Deterioration and Microstructural Evolution of the Fly Ash Geopolymer Concrete against MgSO₄ Solution

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1. Introduction

Geopolymer concrete has increasingly attracted attention due to its environmentally beneficial applications as the process of alkali activation will utilize the industrial refuse such as fly ash and slag to reduce greenhouse gas emissions. It is well known that geopolymers exhibit high early age strength, low penetrability, and good fire resistance due to their greatly cross-linked triaxial aluminosilicate structure [1, 2]. Hence, they are regarded as a new alternative binder to replace ordinary Portland cement (OPC). Besides, sulfate attack on concrete is a major aggressive environmental deterioration, which affects the long-term durability of civil infrastructures. This is because when these infrastructures are exposed to sulfate industrial wastewater and ocean environments and saline-alkali land, the reaction between concrete and sulfate could induce cracking, spalling, or expansion of structures, further degrading their mechanical strength [3]. The rate and mechanism of sulfate attack on concrete depend on many factors, including the cation accompanying the sulfate ions, permeability, paste chemistry, and aggregate mineralogy. The mechanism of MgSO₄ attack on OPC is that the composite layers of Mg(OH)₂ and CaSO₄ are generated on the surface region, and in the inner zone near the surface, calcium silicate hydrate (C-S-H) tends to be exhausted in Ca [4, 5]. Nevertheless, the investigation on the sulfate exposure in FAGC is limited up till now. Some previous research reports [6–9] concluded that geopolymers are more durable than OPC under sulfate attack as the cross-linked aluminosilicate polymer structure is steadier than calcium silicate hydrate gel. C-S-H phases tend to react with MgSO₄ solution to constitute ettringite and gypsum, while the Na-Al-Si-H cross-linked structure of geopolymers resists sulfate corrosion. There are two different opinions on the sulfate attack mechanism of geopolymers. Some scholars [6, 8, 10] suggested that the deterioration of geopolymers in sulfate solution was due to the removal of hydroxyl ions from the matrix into the solution, as a remarkable increase in pH value was observed in the immersion solution accompanied by a largely decreased
mechanical strength of the specimen measured. Baščarević et al. [11] approved the first opinion by using nuclear magnetic resonance, claiming that the settlement of geopolymeric samples with the SO$_4^{2-}$ solution caused the destruction of silicon-oxygen-silicon bonds in $x$Al$_2$O$_3$·ySiO$_2$ gel structure. Both destruction of the silicon-oxygen-silicon bonds and extracting of silicon were responsible for the enhancement of hydroxide ion concentration of the sulfate solution during the experiment. The second opinion was proposed by Ismail et al. [12]. They claimed that the degradation of geopolymers is not due to the sulfate itself, but to the cation accompanying the sulfate anions, since the massive material degradation of the mortars was found during being immersed in MgSO$_4$ solution, but not in Na$_2$SO$_4$ solution. The presence of Mg leads to the migration of Ca$^{2+}$ from the calcium-rich gels in the geopolymer matrix, but sodium does not have this kind of function. In addition, the partial substitute of fly ash by metakaolin [13] and higher Na$_2$O content [14] can contribute to improving the sulfate resistance of geopolymer specimens. This is because the metakaolin substitution and Na$_2$O addition are associated with each other to form an optimal microstructure, which impedes the damage of the matrix by sulfate attacks. It is well known that the resistance to sulfate attack is highly correlated with the dense microscopic structure and the high compressive strength. Chindaprasirt et al. [15] demonstrated that the microwave-heated high calcium fly ash geopolymer has a lower strength loss under sulfate attacks compared with the conventional heat cured samples.

In sulfate environment, structures located in water-level fluctuation, littoral area, and spray zone will experience more complicated environmental damage through the drying-wetting cycles, which tends to deteriorate the concrete more rapidly [16]. Jiang and Niu [17] proved that the degree of degradation of OPC concrete in MgSO$_4$ solution under drying-wetting cycles was more rigorous than that only immersed in the same sulfate solution without drying-wetting cycles. Sahmaran et al. [18] suggested that, for the structures subjected to sulfate solution under the wetting-drying and heating-cooling cycles, the sulfate resistant Portland cement was observed to achieve better compressive strength losses than blended cement.

