Influence of air-cooled blast furnace slag aggregate on sulfate attack resistance

Hong-Gi Kim and Jae-Suk Ryou*
Department of Civil Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul 133-79, Korea

This study evaluated the effect of the use of slag, metakaolin and air-cooled blast furnace slag aggregate on sulfate attack resistance by preparing six mixes. Air-cooled blast furnace slag was used as an aggregate in three of these mixes, each of which contained 20% metakaolin, 10% slag, 10% metakaolin and 100% cement. Three other mixes contained natural aggregate with the above ratios of binders. Slump and compressive strength tests were performed, after which the mixes were immersed in a 3% H₂SO₄ solution. The compressive strength loss and the concrete mass change rate were then measured after 28, 56, and 91 days. The microstructural properties were studied via SEM and EDAX. Based on the results of the above tests, it can be concluded that metakaolin improves sulfate attack resistance and air-cooled blast furnace slag aggregate shows better sulfate attack resistance compared to natural aggregate.

Key words: Sulfate attack resistance; Air-cooled blast furnace slag aggregate; Metakaolin; gypsum formation.

Introduction

Sulfate attack is one of the important causes of deterioration in concrete structures. When cement or concrete is exposed to a sulfate environment, the sulfate ions react with the hydrating products, generating expansive products and causing expansion and cracking [1], which are generally attributed to the formation of ettringite and gypsum [2, 3]. Ettringite and gypsum formation is generated by the reaction of the sulfate ions with calcium hydroxide and calcium aluminate hydrate. The gypsum and ettringite generated by sulfate attack is considerably voluminous (1.2-2.2 times) compared to the first generation [4]. Furthermore, the formation of ettringite and gypsum from deterioration due to sulfate attack is primarily caused by the degradation of C-S-H gel by the calcium composition. The process generally causes loss of stiffness of the C-S-H gel and degradation of the cement and concrete matrix [5]. Several methods have been suggested to improve the performance of concretes against sulfate attack [6-8]. The use of SCM (supplementary cementitious materials) is the common method for addressing sulfate attack. There is a growing interest in the use of MK (metakaolin) as an SCM in concrete structures. MK is generally used when making high-strength and high-performance concrete with improved durability. Many researches have reported properties of MK that it reduces the porosity of the microstructures due to the filler effect, and then activated pozzolanic reaction in the concrete matrix with cement. There have not been many studies, however, that evaluated the effect of the MK properties on sulfate attack. The use of waste or recycled aggregates in concrete has drawn much interest due to the concern about and need for environmental protection, but limited studies on sulfate resistance with the use of such aggregates have been conducted [9].

Air-cooled blast furnace aggregate is a byproduct of the steel industry. It is produced as a residue of the steel manufacturing process, slowly cooled in the air, and finally crushed [10]. The properties and composition of the slag vary among the kilns. The crushed slag is stockpiled on the land and is sometimes used for land and road filling. The use of the crushed slag as an aggregate in concrete will help to fix the problem of industrial waste disposal and will also reduce natural aggregate excavation for use in concrete. The use of the air-cooled blast furnace slag aggregate is currently limited because engineers and contractors are less confident about its use due to their limited knowledge about the concrete containing this industrial waste. Faleschin et al. studied the carbon footprint of the slag aggregate if used in concrete and concluded that it is more environment-friendly than natural aggregate extraction [11].

This study aimed to efficiently use air-cooled blast furnace slag as an aggregate in concrete to create a green, durable and sustainable concrete and to replace cement with the mineral admixtures slag and metakaolin. Both are used to replace a fraction of cement. The durability and especially sulfate attack resistance of the air-cooled blast furnace slag aggregate concrete were studied in detail and were compared with those of natural aggregate concrete.

