS dosage ratios listed in Table 2 were determined as the total value including the aforementioned amounts included in the cement. Likewise, the SO₃ dosage ratios are the value taking into consideration the amount contained in the cement.

2.2. Hydration analysis experiment

In this experiment, paste that simulates the binder part of concrete was mixed and hydration reaction analysis by the XRD/Rietveld method was conducted. As shown in Table 4, the cement pastes used in the hydration analysis consisted of cement paste with the same mix proportions as BLS(A)-4.5-3 (denoted as BLS(A) in this experiment), cement paste equivalent to N-2.2-0 using only ordinary Portland cement (N), and cement paste equivalent to BA-2.2-0 (BA) used in the free shrinkage experiment.

The cement paste specimens for hydration analysis were mixed using the cement and binder ratios given in Table 4, and the materials listed in Table 3. Cement for chemical analysis from the Japan Cement Association was used, and BFS without added gypsum like that used for the free shrinkage experiment was selected. The chemical composition of each material is given in Table 5. The mixing was carried out in a 20°C environment in accordance with JIS R5201, and after mixing, mixed pastes were transferred to rooms at the respective temperatures of 10°C, 20°C and 30°C according to the temperature conditions, and the paste was then cast in a 4 × 4 × 16 cm formwork. After being kept sealed until the following day, the hardened paste was demolded, cut in 3 mm thick slices that were water cured at the various specified temperatures. At the material ages of 3, 7, 28, 91 days, the specimens were taken out from the water for hydration analysis. After measurement of the surface-dry condition mass, they were immersed in acetone for 3 hours to stop hydration. The specimens were then dried at 40°C for 3 hours, and they were then crushed and subjected to XRD measurement. XRD measurement and Rietveld analysis were performed on the above-described specimens. XRD measurement was performed using a rotating specimen stage and high-speed solid state detector, using as conditions target CuKα, tube voltage of 40 kV, tube current of 15 mA, scanning range of 5 to 70 deg. (2θ), and step of 0.02 deg. For Rietveld analysis, SIROQUANT Ver. 3 was used. For additional information about XRD measurement and Rietveld analysis, refer to Sagawa 2014.[5]

Table 3. Constitutive materials in experiments.

| Exp. type | Material | Symbol | Type | Density (g/cm³) |
|-----------|----------|--------|------|----------------|
| Shrinkage experiment | Portland cement | OPC1 | Ordinary Portland cement | 3.16 |
|             | BFS additive | BFS1 | BFS powder | 2.91 |
|             | CaSO₄ | CaSO₄ | Gypsum | 2.91 |
| Fine aggregate | CaCO₃ | CaCO₃ | Calcium carbonate powder | 2.71 |
|             | S1 | S1 | Crushed sand stone | 2.64 |
|             | S2 | S2 | Land sand | 2.61 |
| Coarse aggregate | G | G | Crushed sand stone | 2.65 |
| Chem. admix. | SP1 | SP1 | Polycarboxylate water reducer | 1.02 |
| Hydration Analysis experiment | Portland cement | OPC2 | Ordinary Portland cement | 3.16 |
|             | BFS additive | BFS2 | BFS powder | 2.91 |
|             | CaSO₄ | CaSO₄ | Same as in shrinkage exp. | 2.91 |
|             | CaCO₃ | CaCO₃ | Same as in shrinkage exp. | 2.71 |
3. Experimental results and discussion

Table 4. Mix proportion in hydration analysis constitutive experiment.

| Mix   | Water to Binder ratio | SO₃ Dosage Ratio (%) | CaCO₃ Dosage Ratio (%) | Mass ratio |
|-------|-----------------------|----------------------|------------------------|------------|
| N     | 2.0                   | -                    | 1.00                   | 2.00       |
| BA    | 50%                   | 2.0                  | 1.00                   | 1.59       |
| BLS(A)| 4.5                   | 3.0                  | 1.00                   | 1.43       |

Table 5. Chemical composition in materials.

