Effects of air-cooled blast furnace slag fine aggregate in mortar with self-healing capability exposed to sulfurous acid attack

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This study focuses on high durability mortar against sulfurous acid attack by replacing binary and ternary blend of binder with fully substituted Air-Cooled Blast Furnace Slag (ACBFS) fine aggregate. Two replacement ratio of binder were considered in this study and ten types of binder mix were designed to conduct experiment. And cementitious materials with self-healing capability were prepared in order to apply for theses mortars. Each specimen was manufactured into 3 cm diameter with 5 cm height in cylindrical mould. After demolding, specimens were water cured for 28 days. All specimens were immersed into 3\% concentrated solution for 60 days and solutions were replaced regularly in consider with loss of sulfurous acid concentration. Mass change of all specimens was measured after removing detached particles gently. From 60days observation, it was shown that specimens with ACBFS performed high resistance to sulfurous acid attack compared to normal fine aggregates in same binder mix. Also, ternary blend mix showed higher resistance than binary blend specimens.

Key words: Mortar, Sulfurous acid attack, Air-Cooled Blast Furnace Slag fine aggregate, Self-healing capability.

Introduction

Concrete is the most widely used construction material with high strength and durability compared to the other materials in large fields such as sewage pipe, drainage etc. Organic compounds contained in sewage water are reported to induce corrosion of concrete in accordance with specific mechanism by bacteria, Thioacillus. Sulfate ions inside sewage water change to hydrogen sulfide and it transfers to sulfurous acid by interruption of bacteria. Those dissolved sulfurous acid in sewage water deteriorates concrete structures not only internal surface but also possible to contaminate soil or other interfacing environments. Main mechanisms of deterioration in cement matrix by sulfurous acid attack are divided into two steps which are:

\begin{enumerate}
  \item Formation of gypsum (CaSO\textsubscript{4} \cdot 2H\textsubscript{2}O) which expands due to ingress of sulfate ion
  \item Ettringite formation by gypsum and aluminates
\end{enumerate}

In order to enhance durability of above mentioned concrete structure, many researches are conducted by using Supplementary Cementitious Materials (SCMs). It was verified that by substituting cement with SCMs is able to increase not only physical properties of concrete, but also chemical resistance due to its impermeable matrix in the long term. It is due to pozzolan reaction in the late hydration of cement matrix which produce calcium silicate hydrate while consuming calcium hydroxide produced in early stage of cement hydration and makes matrix more impermeable. In this view point, ternary blend mix designs are reported as better option in severely hazardous environments [1]. However, most of researches to enhance durability of concrete with binary or ternary mix were combined with natural aggregate. Meanwhile, due to environmental view point, it is essential to use recycled materials or industrial by-products to reduce environmental load such as recycled aggregate or various slag aggregate with improved physical properties or chemical resistance nowadays. One of representative fillers is slag aggregate which is formed during steel manufacturing. Many studies were conducted to use slag aggregate as an inert filler such as asphalt, back filler etc. to reduce environmental load which occurs with quarrying stones. Hence, in this study, normal aggregate and Air-Cooled Blast Furnace Slag (ACBFS) fine aggregate were used to verify feasibility against the sulfurous resistance [2]. Also, various SCMs with binary and ternary mixes in different aggregate components were compared. Mass change and reduction rates were used as comparison parameter between binders and aggregates.

Experimental

Supplementary cementitious materials

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Five types of SCMs were used with Ordinary Portland Cement (OPC) in binary and ternary mix of this study. Fly ash (FA), silica fume (SF), blast furnace slag (BFS) and metakaolin (MK) [3,4] were studied by many researchers that those materials are able to enhance durability of concrete by producing additional calcium silicate hydrate, mainly, which leads to dense structure. Each SCMs was replaced to 20% in total weight of binder and also same as in 10% of each in ternary blend mix. Basic properties of each SCMs are as shown in Table 1.

Normal fine aggregate
Washed sand was used in normal aggregate mix type and its characteristics are as shown in Table 2.