*Corresponding author:
Tel: +82-02-2220-4323
Fax: +82-02-2293-9977
E-mail: jsryou@hanyang.ac.kr
Experiment Program

Materials
Ordinary Portland cement satisfying KS L 5201 from a company and the commercially available mineral admixtures ground granulated blast furnace slag powder and metakaolin were used as binder materials. The physical and chemical properties of all the binder materials that were used in this study are presented in Table 1. Natural river sand and coarse aggregates, air-cooled blast furnace slag aggregates (from H Company, Gwang Yang, Jeonnam) were used. The physical properties of all the aggregates that were used in this study are listed in Table 2 while the chemical properties of the slag aggregates that were used are presented in Table 3. The polycarbon-acid-type water reducer produced in S Company was used to control the workability.

Specimen preparation and measurements
Six different mix proportions were prepared, as shown in Table 4. All the mixes were prepared with different binder replacement ratios, three of them with natural aggregates and the remaining three with air-cooled blast furnace slag aggregates. The W/B ratio and binder content for all the mixes were fixed to 0.37 and 499 kg/m$^3$, respectively. Concrete cylinder specimens (Ø100 × 200 mm) were prepared according to KS F2403 after testing for slump and air content. The samples were demolded after 24 hrs and were subsequently immersed in water for curing at 20±2 °C.

Workability is of prime importance while dealing with a concrete mix proportion containing mineral admixtures. Furthermore, in this study, workability was a main concern as air-cooled blast furnace slag fine aggregate (ACBFS) was used, which contains fine dusts. For this purpose, a slump test was conducted according to KS F2402.

Concrete cylindrical specimens were used to evaluate the compressive strength of concrete. The specimens were removed after 3, 7, 14, 28, and 56 days of water curing, and a compressive strength test was performed using a universal testing machine conforming to KS F2405. The strength reduction rate was obtained by comparing the compressive strengths of the specimens before and after water curing.

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### Table 1. Chemical and physical properties of OPC and SCMs.

<table>
<thead>
<tr>
<th>Items</th>
<th>OPC</th>
<th>MK</th>
<th>GGBFS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>20.8</td>
<td>56</td>
<td>34.1</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>6.3</td>
<td>37</td>
<td>16.1</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>3.2</td>
<td>2.4</td>
<td>0.4</td>
</tr>
<tr>
<td>CaO</td>
<td>62</td>
<td>0.2</td>
<td>42.3</td>
</tr>
<tr>
<td>MgO</td>
<td>3.3</td>
<td>0.3</td>
<td>4.1</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.9</td>
<td>0.9</td>
<td>0.7</td>
</tr>
<tr>
<td>Physical properties</td>
<td>***</td>
<td>***</td>
<td>***</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>3.15</td>
<td>2.63</td>
<td>2.89</td>
</tr>
<tr>
<td>Blaine (cm$^2$/g)</td>
<td>3,200</td>
<td>12,000</td>
<td>4,893</td>
</tr>
<tr>
<td>IL (%)</td>
<td>1.3</td>
<td>1.95</td>
<td>0.05</td>
</tr>
</tbody>
</table>

### Table 2. Physical properties of aggregates.

<table>
<thead>
<tr>
<th>Aggregates</th>
<th>$G_{\text{max}}$ (mm)</th>
<th>Density (g/cm$^3$)</th>
<th>Absorption rate (%)</th>
<th>F:M</th>
<th>Abrasion rate (%)</th>
<th>Unit weight (Kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural fine aggregate</td>
<td>2.80</td>
<td>2.60</td>
<td>0.96</td>
<td>2.81</td>
<td>25</td>
<td>1489</td>
</tr>
<tr>
<td>Natural coarse aggregate</td>
<td>25</td>
<td>2.80</td>
<td>0.72</td>
<td>7</td>
<td>25.1</td>
<td>1530</td>
</tr>
<tr>
<td>ACBFS fine aggregate</td>
<td>2.75</td>
<td>2.42</td>
<td>2.8</td>
<td>3.1</td>
<td>30</td>
<td>1256</td>
</tr>
<tr>
<td>ACBFS coarse aggregate</td>
<td>25</td>
<td>2.12</td>
<td>2.9</td>
<td>7.1</td>
<td>32</td>
<td>1217</td>
</tr>
</tbody>
</table>