However, the pattern of sulfate attack which is chosen by most researchers for geopolymers is immersion [19, 20]. Few literatures presented the property of FAGC subjected to the sulfate attack under drying-wetting and heating-cooling cycles, which could expedite the deterioration process of concrete. Therefore, this research reported an observation of both the compressive behavior and the microstructural characteristics of FAGC. It revealed the performance deterioration mechanism of the concrete in the MgSO$_4$ solution under drying-wetting and heating-cooling cycles.

2. Experiment Procedure

2.1. Materials. Fine and coarse aggregate, OPC (PO 42.5R, Sichuan Lanfeng Cement Limited Company, China), fly ash (Class F, Tianjin Dagang Power Plant), alkaline activating solution, and magnesium sulfate solution were used as raw materials for the experimental work. The properties of aggregates and the chemical constitutions of OPC and fly ash are shown in Tables 1 and 2, respectively. The gradation curves for aggregates and fly ash are shown in Figure 1. The alkaline activating solution contained Na$_2$SiO$_3$ and NaOH. The chemical compositions of the Na$_2$SiO$_3$ solution (Foshan Zhongfa Water Glass Factory) were Na$_2$O (8.83%), SiO$_2$ (27.64%), and H$_2$O (63.53%) by mass. NaOH solution was prepared by distilled water to provide 10 mol/L concentration. The pH value of the final alkaline activating solution was 13.3 by using model 8601 pH meter. The concentration of magnesium sulfate solution was 5% by mass, and the pH of magnesium sulfate solution was 7.

2.2. Specimen Preparation. Two mixtures were projected to compare the property of OPCC and FAGC exposed to sulfate solution. The concrete mixture ratio designs are outlined in Table 3. OPCC was demolded after being cast by 24 hours and cured in a standard condition of 20 ± 2°C and 95% relative humidity for 28 days. The alkali-activated solution was prepared one day prior to the mixing of the geopolymer concrete. The mixing of the geopolymer concrete was completed in a pan mixer. Dry coarse/fine aggregates and fly ash were mixed in the mixer for about 3 minutes. The prepared alkali-activated solution was then sequentially added and the wet mixing was continued for another 5 minutes. Before casting, the inner sides of the mold were layered with lubricating oil to prevent adhesion with the geopolymer concrete specimens. The molds were filled in three layers, and each layer was well compacted. The molds were vibrated for about one minute on the vibration table. FAGC was cured at 80°C for 24 hours after casting, followed by curing under the same standard condition with the OPCC specimens for 28 days.

2.3. Testing Procedures

2.3.1. Cyclic Test and Compression Strength Test. The drying-wetting and heating-cooling processes were performed on the concrete sulfate drying-wetting test machine (CABR-LSB, China Academy of Building Research Co., Ltd., China). The duration of one cycle was 24 hours. The drying-wetting and heating-cooling cycles were carried out as follows. At first, the specimens were soaked for 14 hours, with the temperature of the solution being set as 20°C. This was followed by 5 hours of drying with 80°C heating. Then, the samples were kept for 5 hours under 20°C cooling. The standard for the drying-wetting and heating-cooling test to be carried out for concrete was the standard for test methods of long-term performance and durability of ordinary concrete, GB/T 50082-2009, Test Method for Resistance of Concrete to Sulfate Attack. The procedure above was repeated for 32 cycles. The compressive strength of specimens (100 mm × 100 mm × 100 mm cubes) was measured using an electrohydraulic servo controlled compression test machine (YAW-2000, Changchun New Testing Machine Co., Ltd., China) with a loading capacity of 2000 kN, before the exposure test and at every 8 cycles. The loading rate during the compression tests was 5 kN/s.
Table 1: Properties of aggregates.

<table>
<thead>
<tr>
<th>Category</th>
<th>Bulk density (kg/m$^3$)</th>
<th>Apparent density (kg/m$^3$)</th>
<th>Moisture content (%)</th>
<th>Maximum particle size (mm)</th>
<th>Average particle size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse aggregate</td>
<td>1479</td>
<td>2632</td>
<td>0.3</td>
<td>22</td>
<td>12.38</td>
</tr>
<tr>
<td>Fine aggregate</td>
<td>1342</td>
<td>2381</td>
<td>0.1</td>
<td>4</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Table 2: Chemical compositions of OPC and fly ash.

