Fluidity of slag cement paste depending on types and replacement ratios of gypsum

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The aim of this research is evaluating the flow behavior of slag cement paste depending on various types of gypsum and their replacement ratio. In this research, gypsum was added for the slag cement to induce ettringite formation and thus achieve improved and stable strength. Although natural anhydrite gypsum is primarily used for this purpose, various other types of gypsum have been studied as potential additives for slag cement. However, these studies have focused on the reaction mechanisms or hardened properties. Hence, in this research, using workability measurement methods and a rheological test method, six different types of gypsum were evaluated: anhydrite, \( \alpha \), and \( \beta \) hemihydrate, dihydrate, desulfurized gypsums and combined gypsum of desulfurized and anhydrite gypsums. Experiment results showed that the dissolution rate of different gypsums can significantly influence the fluidity of the pastes.

Key words: Slag cement paste, Gypsum type, Gypsum replacing ratio, Rheology.

\section*{Introduction}

Today’s complex infrastructure requires that concrete have high performance of high workability, strength, and durability. To achieve these high performance characteristics, supplementary cementitious materials (SCMs) have been used, especially blast furnace slag-which has been used widely as an essential additive for high performance concrete due to its low cost, improved long-term strength [1-4], decreased heat of hydration [5-9], and improved permeability of concrete [10-14].

Blast furnace slag (BFS), a byproduct of the steel manufacturing industry, is obtained through the quenching process, and surfaces as an amorphous or glassy material [15]. Because of the characteristics of the glassy material, the hydration of BFS is defined as latent hydraulic material which hydrates at a very slow reaction speed [5-7, 10, 16]. Additionally, when BFS in mixture contacts water, \( \text{Ca}^{2+} \) ion is dissolved and thus a less permeable membrane is produced on the surface of the blast furnace slag. Since this membrane prevents intrusion of water to the BFS particle and additional dissolution of ions from the BFS particle, the hydration of BFS is delayed and giving it less initial strength and an extended setup of remaining formwork. As a solution to this drawback, gypsum is added 1-4\% during the milling process of BFS to produce ettringite [17-19] continuously with aluminate in cement after the setting for improving initial strength of slag cement concrete. As for the type of added gypsum in BFS, natural anhydrite gypsum is used and recently desulfurized gypsum obtained from the desulfurizing process was used partially, or entirely. Additionally, the properties of slag cement concrete including various types of gypsum have been researched [20, 21]. Regarding the influence of gypsums, Seo \textit{et al.} [22] evaluated the influence of type II anhydrite gypsum and various types of dihydrate gypsums with their replacing ratios. By Jeong \textit{et al.} [23], to improve the initial strength of slag cement concrete, six different types of gypsum including natural gypsum, phosphor gypsum, and desulfurized gypsum were tested depending on the replacing ratios.

Although former studies [24-26] have been done on various gypsum based on their physical properties, setting time, and compressive strength at different replacement ratios in cement mixes, there is limited research [27] on the fresh state properties of cement paste incorporating gypsum and BFS through the slump flow test method. However, the slump flow test method cannot assess the performance of the fresh state slag cement paste quantitatively [28]. Therefore, in this research, by evaluating the influence of gypsum types and gypsum replacement rate on the fresh state properties, especially on the workability of slag cement paste, fundamental data needed to improve the quality of concrete incorporating BFS and gypsum was obtained.

\section*{Experiment}

\subsection*{Experimental design}

The experiment was designed to evaluate the influence
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of gypsum on rheological properties of slag cement paste incorporating blast furnace slag. The detailed experimental plan is summarized in Table 1, and the mixing designs of the tested mixtures are shown in Table 2. For the mixtures, water-to-binder ratio was fixed at 0.45 for all mixtures. For the binder, blast furnace slag replaced 40% of cement powder mass. To evaluate the influence of gypsum type and replacement ratio, control mixture was tested without gypsum. In addition, six different mixtures with six different types of gypsum (dihydrate, anhydrite, α-hemihydrate, β-hemihydrate, desulfurized gypsum, and mixed gypsum of desulfurized gypsum and anhydrite gypsum) were prepared. The replacement ratios of the gypsum to blast furnace slag were 0, 2, 4, and 6% based on the mass of blast furnace slag in the binder. Only fresh state cementitious paste properties were tested within 30 minutes from the time samples were mixed. Comparisons were based on properties of the gypsum/BFS mixtures tested by table flow, grout flow, and rotational rheology.