### Table 3. Chemical composition of ACBFS.

<table>
<thead>
<tr>
<th>Contents (%)</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>Al$_2$O$_3$</th>
<th>T:Fe</th>
<th>MgO</th>
<th>MnO</th>
<th>S</th>
<th>TiO$_2$</th>
<th>C/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blast furnace slag</td>
<td>33.5</td>
<td>41.8</td>
<td>13.6</td>
<td>0.4</td>
<td>6.4</td>
<td>0.5</td>
<td>1.0</td>
<td>1.3</td>
<td>1.23</td>
</tr>
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</table>

### Table 4. Concrete mix proportions.

<table>
<thead>
<tr>
<th>Mix type</th>
<th>Cement (kg/m$^3$)</th>
<th>GGBFS (kg/m$^3$)</th>
<th>MK (kg/m$^3$)</th>
<th>Natural aggregate (kg/m$^3$)</th>
<th>ACBFS aggregate (kg/m$^3$)</th>
<th>Water (kg/m$^3$)</th>
<th>Water reducer (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PN</td>
<td>499</td>
<td>-</td>
<td>-</td>
<td>580.4</td>
<td>913.9</td>
<td>-</td>
<td>184</td>
</tr>
<tr>
<td>M2N</td>
<td>399.2</td>
<td>-</td>
<td>99.8</td>
<td>573.9</td>
<td>903.7</td>
<td>-</td>
<td>184</td>
</tr>
<tr>
<td>MS1N</td>
<td>399.2</td>
<td>44.9</td>
<td>44.9</td>
<td>575.7</td>
<td>906.5</td>
<td>-</td>
<td>184</td>
</tr>
<tr>
<td>PA</td>
<td>499</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>569.3</td>
<td>889.9</td>
</tr>
<tr>
<td>M2A</td>
<td>399.2</td>
<td>-</td>
<td>99.8</td>
<td>-</td>
<td>563</td>
<td>880</td>
<td>184</td>
</tr>
<tr>
<td>MS1A</td>
<td>399.2</td>
<td>44.9</td>
<td>44.9</td>
<td>-</td>
<td>564.7</td>
<td>882.7</td>
<td>184</td>
</tr>
</tbody>
</table>
Influence of air-cooled blast furnace slag aggregate on sulfate attack resistance

after immersion in sulfuric acid solution. The concrete specimens were water-cured for 28 days at 20±2 °C and were then immersed in 3%-concentration sulfuric acid. The specimens were left immersed in the solution for 28, 56 and 91 days. After each interval, the specimens were taken out and dried in an oven at 60±2 °C for 24 hours, and then their compressive strength was obtained according to KS F 2405. The following equation was used to calculate the compressive strength loss.

\[
\text{Compressive strength loss} (\%) = \left( \frac{C_w \cdot C_s}{C_w} \right) \times 100 \quad (1)
\]

where \(C_w\): Compressive strength of concrete water-cured for 28 days (MPa), \(C_s\): Compressive strength of concrete after immersion in an acid solution (MPa)

The mass reduction rates of the concrete specimens were measured after immersing them in an especially manufactured tank containing sulfuric acid solution (3% concentration), as shown in Fig. 1. After being cured for 28 days in water at 20±2°C, the specimens were immersed in a solution. To achieve the perfect immersion of the specimens (200 mm long), the tank was filled with a solution up to 230 mm from the bottom. After five days immersion, the specimens were taken out of the tank and were dried in an oven at 60±2°C for 24 hrs. Furthermore, the mass loss was measured and was compared with the initial mass. The mass reduction rate was then calculated using the following equation:

\[
\text{Mass change rate} (\%) = \left( \frac{M_w \cdot M_s}{M_w} \right) \times 100 \quad (2)
\]

where \(M_w\): Mass of the water-cured concrete specimen before immersion (g), \(M_s\): Mass of the concrete specimen after immersion (g)

A scanning electron microscope with a 0.2-30 kv accelerating voltage, a 10E-12 to 10E-5A probe current, a 3.5 nm SEI resolution (WD = 8 mm; Acc.V = 35 kv), and X10 to X 300,000 magnification was used to analyze the microstructural properties of concrete. The samples were obtained from the specimens that had been immersed in sulfuric acid solution for 91 days, conforming to [12]. Furthermore, EDAX (Falcon Energy System 60SEM) was used in conjunction with SEM to investigate the elements that were formed after sulfuric acid immersion.

