PROPERTIES OF PORTLAND BLAST FURNACE SLAG CEMENTS AFFECTING THEIR AUTOGENOUS SHRINKAGE BEHAVIORS

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Abstract: In Japan, Portland blast furnace slag cements that contain 30-60% of blast furnace slag (BFS) are classified in the slag cement class B in JIS R 5211. Even if slag cements are classified in a category, different autogenous shrinkage behaviors are observed among them. In this study, class B slag cements are collected from eight different plants in Japan. Physical and chemical properties of slag cements are investigated to find the cause of different shrinkage behavior. Physical properties of slag cement are expressed in terms of surface area, mean particle size and particle size distribution. The experimental results showed that the collected slag cements can be differentiated into two different groups based on physical properties. However, different behaviors of autogenous shrinkage cannot be explained, because slag cements, which contain finer particles, have not displayed significant differences in the shrinkage of mortar specimen. Therefore, chemical properties of slag cement could be the main reasons behind the different shrinkage behavior among slag cements. To compare the chemical property of slag cements, the phases of mineral (C₃S, C₃A, etc.) and content of cement and slag mineral (%) in slag cements are analyzed by thermal gravimetric analysis (TGA) and X-ray diffraction (XRD) Rietveld analysis. The results showed that in each plant, different types of BFS are used for producing the slag blended cements, and different quantity levels of slag minerals are found in BFS used in each cement plant. In slag cements classified as Class B in JIS R 5211, different physical and chemical properties are observed. However, the chemical properties of BFS in slag cement mainly influence the shrinkage behavior of slag cement. If the user of BFS cement is concerned about the shrinkage behavior of the concrete, the chemical composition of BFS should be checked to ensure that the concrete has sufficient resistivity against shrinkage.

Keywords: Portland blast furnace slag cements; phase of mineral; particle size distribution; Thermo-gravimetric analysis; X-ray deflection measurement.

1. Introduction

Blast furnace slag (BFS) is a by-product of the steel industry that is considered a sustainable alternative to Ordinary Portland cement (OPC). Concrete with slag cement is known for good durability properties and long-term strength development due to its dense microstructure. Japan is one of the major users of blended cements containing BFS and the common slag blended cement is specified as class B in JIS 5211 and it contains blast furnace slag in the range of 30% to 60%.

However, even if supplied class B in JIS 5211 Slag cement concrete is satisfying the demand, different behaviors such as setting time, heat of hydration, shrinkage, etc. in concrete are observed, and some previous research (Sagawa et al., 2010, Nito et al., 2005, Ekaputri et al., 2010) has also reported that commercial cements, classified in slag cement class B with satisfactory existing allowable range of cement properties, are exhibiting different behavior in autogenous shrinkage.

Therefore, slag cements, which are commercially available in Japan, should be differentiated through the physical and chemical properties, to determine the cause of different shrinkage behavior among slag cements; additionally, an investigation should be conducted into what properties of slag cement are mainly influencing the behavior of shrinkage of concrete.

In this study, physical properties of slag cements are analyzed through laser diffraction test; to compare the chemical properties of slag cements, thermal gravimetric analysis (TGA) and X-ray diffraction (XRD) Rietveld analysis are conducted.
2. Properties, behavior of compressive strength and autogenous shrinkage of OPC and Slag cements

2.1 Properties of OPC and Slag cements

In this experimental study, eight different commercially use slag cements that are available in Japan, are collected and they are coded as sca, scb, scc, scd, sce, scf, scg, sch and opc which is used as a check system. Table 1 shows that, the percentages of BFS and physical properties of OPC and slag cements.

Table 1: Properties of OPC and Slag cements

| No | Symbol | Cement type | BFS [%] | Density [kg/m³] | Surface area [cm²/g] |
|----|--------|-------------|---------|-----------------|---------------------|
| 1  | opc    | Ordinary Portland cement, JIS R 5210 | 0       | 3.15            | 3430                |
| 2  | sca    | Slag cement class B, JIS R 5211     | 40-45   | 3.02            | 3620                |
| 3  | scb    |                                          | 40-45   | 3.04            | 3750                |
| 4  | sce    |                                          | 40-45   | 3.04            | 3820                |
| 5  | scd    |                                          | 40-45   | 3.04            | 4140                |
| 6  | sce    |                                          | 40-45   | 3.04            | 4170                |
| 7  | scf    |                                          | 40-45   | 3.05            | 3790                |
| 8  | scg    |                                          | 40-45   | 3.04            | 3860                |