Air-cooled blast furnace slag fine aggregate
ACBFS is divided into few types by different procedure in steel factory. BFS is a non-metallic material, consists of silicates and aluminosilicates of calcium and magnesium together with other compounds of sulfur, iron, manganese and others. It is produced from a molten state simultaneously with pig iron in a blast furnace. The solidified product is further classified according to the process by which it was brought from the molten state (Fig. 1). ACBFS is produced through relatively slow solidification of molten blast furnace slag under atmospheric conditions, resulting in crystalline mineral formation. However, ACBFS fine aggregate, were hardly commercialized and standardized, it was separated by manufactured sieve following to KS F 2502. Also, it was verified that used ACBFS satisfied KS F 2544 which is the standard of Blast furnace slag aggregate in concrete. Properties of used ACBFS are as shown in Table 3.

Design of high durability mortars
Mortar mix was designed to compare each binder with different fine aggregates. 22 types of mix were considered in total, simultaneously, 11 types of mix for each aggregate. W/B ratio of all the specimens were

### Table 1. Characteristics of SCMs.

<table>
<thead>
<tr>
<th></th>
<th>Ordinary Portland Cement</th>
<th>Fly ash</th>
<th>Blast Furnace Slag</th>
<th>Silica fume</th>
<th>Meta-kaolin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical composition (%)</td>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>20.71</td>
<td>61.20</td>
<td>32.29</td>
<td>92.00</td>
</tr>
<tr>
<td></td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>5.56</td>
<td>24.92</td>
<td>13.19</td>
<td>2.01</td>
</tr>
<tr>
<td></td>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3.03</td>
<td>4.63</td>
<td>6.12</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>62.25</td>
<td>1.82</td>
<td>42.41</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>MgO</td>
<td>3.40</td>
<td>0.62</td>
<td>0.43</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>SO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.5</td>
<td>–</td>
<td>3.17</td>
<td>–</td>
</tr>
<tr>
<td>Ignition Loss (%)</td>
<td>–</td>
<td>1.34</td>
<td>–</td>
<td>–</td>
<td>0.40</td>
</tr>
<tr>
<td>Physical properties</td>
<td>Blaine</td>
<td>3.266</td>
<td>4.847</td>
<td>4.847</td>
<td>6.192</td>
</tr>
<tr>
<td></td>
<td>Specific gravity</td>
<td>3.15</td>
<td>2.15</td>
<td>2.15</td>
<td>2.90</td>
</tr>
</tbody>
</table>

### Table 2. Properties of washed sand.

<table>
<thead>
<tr>
<th>Absorption (%)</th>
<th>Specific gravity</th>
<th>F.M</th>
<th>Unit Weight (kg/m&lt;sup&gt;3&lt;/sup&gt;)</th>
</tr>
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<tbody>
<tr>
<td>0.96</td>
<td>2.60</td>
<td>2.81</td>
<td>1,489</td>
</tr>
</tbody>
</table>

### Table 3. Properties of ACBS aggregate.

<table>
<thead>
<tr>
<th>Absorption (%)</th>
<th>Specific gravity</th>
<th>F.M</th>
<th>Unit Weight (kg/m&lt;sup&gt;3&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8</td>
<td>2.42</td>
<td>3.1</td>
<td>1,356</td>
</tr>
</tbody>
</table>

### Table 4. Mix-proportions of SCMs Mortars.

<table>
<thead>
<tr>
<th>Mix-Proportions</th>
</tr>
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<tbody>
<tr>
<td>* W/B = 0.4</td>
</tr>
<tr>
<td>* Binder: Washed sand = 1 : 3</td>
</tr>
<tr>
<td>Plain</td>
</tr>
<tr>
<td>Only cement as a binder</td>
</tr>
<tr>
<td><strong>Series 1</strong></td>
</tr>
<tr>
<td>Binary blend mix Mix (Binder/Cement = 0.2)</td>
</tr>
<tr>
<td>Ternary blend mix (Binder/Cement = 0.1 for each)</td>
</tr>
<tr>
<td>Washed sand is fully replaced to ‘ACBFS’ with same mixture</td>
</tr>
<tr>
<td><strong>Series 2</strong></td>
</tr>
<tr>
<td>*FA : Fly Ash, SF : Silica Fume, SG : Slag, MK : Metakaolin</td>
</tr>
</tbody>
</table>

Fig. 1. Procedure of manufacturing Air-Cooled Blast Furnace Slag aggregate.
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fixed to 0.4 and binder to sand ratio were 1 : 3 according to ISO 679. Binary and ternary blends were considered with different combination with different aggregate but same proportion of materials as shown in Table 4.