Results and Discussion

Properties of fresh concrete

The slump test was conducted to confirm the workability. The before and after results of the air content and slump test in fresh concrete for each mix are presented in Table 5. The values of the general concrete specimens that used normal aggregate were determined to be 115-120 mm. In the case of ACBFS, however, the values were determined to be 100-120 mm. These results were relatively low due to the remaining dusts and the high absorption rate of ACBFS.

Table 5. Slump test and air content results of fresh concrete.

<table>
<thead>
<tr>
<th>Type</th>
<th>Slump (mm)</th>
<th>Air content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLAIN.NA</td>
<td>115-120</td>
<td>3.4</td>
</tr>
<tr>
<td>MK20.NA</td>
<td>115</td>
<td>3.6</td>
</tr>
<tr>
<td>MKGS10.NA</td>
<td>120</td>
<td>3.2</td>
</tr>
<tr>
<td>PLAIN.ACBFS</td>
<td>110-120</td>
<td>3.9</td>
</tr>
<tr>
<td>MK20.ACBFS</td>
<td>120</td>
<td>4</td>
</tr>
<tr>
<td>MKGS10.ACBFS</td>
<td>115-120</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Compressive strength of concrete

Fig. 2 shows the compressive strength measurements for the specimens after curing for 56 days. In the initial stages, it was verified that the ACBFS specimens’ strength was lower than those of the specimens with normal aggregate because of the porous structure of the ACBFS surface. In the case of the concrete with natural aggregate, the compressive strength of MK 20 was higher than those of the others since the 14th curing day. It is considered that the fine particles of MK may be used to fill the voids in the cement matrix, which will make the microstructure denser. The compressive strength of MKGS10 was also found to be higher than that of the plain concrete. The hydration
from a less dense CSH, 2CaO·SiO$_2$ cement pastes with MK and/or to transform them to a denser matrix could be formed to reduce the products on the pore volume. These results indicate that an inhibiting layer could be formed to reduce the products on the pore volume. The densification process of the cement paste with MK seems to have been completed after 14 days. On the other hand, the pore volume slightly increased between the 14th and 28th curing day, with a high calcium hydroxide content. These results indicate that an inhibiting layer could be formed to reduce the products on cement pastes with MK and/or to transform them from a less dense CSH, 2CaO·SiO$_2$·Al$_2$O$_3$·8H$_2$O (stratlingite), and C$_4$AH$_{13}$ (calcium aluminium hydrate) to a dense hydrogarnet. Based on the results, the compressive strength of the specimens with MK indicated higher values than the others. While BFS is classified as a latent hydraulic material with pozzolanic and cementitious properties after its activation, its chemistry and hydration process are well known for CaO-SiO$_2$-Al$_2$O$_3$ [18-20]. It has been well demonstrated by several researchers that the principal hydration products of BFS in the cement phases are calcium silicate hydrate (CSH) and calcium hydroxide (CH). The properties of the ternary matrix that included PC, BFS, and MK could be improved. The addition of BFS with MK can improve the workability of fresh concrete as well as the early strength of concrete due to the presence of MK [20, 21]. In the previous researches, the compressive strengths of the specimens with MK increased compared with those of the specimens with BFS or only PC. In the case of the specimens with blended MK and BFS, slightly lower values were presented compared to the specimens with MK. The hydration reaction is dependent on the PC+MK content in the concrete matrix. In Fig. 1, it can be confirmed that the increasing content of BFS decreases the compressive strength. Supplementary materials such as BFS decrease the hydration reaction due to low pozzolanic activity and the dilution effect [21, 22]. The increase in compressive strength attributed to the effect of the reactive Al$_2$O$_3$ from MK was due to the indirect stimulation of the C$_3$A and C$_3$S dissolutions to form Aft in a solution rich in sulfate ions [21, 23]. The compressive strengths of the specimens with ACBFS aggregate were also lower than those of the specimens with natural aggregates. The compressive strength would be dependent on the characteristics of the internal structure of the ACBFS aggregate, which has a higher porous structure than natural aggregate. As shown in Fig. 1, however, the compressive strength values of the natural aggregate and the ACBFS aggregate were not significantly different. Therefore, the materials of ACBFS aggregate with MK and BFS used in a cement matrix can improve the compressive strength and can be applied to concrete.