2.2 Compressive strength of OPC and Slag cements

The compression test results are from each data sheet of cement plant, and the experimental procedure was followed according to the JIS B 5201 for all samples. Cube mortar specimens, with 40×40×40 mm dimensions, were casted, to test the compressive strength of OPC, and slag cements and fresh mortar were prepared by 1:3:0.5 mass ratio between cement, sand and water, respectively. All casted specimens were cured under a constant temperature at 20°C and a relative humidity of 50%. All specimens were demolded after 24 hours, and then immersed into water at a constant temperature of 20°C. Compressive strength tests were conducted at 3, 7 and 28 days of age.

Figure 1 shows the compressive strength at 3, 7 and 28 days of collected OPC and slag cements. Different compressive strength developments are observed among the OPC and slag cements at 3 and 7 days. However, it is interesting to note that at 28 days, the OPC and Slag cements are showing an almost equal compressive strength development.

2.3 Autogenous shrinkage of OPC and Slag cements

Cylindrical mortar specimens, of ø 5×10 cm, were used to measure autogenous shrinkage and fresh mortar (Takahashi and Suntharalingam 2018); they were prepared with 35% of water to binder ratio and sand where the maximum aggregate size and density were 2 mm and 2.63 g/cm³, respectively, as fine aggregate for 40% volume of fresh mortar. To improve workability of the fresh mortar, a water-reducing agent of 0.55% cement weight was used (BASF 6500 XD2). Strain gauges of the embedded type (KM-30-120-H2-11) are used to measure the autogenous shrinkages of different OPC and slag cement mortar specimens, under sealed conditions at a constant temperature 20°C (Ekaputri et al., 2010); the results are processed to eliminate the effects of the thermal expansions, through the proposed model of early age heat expansion coefficients by Holt (2001) and temperature histories at the early ages.

The results showed that slag cements had larger autogenous shrinkage than ordinary Portland cement; slag cements, which are classified in a particular category, are showing differences in level of autogenous shrinkage behavior, with the results being presented in Figure 2.
It is clearly shown that, even if collected slag cements are classified in a category in JIS R 5211, different autogenous shrinkage behaviors among slag cements, are observed, while almost equal compressive strength among OPC and slag cements at 56 days of age. Therefore, physical and chemical properties of slag cements are investigated to find the cause of different shrinkage behavior.

3. Physical properties of OPC and Slag cements

The particle size and distributions of OPC and slag cements were measured using a laser diffraction technique, through the SALD-3000J particle Size Analyzer in the range of particle size from 0.1 µm to 2000 µm. The mean particle size and the relationship between surface area and mean particle size of OPC and Slag cements are shown in Figures 3 and 4, respectively.

4. XRD Rietveld and TGA analysis

The Shimadzu XRD 6100 machine was used to determine the diffraction profile pattern for OPC and slag cements sample in XRD test, and the measurement of XRD was conducted using an internal standard substance with an average particle diameter of 3 µm. Corundum (α1 Al2O3) was added by 10% of sample. The XRD measurement conditions were as follows: target Cu-Kα, tube voltage 45 kV, tube current 40 mA;
range of scanning from 5 to 70 degrees; 2θ step width 0.02 deg. Rietveld analysis is distributed by Siroquant version 3 software. Micro absorption was corrected with the particle diameter of quantitative minerals being 10 μm.

4.1 Quantitative value of OPC minerals in Slag cement

In the quantitative value of cement mineral in slag cement, the following minerals were subjected for Rietveld analysis, C₃S (Belov), C₃S (mono.), C₂S, beta, C₃A, alpha, C₃A (cubic), C₃A (ortho.), C₄AF, Periclase, Mayenite, Gypsum, Calcite 2, Portlandite, Bassanite of cement mineral and as internal standard substance corundum (α₁ Al₂O₃). Obtained quantitative values for cement mineral in Rietveld analysis are corrected by the internal standard substance amount and ignition loss according to equation (1).

\[ W_{CX} = \frac{W_x}{W_C} \times 10^* (1 + \frac{Ig}{100}) \]  

Where

- \( W_{CX} \) = Corrected quantitative value (%)
- \( W_x \) = Quantitative value of mineral before correction (%)
- \( W_C \) = Quantitative value of corundum (%)
- \( Ig \) = Ignition loss between 30° C and before starting the crystallization effect of slag materials (%)

In determining ignition loss by TGA test, mass losses are measured between 30 and 1000° C and they can be used for Ordinary Portland cement that does not contain BFS. However, when heating the slag cement in the range between 30 and 1000° C, further losses or increases in weight of slag cement sample nearly above 760° C temperature were observed; this is because of the slag materials being in the form of amorphous material nearly below 760° C temperature. However, when continuously heating slag cement above 760° C, slag materials start to shift into their crystal forms.