Materials
In this research, all tests were conducted using paste phase with various binders. Ordinary Portland cement was used from the South Korean market. The physical properties of the cement are shown in Table 3 with properties similar to Type I cement from ASTM C150 [29]. As a main replacement powder for cement, the blast furnace slag was a commercially available product in South Korea and according to the information provided by manufacturer, its specific gravity was 2.85 and fineness was 4,460 cm$^2$/g. The chemical composition of blast furnace slag and various gypsum additives are summarized in Table 4. The dihydrate gypsum used was a reagent grade product. For the hemihydrate gypsiums used, α, and β hemihydrate gypsyums were commercially available products. The desulfurized gypsum was pulverized from the substance collected by a desulfurizing precipitator during the refining process of the Korean H company. The anhydrite gypsum was a natural anhydrite gypsum.

Tests methods
The slag cement paste mixtures were mixed by following ASTM C305 [30] standard with 5 L planetary mixer. The tests in this research were conducted to evaluate the fluidity of the fresh state mixtures. The

<table>
<thead>
<tr>
<th>Table 1. Experimental design.</th>
<th>W/B (%)*</th>
<th>45</th>
<th>BS/B (%)**</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture conditions</td>
<td>Gypsum type</td>
<td>Anhydrite gypsum</td>
<td>α- hemihydrate gypsum</td>
<td>β-hemihydrate gypsum</td>
</tr>
<tr>
<td>Gypsum replacement ratio (%)</td>
<td>0, 2, 4, 6</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Tests</td>
<td>Table flow</td>
<td>Grout flow</td>
<td>Rheometer test (flow curve)</td>
<td></td>
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<tr>
<td>*W/B: water-to-binder ratio.**BS/B: blast furnace slag-to-binder ratio</td>
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</table>

<table>
<thead>
<tr>
<th>Table 2. Mix proportions.</th>
<th>W/B (%)*</th>
<th>BS/B (%)**</th>
<th>Gypsum replacement ratio (%)</th>
<th>Unit weight (kg/m$^3$)***</th>
</tr>
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<tr>
<td></td>
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<td></td>
<td></td>
<td>W</td>
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<td>2</td>
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<td>227</td>
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<tr>
<td></td>
<td></td>
<td>6</td>
<td>170</td>
<td>227</td>
</tr>
</tbody>
</table>

*W/B: water-to-binder ratio.
**BS/B: blast furnace slag-to-binder ratio.
***W: water, C: cement, BS: blast furnace slag, S: sand (crushed sand).

Materials

<table>
<thead>
<tr>
<th>Table 3. Physical properties of cement.</th>
<th>Density (g/cm$^3$)</th>
<th>Fineness (cm$^2$/g)</th>
<th>Setting time (min.)</th>
<th>Compressive strength (MPa)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Final</td>
<td>3 D</td>
<td>7 D</td>
</tr>
<tr>
<td></td>
<td>3.15</td>
<td>3.483</td>
<td>208</td>
<td>351</td>
</tr>
</tbody>
</table>

<table>
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<tr>
<th>Table 4. Chemical composition of the binding materials.</th>
<th>Chemical composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blast furnace slag</td>
<td>CaO</td>
</tr>
<tr>
<td>39.8</td>
<td>32.0</td>
</tr>
<tr>
<td>Anhydrite gypsum</td>
<td>33.7</td>
</tr>
<tr>
<td>α-hemihydrate gypsum</td>
<td>32.6</td>
</tr>
<tr>
<td>β-hemihydrate gypsum</td>
<td>34.9</td>
</tr>
<tr>
<td>Dihydrate gypsum</td>
<td>33.4</td>
</tr>
<tr>
<td>Desulfurized gypsum</td>
<td>44.7</td>
</tr>
</tbody>
</table>
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Table flow test was conducted following ASTM C1437 [31] standard. The grout flow test was similar to the test method of ASTM C939 [32], while the dimension of the funnel was different as shown in Figure 1. For the grout flow test, the flow time for every 100 ml of pastes were measured and recorded. For the rheological test, R/S Solids type rheometer from Brookfield, (Middleboro, Massachusetts, USA) was used. The spindle was vane-shaped with a width and height of 30 × 60 mm, respectively, as shown in Figure 2. To measure the flow curve of the mixtures, the shear rate was applied with an increased shear rate from 0.1 s⁻¹ to 10 s⁻¹, and 10 points of the shear stress values were measured and recorded. The applied shear rate range with relatively low values were determined to prevent the slip of the spindle and to simulate the actual level of shear force on the slag cement paste in concrete flow. Since the flow curve of the cementitious materials is generally linear, rheological parameters were calculated based on the Bingham model [33] as follows:

\[ \tau = \tau_y + \mu \gamma \]  

where, \( \tau \), \( \dot{\gamma} \) and are shear stress and shear rate, respectively, from the vertical and horizontal axis of the flow curve. \( \tau_y \) is yield stress, which can be obtained from the intersection of the flow curve to the vertical axis (shear stress), and \( \mu \) is plastic viscosity obtained from the slope of the flow curve.