**Compressive strength reduction rate**

The compressive strength values of the concrete specimens with metakaolin, slag, and ACBFS aggregate, respectively, and those of the concrete specimens without any of these were tested after being exposed to a 3% sulfuric acid solution for 28, 56, and 91 days, and the results are indicated in Figs. 3 and 4. The reduction rate of the compressive strength of PN was decreased by 22.67% and 37.56% after 28 and 56 days, respectively. Finally, it decreased by 59.73% after 56 days. The compressive strength values of the M2.N and M31.N specimens decreased by 31.29% and 24.46% after 28 days, respectively, and then, after 56 days, they were reduced by 45.81% and 33.94%, respectively. After 91 days, it was reduced by 48.80% and 38.69%, respectively. The chemical mechanism between the sulfuric acid and hydrated cement components described the following reactive products [24]: secondary gypsum (CaSO$_4$·2H$_2$O) and secondary ettringite (3CaO·Al$_2$O$_3$·3CaSO$_4$·32H$_2$O). The formation of secondary ettringite...
caused expansion and cracking. In the case of gypsum formation, it caused expansion based on the literature [3]. According to the researchers, ettringite as well as gypsum have expansion and destruction characteristics [25, 26]. The other researchers insisted, however, that the contribution of expansion through gypsum is limited while the expansion through ettringite was primarily characterized [27]. The formation of gypsum and ettringite generated expansion, strength loss, and cracking of the concrete matrix. The cement has CaO and a high proportion of C$_3$S. These materials generated comparatively greater amounts of Portlandite then blended the cements or geo-polymers. The leaching of Portlandite can thus penetrate the sulfuric ions in the cement matrix. Furthermore, the reaction with sulfuric solution may be able to produce more gypsum and ettringite, which are responsible for the expansion and cracking [28]. Therefore, the specimens used only cement that presented a low resistance to sulfuric attack, such as P.N and P.NA, compared with the other specimens. While the other specimens with slag and metakaolin or natural and ACBFS aggregate showed an improvement of their resistance to sulfuric attack. Especially, M2.A showed that its compressive strength reduction rate and resistance to sulfuric attack are higher than those of the other specimens. The reduction rates of the P.A and MG1.A specimens were found to be 16.33 and 22.47% after 28 days. After 56 and 91 days, the reduction rates were shown to be 26.86, 24.36, 28.80, and 30.61% while the M2.A specimens showed 22.47, 25.32, and 28.80 reduction rates after 28, 56, and 91 days. By considering these mechanical properties and microstructure aspects, the effects of metakaolin with slag and ACBFS aggregate were constituted by several aspects. First, it can consider the pozzolanic reactivity [29, 30], which means that metakaolin reacts chemically with CH in water to form a modified microstructure, and thus improves the mechanical properties and durability. This consumption of CH by amorphous silica and amorphous alumina in metakaolin generates the formation of CSH and C$_2$ASH$_8$ [31]. Furthermore, the pozzolanic reaction between metakaolin and CH can help improve the capillary porosity in the binder [32] from the direct consequence of the compressive strength reduction rate improvement. The second is the microaggregate filling effect [33, 34]. The particles of metakaolin are smaller than those of cement and slag. Therefore, the replacement of cement by metakaolin will decrease the porosity and may make the microstructure denser [35]. The fine particles of metakaolin can contribute to the compaction of concrete. Based on these reasons, the specimens with metakaolin presented better results compared to the others. Also, when generating expansion by gypsum and ettringite, the ACBFS aggregate has an important role in reducing the expansion. The ACBFS aggregate has a higher porous characteristic than natural aggregate. This property of the ACBFS aggregate can be protected from sulfuric attack by expansion and