| Constitutive material | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ | Na₂O | K₂O |
|-----------------------|------|-------|-------|-----|-----|-----|------|-----|
| OPC2                  | 21.3 | 5.09  | 3.15  | 65.4| 1.01| 2.01| 0.32 | 0.41|
| BFS2                  | 33.8 | 14.4  | 0.37  | 42.6| 6.15| 0.03| 0.21 | 0.29|
| CaCO₃                | 0.14 | 0.06  | 0.02  | 56.1| 0.21| -   | 0.01 | 0.01|
| CaSO₄              | 1.20 | 0.30  | 0.10  | 39.3| 0.20| 57.9| -    | -   |

3.1. Free shrinkage experimental results

Three diagrams in Figure 2 demonstrate the time-dependent change in free shrinkage strain of BLS(A), depending on different SO₃ dosage ratio. These diagrams show that the CaCO₃ dosage ratio does not have a significant influence on time-dependent change in free shrinkage strain. Further, they clearly show that the SO₃ dosage ratio has an important influence on strain behaviour prior to commencement of drying, and that the higher the dosage ratio, the smaller the amount of autogenous shrinkage strain prior to commencement of drying.

Figure 3 and Figure 4 show the influence of SO₃ and CaCO₃ on strain behaviour. Figure 3 shows the findings with regard to maximum expansion strain. Whereas the CaCO₃ dosage ratio has only a minor influence on maximum expansion strain, this figure demonstrates that increases in maximum expansion strain presumed to be due to increased ettringite production become conspicuous as the SO₃ dosage ratio increases. Figure 4 shows the influence of maximum expansion strain on free shrinkage strain after the drying period 182 days. As the maximum expansion strain becomes larger, the free shrinkage strain becomes smaller, and initial expansion can be seen to contribute to long term shrinkage strain reduction, as would be expected.

Figure 5 shows the influence of the SO₃ and CaCO₃ dosage ratios on compressive strength. Compared with N and BA, BLS(A), which uses a larger SO₃ dosage ratio and CaCO₃ dosage ratio, shows increased compressive strength. Moreover, in the same figure, compressive strength shows a tendency to increase as the SO₃ dosage ratio increases, except when the CaCO₃ dosage ratio is 7%. It is conceivable that the higher than usual amount of SO₃ causes increased generation of ettringite, which in turn promotes densification of the pore structure. Further, while there are cases when higher CaCO₃ dosage ratios result in decreased strength, at the higher SO₃ dosage ratios within the range considered in this study, an increase in compressive strength was actually seen for CaCO₃ dosage ratios up to about 5%.

3.2. Hydration analysis experiment results

Figure 6 shows the analysis results pertaining to the hydration degree of cement and BSF. In the legend for this figure, the numbers at the end indicate the ambient temperature (the same holds for the
following figures). In this figure, the hydration degree of both the cement and BFS clearly show a tendency to increase as the ambient temperature becomes higher. At the ambient temperature of 30°C, no significant difference in the hydration degree of cement and blast furnace slag is seen for BA-30 and BLS(A)-30, and the influence of increases of SO\(_3\) and CaCO\(_3\) is negligible. The hydration degree of BFS is known to be low compared with cement [4], and in this study too, whereas the hydration degree of cement at 30°C in upper diagram of Figure 6 exceeded 90% at 91 days, the hydration degree of BFS in lower diagram of Figure 6 is only about 70%.

Figure 7 shows the change with time of the hydration degree of C\(_3\)S and C\(_3\)A. The hydration degree of C\(_3\)S in upper diagram of Figure 7 increases with the ambient temperature for BLS(A), as expected. Comparing the results of N, BA and BLS(A) at the ambient temperature of 30°C, there is no remarkable difference in the hydration degree of C\(_3\)S. On the other hand, the hydration degree of C\(_3\)A at the ambient temperature of 30°C in lower diagram of Figure 7 tends to be slightly delayed for BLS(A). Given that gypsum works to delay the hydration of C\(_3\)A, it can be inferred that this delaying effect was stronger in BLS(A) owing to its higher gypsum content. This tendency is consistent with what is reported in the referenced literature [4] for the test conducted at 20°C.