Results and Discussions

Flow

The influence of types and replacement ratios of gypsums on flow of slag cement paste right after the mixing and in 30 minutes is shown in Figure 3. For flow values obtained from the test conducted right after the mixing, the control mixture without gypsum showed 175 mm of flow value and all the mixtures with various gypsums except for \( \beta \) hemihydrate gypsum showed flow values within the range of 175 ± 5 mm. These trends indicate no significant effect depending on the types and replacement ratios of the gypsums except for \( \beta \) hemihydrate gypsum. In the case of the mixture with \( \beta \) hemihydrate gypsum, the flow values clearly decreased as the replacement ratio increased.

Thirty minutes after mixing, the general values of flow were decreased over 15 mm compared to the flow values measured right after mixing. The influence of the replacement ratios was very little for dihydrate gypsum.
and anhydrite gypsum while $\alpha$ and $\beta$ hemihydrate, desulfurized gypsums and the combined gypsum of desulfurized gypsum and anhydrite gypsum showed decreased flow with increased replacement ratio. Especially, in the case of $\alpha$ hemihydrate gypsum, a flow value decreased significantly as the replacement ratio was increased. Hemihydrate gypsums have a fast dissolution rate and thus dissolve $\text{Ca}^{2+}$ and $\text{SO}_4^{2-}$ ions into the suspension (slag cement paste), which causes supersaturating conditions of the suspension. Consequently, this supersaturated $\text{Ca}^{2+}$ and $\text{SO}_4^{2-}$ ions of the suspension causes reprecipitation of the dihydrate gypsum, and thus the suspension lost fluidity. Meanwhile, in the case of $\beta$ hemihydrate gypsum, the most decreased trend of flow value was observed from the flow test result conducted right after the mixing. It can be state that the $\beta$ hemihydrate gypsum which has faster dissolution rate than $\alpha$ hemihydrate gypsum produced supersaturated conditions with $\text{SO}_3$ right after the mixing with a so-called false set where recrystallization of hemihydrate gypsum to dihydrate gypsum so that the suspension lost fluidity. Therefore, in the case of adopting hemihydrate gypsum for slag cement, additional solution would be needed to maintain the desired range of fluidity.

**Grout flow**

The original purpose of the grout flow test is evaluating the filling performance of the hydraulic grout for pre-placed aggregate concrete. However, in this research, this test method was used to evaluate the fluidity of the paste-phase material of slag cement. Figures 4 and 5 show the influences of various types of gypsum and gypsum replacement ratios on grout flow values right after the mixing and at 30 minutes after the mixing. The grout flow value means the flowing down time duration for 100 ml of the paste sample. The grout flow time durations for the suspensions measured right after mixing were for all mixtures with gypsum except for $\beta$ hemihydrate gypsum, which showed a shorter flow duration than the control mixture without gypsum. However, the differences are not significant, so it is considered that there was no influence on fluidity of slag cement paste depending on gypsum types and replacement ratios except for $\beta$ hemihydrate gypsum at early age. On the other hand, in the case of the mixture including $\beta$ hemihydrate gypsum, a very long time was taken for the mixture to flow through including 2% of $\alpha$ hemihydrate gypsum; in fact, the flow time could not be measured because the flow time duration was too long for the mixtures with more than 4% gypsum.

The grout flow values at 30 minutes after mixing generally increased about 10 to 30 seconds comparing the grout flow values right after the mixing. Especially, for the mixtures including $\alpha$, and $\beta$ hemihydrate, and desulfurized gypsums, this increased grout flow time was clearly shown while other mixtures with different gypsum showed shorter time durations than the control mixture. In the case of the mixtures with $\alpha$, and $\beta$ hemihydrate gypsum, when the replacement ratio was 2%, the entire sample volume (500 ml) in the cone could not be flown out. Furthermore, when the replacement ratio was higher than 4%, it was impossible to measure the grout flow time duration for 100 ml because the sample could not flow out 100 ml in the time given. It is similar to the result in Chapter 3.1 where a very high dissolution rate of hemihydrate gypsums contributed to losing the fluidity of the suspension by rapid setting of the binder system. Therefore, the mixture with hemihydrate needs more mixing water to overcome the aggregation of the binder particles and add adequate fluidity to the paste. The trend of increasing grout flow time duration
Fluidity of slag cement paste depending on types and replacement ratios of gypsum was enhanced with the order of \( \beta \) hemihydrate, \( \alpha \) hemihydrate, desulfurized gypsum, and the combined gypsum of desulfurized and anhydrite gypsums. In spite of this increasing trend, in the case of dihydrate and anhydrite gypsums, as the replacement ratio increased, the grout flow time duration was shortened instead of the control mixture without gypsum. It can be stated that although dihydrate and anhydrite gypsums with low dissolution rates did not produce rapid setting, as the dissolution of gypsum proceeds, the concentration of SO\(_{3}^{2-}\) anion ions increases. This increased concentration of SO\(_{3}^{2-}\) anion ions covered reactive cementitious particles, so the concentration of reactive cementitious powder decreased compared to the control mixture without gypsum.