Figure 5 shows that slag materials in scd start to transform from amorphous phase to crystal form, above 760° C. Therefore, the quantitative value of each mineral should be corrected with ignition loss, to compare the percentage of each minerals in slag cement before the start crystallization effect, for an accurate analysis. Here, to correct quantitative values of each mineral, ignition loss of slag cements is calculated at weight loss temperature between 30° C, and before starting the crystallization effect of slag materials.

![Figure 5: Mean particle size of OPC and Slag cements](image)

Figure 6 shows that the corrected quantitative value of main cement mineral (C₃S and C₂S) in OPC, which were used to blend with blast furnace slag to produce slag cements in each plant (here, the percentage of each cement minerals were calculated without considering the blast furnace slag portion in slag cement). The result shows that significant differences were observed in percentages of C₃S and C₂S of used OPC for producing slag cement. However, the pozzolanic reaction in slag cement is what mainly decides the long-term behavior of autogenous shrinkage of mortar specimen. Therefore, the content of slag material should be analyzed to understand behavior of autogenous shrinkage.

![Figure 6: Corrected quantitative value of main mineral (C₃S and C₂S)](image)
4.2. Quantitative value of crystallized BFS minerals in slag cements

BFS fine powder is in amorphous phase in slag cement. Therefore, BFS should be transformed into a crystal, through heat treatment for XRD test. In TGA test, it is clearly observed that if heated nearly above 760 °C, the blast furnace slag starts to obtain a crystal structure. Sagawa and Nawa (2006) proposed that, for determining the content of BFS in slag cement, the sample should be heat-treated at 900 °C for 30 minutes to crystallize slag material; as for the above crystallization conditions, a complete crystallization of the slag, and a minimization the decomposition of the cement mineral, can be achieved.

Due to the aforementioned heating process, there was C$_2$S (α'L), which was thought to have been generated by decomposition of C$_3$S in cement mineral and blast furnace slag fine powder changed into Gehlenite (2CaO·Al$_2$O$_3$·SiO$_2$), Akermanite(2CaO·MgO·2SiO$_2$), Merwinite(3CaO·MgO·2SiO$_2$), which are represented by abbreviations of C$_2$AS, C$_2$MS$_2$ and C$_3$MS$_2$, respectively. The crystal structure of the above minerals was based on data preset in Rietveld analysis software (Siroquant version3).

The following cement and crystallized slag minerals were the subject of Rietveld analysis: C$_2$S (Belov), C$_3$S (mono.), C$_2$S(beta, C$_2$S, alpha, C$_3$A, (cubic), C$_4$AF, Anhydrite, Wollastonite, Lime of cement mineral, Akermanite, Gehlenite, Merwinite, Mayenite of crystallized slag mineral and as internal standard substance corundum (α 1 Al$_2$O$_3$).

Obtained quantitative values of cement and crystallized slag mineral in Rietveld analysis are corrected by the internal standard substance amount and ignition loss according to equation (2).

$$W_{CX} = \frac{W_X}{W_C} \times 10^* (1-Ig/100) \quad (2)$$

Where
- $W_{CX}$ = Corrected quantitative value (%)
- $W_X$ = Quantitative value of mineral before correction (%)
- $W_C$ = Quantitative value of corundum (%)
- Ig = Ignition loss between starting point of the crystallization of slag materials and end of heat-treatment (%)

The quantitative value of each slag and cement mineral in heat-treated samples (at 900 °C for 30 minutes) are listed with a degree of crystallization effect in slag material between the starting temperature of crystallization (at nearly 760 °C) and the end of heat treatment. Therefore, to accurately analyzing, the quantitative value should be corrected with ignition loss when comparing the percentage of each mineral in slag cement, at the starting point of crystallization effect. In this heat-treated sample analysis, Ignition losses are calculated for correcting quantitative value of each mineral weight loss between the starting point of the crystallization of slag materials and end of heat treatment.