In order to ensure Surface Saturated Dry (SSD) condition of normal and ACBFS, tests were held according to ASTM C 128. To meet SSD condition, aggregates in pan were mixed every 5 hours. To verify whether aggregates meet SSD condition, cone type mould with 40 mm × 90 mm dimension with 75 mm height were used. Also, cylindrical mould for each mortar specimens were regularly manufactured with 3 cm diameter and 5 cm of height by PVC (Poly Vinyl Chloride) pipe as shown in Fig. 2. After casting, specimens were removed in 24 hours and water cured in 20 ± 5 °C for 28 days.

After curing, each specimen was immersed into glass cylinder with 3% concentration by mass of sulfuric acid for 60 days. Concentration was decided referring ACI Building Code 318 which defines concrete exposure depending on concentration of sulfuric acid (Table 5). In order to prevent corrosion inner side of plastic cap glass cylinder, it was coated with Teflon film. Sulfuric acid was poured into glass cylinders which the volume ratio of specimen to liquid is 3. Also, liquid were changed regularly considering concentration loss.

After 60 days of immersion, mass reductions were calculated by initial weight of specimens after curing. All specimens were dried in oven for 48 hrs with 60 ± 3 °C before and after immersion. Finally, mass reduction rate were calculated by following equation;

\[
\text{Mass reduction rate(%) } = \frac{W_1-W_2}{W_1} \times 100
\]  

where \(W_1\) is the initial mass (g) of specimen after oven drying (before immersion) and \(W_2\) is the mass (g) after 60 days of immersion.

Results and Discussion

Verification of High durability of Series I

From the measuring mass change of specimens, it was found that ternary blend mix showed better performance compare to the binary blend mix. Although SCMs in binary blend mix were effective to resist against corrosion of sulfate attack more than OPC, but specimen with FA showed lower resistance than other binders. Previous studies have reported replacing SF as a binder were effective, however, BFS showed better performance in this study.

Also, specimen with MK showed similar value to SF. Especially, result of specimens which involve MK indicated lower mass reduction compared to SF. It is also regarded as a low permeability, in similar case as in binary blend mix, in terms of sulfate penetration as shown in Fig. 3.
Verification of high durability of Series 2

Similar tendency of mass reduction was observed in Type 2. However, in binary blend mix, specimen which contains FA showed better performance than other binders except BFS. As mentioned above in Series 1, it was verified that using SCMs as a partial replacement in binder showed better performance compared to the specimen with only OPC. In ternary blend mix, SF with BFS showed highest performance in mass reduction. Also, from the results of mass change, ternary blend mix showed better performance than binary blend mixes, simultaneously, specimens containing MK presented lower mass reduction generally as shown in Fig. 4.

Effects of Air-cooled blast furnace slag fine aggregate

Main difference between Series 1 and 2 mixes were investigated by physical or chemical component of used aggregate. Especially, tendency in terms of scaling in both Series were observed as compared as plain. Durability of plain was the worst compared to others. Mass reduction of Series 1 were tend to loosen and crumbled constantly during immersion, meanwhile, that of Series 2 were relatively stable by forming thick layer which regarded as gypsum. Due to its layer, several weeks were taken to observe exposed aggregate surface.

After 28 days of immersion, surface of Series 2 specimens were seem to be expand and, finally, a large

![Fig. 4. Mass change of Series 2 specimens (60 days of immersion).](image)

![Fig. 5. Reduction rate of Series 1 and Series 2 (60 days immersion).](image)

![Fig. 6. Specimens after 60 days immersion.](image)
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In this study, high durability mortars against sulfuric acid attack by replacing binary and ternary blend of binder with fully substituted Air-Cooled Blast Furnace Slag (ACBFS) fine aggregate were investigated. In addition, the new method of self-healing design to repair cracks in cracked mortar and concrete was suggested.

1. The ACBFS fine aggregate significantly affected the resistance to sulfuric acid attack
2. It was verified that using SCMs as a partial replacement in binder showed better performance compared to the specimen with only OPC.
3. In ternary blend mix, SF with BFS showed highest performance in mass reduction. Also, from the results of mass change, ternary blend mix showed better performance than binary blend mixes.
4. The addition of industrial wastes (SCMs) such as fly ash, slag and metakaolin to normal cement paste contributed to an increase in self-healing capability in the cracked cement paste by cementitious recrystallization and precipitated particles.

Conclusions

Acknowledgments

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References