![Surface observation of the specimens after 56- and 91-day immersion in sulfuric acid solution.](image)
cracking. Generating ettringite and gypsum formation in a cement matrix is likely to terminate the structure of the matrix caused by the physical characteristics. When this reaction took place in this study, the structure of the cement matrix collapsed after the cement matrix reached a critical point in terms of strength, which resists the expansion force. The specimens with ACBFS aggregate showed superior efficiency compared to the specimens with natural aggregates. This may have been due to the fact that the pores in the ACBFS aggregate absorbed the stresses caused by expansion and provided enough space for the expansive products to occupy.

**Mass change of concrete**

Surface observation of the specimens was conducted after 56 and 91 days of immersion in a sulfuric acid solution. Fig. 5 shows the deterioration results on all the specimens. In the case of P.N, it deteriorated noticeably compared to the other specimens. The MS1.N specimen also deteriorated, unlike the others. The mass changes of the specimens immersed in a 3%-concentration sulfuric acid solution (H₂SO₄) for 91 days are presented in Fig. 6. The P.N specimen with natural aggregates presented low resistance to H₂SO₄ attack, which was decreased by 13.03% after 91-day immersion. In the case of the M2.N and MS1.N specimens with natural aggregates, the 5.8% and 3.1% mass change rates decreased after 56 days, and then, after 91 days, the 7.15% and 5.16% mass change rates finally decreased, respectively. On the other hand, the specimens with ACBFS aggregate presented divergent trends. The value of the mass change of P.A was decreased by 0.49% and 0.95% after 56 and 91 days, respectively. Also, in the case of the M2.A and MS1.A specimens, it was indicated that the mass change rates decreased by 0.17% and 0.24% after 56 days, then finally, they were shown to be 0.07 and 0.46% after 91 days. These results showed that the mass change rate of M2.A will increase by 0.1% after 91 days compared with that after 56 days. According to the previous literature, the increase in the sulfate resistance of concrete with metakaolin was established through two mechanisms [36]. First, the replacement of a portion of the Portland cement with metakaolin reduces the total amount of C₃S in the cement matrix of concrete. The second mechanism is the pozzolanic reaction between the metakaolin and the CH produced during the hydration of the cement matrix, which was consumed as part of the calcium hydroxide. Therefore, the quantity of expansive gypsum formed through the
reaction of CH will be reduced in metakaolin concrete rather than in general concrete [37]. Furthermore, the recent formation of calcium silicate hydroxide gel through the pozzolanic reaction, although less dense than that produced through the primary pozzolanic reaction, is effective in filling and segmenting large capillary pores into small ones. In addition to the pozzolanic reaction, the filler action of metakaolin due to its higher fine particle size compared to cement may be further densified in the pore structure of concrete with metakaolin to improve the concrete structure’s sulfate attack resistance.

**SEM and EDAX analyses**

Microstructure analysis of the concrete specimens was carried out through SEM and EDAX tests after exposure to sulfuric acid solution. Fig. 7 shows the SEM microphotographs of the specimens with natural aggregates while Fig. 8 shows those of the specimens with ACBFS. It was observed from the SEM results that a massive amount of hexagonal crystals was generated, as indicated. Furthermore, EDAX analysis was carried out to verify the indicated crystals, as shown in Fig. 9. Samples for EDAX analysis were taken from the plain specimens with natural and ACBFS aggregates. The EDAX analysis presented the peaks of Ca, S, and O. It was considered that the generated crystals were gypsum, formed as the sulfate ions reacted with Ca(OH)$_2$. Interestingly, it was concluded that gypsum formation was the only cause of expansion in the concrete specimens exposed to sulfuric acid solution. Ettringite, however, which is also a vital expansive product, was not formed. It may be considered that the formation of ettringite was delayed.