**Rheology test**

*Flow curve*

For rheological behaviors of the mixtures with various types and replacement ratios of gypsum, flow curves of each mixture were measured right after the mixing and at 30 minutes after the mixing as shown in Figures 6 and 7, respectively. The shear stress of the control mixture without gypsum showed about 57 to 164 Pa range. The mixtures with dihydrate, anhydrite, desulfurized gypsums and combined gypsum of desulfurized and anhydrite gypsums showed lower shear stress in the range of 46 to 163 Pa, so the values were similar or lower than the shear stress of the control mixture without gypsum.

![Flow curve](image)

Fig. 5. Influence of various gypsums replacement ratio on grout flow results at 30 minutes after the mixing.

![Flow curve](image)

Fig. 6. Influence of various gypsums replacement ratio on flow curves right after the mixing.
For $\alpha$ and $\beta$ dihydrate gypsum, however, a shear stress was range of 72 to 188 Pa, and 103 to 327 Pa, respectively; thus, they showed higher shear stress values than the control mixture. At 30 minute after the mixing, the shear stress was increased generally 50 to 200 Pa. In the case of the mixtures with dihydrate and anhydrite gypsums, the shear stress was 28 to 44 Pa lower than control mixture. This means less viscosity of the suspension and can be caused by losing aggregation between the particles due to covering the reactive cementitious powder by $SO_3^{2-}$ ions dissolved from the gypsums while the dihydrate and anhydrite gypsum had a low dissolution rate making it unable to provide rapid setting by the hydration. For the mixtures with $\alpha$ and $\beta$ hemihydrate, and desulfurized gypsum, the shear stress was increased from 6 to 18 Pa. When gypsums have high dissolution rates, the suspension with these kinds of gypsums experiences aggregation of the particles. Between $\alpha$ and $\beta$ dihydrate gypsums, $\alpha$ dihydrate gypsum contributed to a higher increase of the shear stress than $\beta$ dihydrate gypsum at 30 minutes after the mixing while $\beta$ dihydrate gypsum did not show the increase of the shear stress right after the mixing. From this result, it was determined that $\beta$ dihydrate gypsum produces a very rapid setting right after the mixing while the development of the microstructure development is not significant. On the other hand, it is considered that $\alpha$ dihydrate gypsum provides slow reaction at early age, while the setting of the mixture proceeds rapidly as the time passes.

**Rheological parameters**

Based on the flow curves obtained, rheological parameters were calculated using the Bingham model. Among the calculated rheological parameters of each mixture, yield stress values were summarized depending on the replacement ratio of the gypsums in Figure 8. Depending on the measuring time, Figure 8(a), and Figure 8(b) show the yield stress values measured as the mixing began, and 30 minutes later, respectively. The yield stress values were measured right after the mixing showed around 100 Pa except for the mixture with hemihydrate gypsums. In the case of the mixture mixture.

![Fig. 7. Influence of various gypsums replacement ratio on flow curves at 30 minutes after mixing.](image)

![Fig. 8. Influence of various gypsums replacement ratio on yield stress.](image)
Fluidity of slag cement paste depending on types and replacement ratios of gypsum

including β hemihydrate gypsum, the yield stress increased with replacement ratio of the gypsum, and approximately 400 Pa of yield stress was achieved at 6% of replacement ratio.