Figure 7 shows the corrected quantitative value of crystallized slag minerals (C$_2$AS, C$_2$MS$_2$ and C$_3$MS$_2$) at the starting point of slag mineral crystallization (at nearly 760 °C) through XRD Rietveld method in blended slag cements. Among slag cements, several percentage differences are observed in each crystallized slag minerals: sca have the higher content of Merwinite and Gehlenite, compared with other slag cements and Akermanite in sce. Figure 8 shows the sum of corrected quantitative value of crystallized slag minerals (C$_2$AS, C$_2$MS$_2$ and C$_3$MS$_2$) at the starting point of crystallization of slag mineral in slag cements: among these, several percentage changes were observed in total crystallized slag minerals. There are two possibilities for this difference in content of total crystallized slag mineral in slag cements, which are
Figure 7: Content of crystalized slag minerals in slag cements

Figure 8: Content of crystalized slag minerals in slag cements

a) Mixing percentage of blast furnace slag and

b) Chemical composition of blast furnace slag (CaO, SiO$_2$, etc.)

The autogenous shrinkages of slag cements at 3, 7, 28 and 56 days are compared with the sum of crystalized slag minerals (Akermanite + Gehlenite + Merwinite), which is shown in Figure 9. The higher the content of crystalized slag in cement, the greater the autogenous shrinkage. The strong relationship between content of crystallized slag and autogenous shrinkage can be observed at the 56 days period, because of the pozzolanic reaction by slag mineral will be influenced at a later stage. Therefore, behavior differences in autogenous shrinkage among slag cements are affected by the level of crystalized slag mineral in heat treated slag cements.

Figure 9: Relationship between Autogenous shrinkage and crystalized slag minerals of Slag cements

Additionally, the types of BFS used for producing the blending slag cements in each manufacturing plant, are analyzed in terms of crystalized slag minerals composition. Compositions of crystalized slag minerals in blended slag cements is shown in Figure 10, and they are calculated through the percentage of each crystallized slag mineral in total crystallized slag mineral by equation (3).

\[ P_s = \left[ \frac{W_s}{\Sigma W_s} \right] \times 100 \]  

(3)

Where

- \( P_s \) = The percentage of mineral in blast furnace slag (%)
- \( W_s \) = Quantitative value of each slag mineral in slag cement (%)
- \( \Sigma W_s \) = Sum of Quantitative value of slag mineral in slag cement (%)

From this analysis, different compositions of crystallized slag minerals are observed in slag cements from each plant. sca has the higher percentage of Merwinite among crystalized slag minerals, compared with other slag cements. Similar types of slags were used for blending with OPC to produce scb and scd, and, in sce and scf, nearly same type of slag without containing Gehlenite mineral were observed in heat treated samples.
From studies about slag cement chemical properties, different quantities and chemical compositions of slag are observed in collected slag cements (Class B in JIS 5211). These different blast furnace chemical compositions change the Ca/Si ratio and the density of C-S-H product among slag cements, due to the pozzolanic reaction (Sagawa and Nawa, 2010), which is shown in Figure 12. The Ca/Si ratio and the density of C-S-H product are mainly influencing the autogenous shrinkage behavior of cement, and low densities of C-S-H produces larger shrinkage than high densities of C-S-H product, a fact reported by Maruyama and Kurihara (2016).

5. Conclusion

In this study, slag cement (Class B in JIS 5211), which is commercially available in Japan, is differentiated in two different groups based on their physical properties. However, the physical properties of slag cement do not constitute a major influencing factor for the different shrinkage behavior, because slag cements contain finer particles that do not significantly affect autogenous shrinkage behavior. In chemical property analysis, the different quantities and types of BFS that were used to produce slag cements, are studied by TGA and XRD Rietveld analysis; autogenous shrinkage is more correlated with the content of crystallized slag minerals in slag cement at 56 days of hydration. If the user of BFS cement is concerned about the shrinkage behavior of the concrete, the chemical composition of BFS should be
checked, to ensure that the concrete has sufficient resistivity against shrinkage.

Acknowledgements

This study was financially supported by JSPS KAKENHI Grant No. 17H01284 and Research scholarship by Asian Development Bank-JSP.

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