Sulfate attack is one of the main triggers for concrete deterioration by causing expansion and reducing the cohesion among hydration products. It also affects the bond between aggregates and cement paste [36, 38]. Furthermore, deterioration due to sulfate attack is caused by the formation of either expansive ettringite or gypsum, as considered in this case. Gypsum formation may induce tensile stresses, causing the further expansion and cracking of the cement matrix [3]. Gypsum and ettringite, however, are generated through the following mechanism [38]:

**Relevant chemical equations**

\[
\text{Na}_2\text{SO}_4 + \text{Ca(OH)}_2 + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} \quad (3)
\]

\[
\text{MgSO}_4 + \text{Ca(OH)}_2 + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{Mg(OH)}_2 \quad (4)
\]

\[
3\text{MgSO}_4 + 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + 8\text{H}_2\text{O} \rightarrow 3(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) + 3\text{Mg(OH)}_2 + 2\text{SiO}_2 \cdot \text{H}_2\text{O} \quad (5)
\]

\[
\text{C}_3\text{A} \cdot \text{CaS} \cdot \text{H}_{18} + 2\text{CH} + 2\text{S} + 12\text{H} \rightarrow \text{C}_3\text{A} \cdot 3\text{CaS} \cdot \text{H}_{32} \quad (6)
\]

\[
\text{C}_3\text{A} \cdot \text{H} \cdot \text{CH}_{18} + 2\text{CH} + 3\text{S} + 1\text{H} \rightarrow \text{C}_3\text{A} \cdot 3\text{CaS} \cdot 3\text{H}_{32} \quad (7)
\]

The considerable efforts to mitigate sulfate attack suggest, however, that low-C$_3$A-content cement be used or that the Ca(OH)$_2$ amount in cement paste be
reduced by blending the cement with pozzolans. Blast furnace slag cement plays an important role in the reduction of the Ca(OH)₂ content. In addition, densifying the cement matrix to avoid the intrusion of sulfate and other vulnerable ions is the key to reducing concrete deterioration [36, 41]. Cement replacement with GGBS and MK together presented a significant reduction in pore volume due to their characteristic filling and pozzolanic effect [39]. Moreover, MK improves the pore structure of the cement matrix, resulting in an enhanced resistance to harmful-ion penetration. It was concluded that the replacement of cement with concrete with MK up to 15% showed excellent sulfate attack resistance [41]. This implies that a considerable amount of gypsum was formed in the concrete specimens, without incorporating any pozzolanic material. This may be due to the fact that the concrete specimens with only OPC did not have a dense microstructure, which permitted the sulfate ions to enter the matrix, subsequently generating expansive products.

## Conclusion

Based on the experimental results of this study, the following conclusions are drawn:

The air-cooled blast furnace slag aggregate reduced the slump of concrete due to its high absorption of water and dusts.

The compressive strength of the air-cooled blast furnace slag aggregate concrete is lower than that of the concrete containing natural aggregate due to the lower strength of the air-cooled blast furnace slag aggregate. Supplementary cementitious materials improve the strength of concrete.

The air-cooled blast furnace slag aggregate improved the concrete resistance to sulfate attack. The reduction of the compressive strength and the loss of mass were lower in the concrete containing ACBFS aggregate and that had been exposed to sulfate attack. This improvement is more pronounced in the concrete that also contains metakaolin as a binder.

The reduction of the compressive strength and the mass changes in the concrete under sulfate attack are attributed to the formation of gypsum in this study. The formation of gypsum inside the cement matrix caused expansion. This expansion in some mixes was high enough to create tensile stresses in the concrete and then the spalling of the mass.

The use of metakaolin and slag further improves the sulfate attack resistance by densifying the microstructure of cement paste, and resists the intrusion of external sulfate ions in concrete.

## References

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