The yield stress values were obtained by the measurement conducted at 30 minutes after the mixing started showed increased yield stress values generally over 30 Pa, while the mixtures with dihydrate and anhydrite gypsums showed lower yield stress than the control mixture. In the case of the mixture with hemihydrate gypsums, an increased yield stress was observed with an increased replacement ratio of gypsums, especially, for α hemihydrate gypsum, where the yield stress of the mixture increased 152 to 295 Pa compared to the yield stress value obtained from the mixture right after mixing, while the mixture with β hemihydrate gypsum showed a similar degree of yield stress compared to the yield stress measured right after the mixing. These changing yield stresses of the mixture with α, and β hemihydrate gypsum between the measurement at the beginning of the mixing process and 30 minutes later showed a low dissolution rate of the α hemihydrate gypsum and developed a setting of the mixture after the initial false set of the mixture with a β hemihydrate gypsum of high dissolution rate.

In Figure 9, plastic viscosity values from flow curves of each mixture are shown depending on the measuring timing: (a) right after the mixing began, and (b) 30 minutes later. The plastic viscosity of the control mixture right after the mixing showed 6.8 Pa·s and other mixtures with various gypsums except for β hemihydrate gypsum showed a similar range of the plastic viscosity values within 1 Pa·s. Hence, the influence of the gypsum type except for β hemihydrate gypsum on plastic viscosity of the slag cement paste is not significant. The plastic viscosity of the mixture with β hemihydrate gypsum was 0 Pa·s when the replacement ratio of the gypsum was higher than 4%.

The plastic viscosity of the mixtures measured at 30 minutes after the mixing increased 3 to 5 Pa·s. This was a result of the increased aggregation between the particles due to the progress of the hydration of cementitious particles. The difference in the plastic viscosity of the mixtures depending on the gypsum types and replacement ratios was slightly within 2 Pa·s. Thus, the influences of the gypsum types and replacement ratio on plastic viscosity of the slag cement paste are barely considered.

**Conclusions**

In this research, using the traditional workability measuring method and rheological test method, the influence of types and replacement ratios of gypsums on the fluidity of the slag cement paste was evaluated to produce the slag cement concrete with improved performance. As a fundamental study within the scope of fluidity of slag cement paste depending on different varieties of gypsum, the result of experiment can be summarized as follows:

1) The influence of types and replacement ratios of gypsum on table flow were not significant for the test conducted right after the mixing except for α hemihydrate gypsum. The measured table flow values of the mixtures were within 175 ± 5 mm including the control mixture without gypsum, while the table flow value of the mixture with α hemihydrate gypsum increased with its replacement ratio. From the table flow measurement 30 minutes after mixing, generally, the table flow values decreased within 15 to 25 mm. Also in this case, hemihydrate gypsums decreased the table flow value of the mixtures. Especially α hemihydrate gypsum showed a remarkable trend of decreasing.

2) From the grout flow test result conducted right after the mixing, for all types of gypsum except for β hemihydrate gypsum, a shorter time duration than that of the control mixture without gypsum was measured. Meanwhile, for the mixture including β hemihydrate gypsum, it was impossible to measure the flow time when the replacement ratio was higher than 4%. At 30 minutes after the mixing, the flow time duration extended to about 10 to 30 seconds, especially, α,
and $\beta$ hemihydrate, and desulfurized gypsums showed a remarkable trend of delayed flow in recorded time duration. Different dissolution rates of different types of gypsum cause these results, and thus the hemihydrate gypsums with a high dissolution rate cause much delayed flow time durations.

3) Using the flow curves obtained from rheological tests, the shear stress values of the mixtures right after the mixing were 57 to 164 Pa except for the mixtures with hemihydrate gypsums. The mixtures with $\alpha$ and $\beta$ hemihydrate gypsums showed 72 to 351 Pa of higher shear stress values than the control and other mixtures. From the test results at 30 minutes after mixing, 50 to 200 Pa increased shear stress values were obtained compared to the shear stress values measured right after the mixing. When hemihydrate gypsums were replaced in the mixtures, the shear stress values were higher than the control mixture and depending on the replacement ratios, the shear stress values were 6 to 183 Pa higher than control mixture.

4) The yield stress values of the mixtures except for the mixture including $\beta$ hemihydrate gypsum showed about 100 Pa. In the case of $\beta$ hemihydrate gypsum, the yield stress value of the mixture was increased with the replacement ratio, and approximately 400 Pa of yield stress was obtained at 6% of replacement ratio. Furthermore, 30 minutes after mixing, the yield stress values generally increased to about 30 MPa, while $\alpha$ hemihydrate gypsum in mixture influenced a remarkable increase of yield stress 30 minutes after the mixing. For plastic viscosity, regardless of gypsum types and replacement ratios, generally 5 to 13 Pa·s of plastic viscosity were measured.

Acknowledgments

This work was supported by the Human Resource Training Program for Regional Innovation and Creativity through the Ministry of Education and National Research Foundation of Korea(NRF-2015H1C1A1035953)

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