![Figure 2. Strain history in free shrinkage test, left: SO3 dosage ratio 2.5%, centre: 3.5%, and right: 4.5%](image)

![Figure 3. Effects of SO3 and CaCO3 on max.expansive strain.](image)

![Figure 4. Effects of max. expansive strain on free shrinkage strain after 182 day dry.](image)

![Figure 5. Impacts of trace additives on compressive strength of BLS(A).](image)
Figure 8 shows the time-dependent change in ettringite (AFt) and monosulfate (AFm) production. The vertical axis in the figure indicates the amount of hydrate product per sample. AFt in upper diagram in Figure 8 is stably generated in the case of BLS(A) regardless of ambient temperature, but is not generated in the case of BA and N. In lower diagram of Figure 8, AFm does not occur in BLS(A) in contrast to AFt, but it occurs in BA and N. Figure 9 shows the time-dependent change in residual C3A amount per sample. In this figure, C3A of BLS(A) remains from the material age of 3 days, and is still not gone at 28 days. Figure 10 shows the time-dependent change in residual gypsum amount per sample. In this figure, gypsum can be seen to be consumed by 28 days regardless of ambient temperature even when it is increased to 4.5% in BLS(A). If a substantial amount of ettringite remains unreacted, problems such as cracking caused by delayed ettringite formation (DEF) may occur. In Figure 10, considering the possibility of Rietveld analysis error, it is possible that the gypsum is not entirely gone. However, this finding in which gypsum does not remain in large amount and hence there is little risk of DEF is important knowledge for the durability of concrete.

3.3 Influence of composition of hydrate product on free shrinkage

Figure 11 shows the influence of the SO3 dosage ratio on free shrinkage strain after 182 days of drying as obtained from the free shrinkage experiment, along with the hydration degree of ettringite and monosulfate hydrate as obtained from the hydration analysis experiment. From this figure, we can see that the aforementioned free shrinkage strain becomes smaller in the SO3 dosage ratio range of 2.5%, where monosulfate is dominant, to 5%, where ettringite dominates. These results show that, in high summer/tropical temperatures using the equivalent of low volume BFS cement in this study, it is possible to reduce free shrinkage by leaving a large amount of ettringite as hydrate product, and that this tendency can be realized by increasing the amount of gypsum. This is consistent with the existing literature reporting on the use of medium volume BFS cement at the ambient temperature of 20°C.
It is known that in BFS cement concrete, ettringite, which is generated in the early stage of hardening due to the reaction of C₃A and C₄AF of Portland cement, the calcium aluminate component of blast furnace slag, and gypsum, reacts again with residual C₃A and C₄AF as gypsum becomes depleted, and then changes into monosulfate[6]. In the case of medium volume BFS cement concrete, it has been reported that the conversion of this ettringite to monosulfate causes a sharp decrease in volume resulting in a significant increase in autogenous shrinkage, and that this conversion is suppressed by an increase in gypsum[7].

However, the results of this study include also differences from the above-mentioned previous findings. In Figure 9, some unreacted C₃A remains in the BLS(A)-30 specimen at the ambient temperature of 30°C even at 28 days, whereas Figure 10 shows all the gypsum to be gone at the same age. Under such circumstances, there is the possibility that AFt changes to AFm, but this did not occur in this experiment. Detailed elucidation of the influence of the amount of gypsum in blast furnace slag cement Class A concrete on the stable formation of ettringite in high summer temperatures will be a future topic of research.

4. Conclusions

This study clarified for blast furnace slag cement Class A concrete the effect that the addition of gypsum and calcium carbonate as trace additives can have on strength and shrinkage under high summertime ambient temperature of 30°C, and also examined the relation between hydrate products and shrinkage when gypsum and calcium carbonate dosages are increased. The following findings were established from the study.

(1) Increasing the amount of gypsum and calcium carbonate caused an increase in compressive strength within the scope of this study. This is considered to be due to the formation of ettringite, which in turn appears to densify the pore structure.

(2) A small increase in the dosage of trace additives was found to have a shrinkage reduction effect along with causing a certain amount of initial expansion.

(3) It is supposed that suppression of the formation of monosulfate in the case of normal low volume blast furnace slag cement, which includes negligible amount of trace additives, contributes to this shrinkage reduction effect.

(4) Even when the amount of gypsum was increased to 4.5%, it was found that only small amounts remained after 28 days regardless of ambient temperature, and that the risk of DEF was small.

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