<table>
<thead>
<tr>
<th></th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>Fe$_2$O$_3$</th>
<th>MgO</th>
<th>K$_2$O</th>
<th>P$_2$O$_5$</th>
<th>TiO$_2$</th>
<th>Na$_2$O</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>18.63</td>
<td>2.49</td>
<td>71.70</td>
<td>2.62</td>
<td>3.24</td>
<td>0.48</td>
<td>/</td>
<td>0.84</td>
<td>/</td>
<td>4.75</td>
</tr>
<tr>
<td>Fly ash</td>
<td>74.18</td>
<td>9.44</td>
<td>5.53</td>
<td>4.22</td>
<td>4.28</td>
<td>1.46</td>
<td>0.96</td>
<td>0.32</td>
<td>0.82</td>
<td></td>
</tr>
</tbody>
</table>

The value presented is the weight percentage. LOI: loss on ignition.

Table 3: The concrete mixture ratio designs (kg/m$^3$).

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Gravel</th>
<th>Sand</th>
<th>Fly ash</th>
<th>Cement</th>
<th>NaOH solution</th>
<th>Na$_2$SiO$_3$ solution</th>
<th>Water</th>
<th>W/G ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPCC</td>
<td>1208</td>
<td>592</td>
<td>—</td>
<td>400</td>
<td>—</td>
<td>—</td>
<td>200</td>
<td>0.5</td>
</tr>
<tr>
<td>FAGC</td>
<td>1318</td>
<td>647</td>
<td>437</td>
<td>—</td>
<td>62</td>
<td>156</td>
<td>—</td>
<td>0.5</td>
</tr>
</tbody>
</table>

2.3.2. Structural Characterization. The surfaces (0-1 mm depth) of the chosen specimens were inspected with XRD, FTIR, SEM, and EDS. XRD analysis was performed on EMPYREAN (PANalytical B.V., Holland), scanning from 5° to 65° 2Θ. FTIR analysis was made with Nicolet 6700 (Thermo Electron Corporation, USA) in the range of 400–4000 cm$^{-1}$. Thermogravimetric analysis was carried out by TGA/DSC2 (Mettler-Toledo, Switzerland), at a heating rate of 20° C/min with the range of 25–1000°C. SEM and EDS analyses were carried out by using S4800 (Hitachi, Japan) equipped with an EDS analyzer (Oxford Image Analysis).

3. Results and Discussion

3.1. Visual Observation. There were no obvious visual changes of OPCC and FAGC specimens after 32-cycles drying-wetting and heating-cooling sulfate attack. The surface of the samples had no deposits and was as smooth as before the test, as shown in Figure 2.

3.2. Compression Strength Evolution. The consequences from the compression strength development of OPCC were presented in Figure 3. As could be seen in the histogram, the initial strength of OPCC exhibited a value of 43.5 MPa. In the standard curing environment, it steadily rose to 51 MPa after 60 days, with an increase of 17.2% compared to the initial strength. Due to the MgSO$_4$ solution attack, the compression strength of specimens was clearly lower than that in the standard curing environment with the same age. Also, the compressive strength of OPCC specimens after 32-cycle attack was mildly higher than that of OPCC samples after 24-cycle attack, which resulted from corrosion deposits being formed in the microcosmic pore structures to make the binder denser [17]. The outcomes revealed that the MgSO$_4$ attack contributed to the reduction of the compressive strength of OPCC.

The variation in the compression strength of FAGC with time is exhibited in Figure 4. From the figure, it is clear that the initial compression strength (28 days) of FAGC was 32 MPa, with some fluctuations on the strength for...
Figure 2: The visual appearance of OPCC and FAGC specimens before and after sulfate attack.

Figure 3: Compression strength evolution of OPCC in the standard curing condition and MgSO$_4$ attack, respectively.
both the standard curing condition and the MgSO₄ attack. The compressive strength of FAGC in the standard curing condition increased by 21.88% after 60 days, but it soared by 71.88% in the MgSO₄ attack after 32 cycles. The compressive strength of FAGC after MgSO₄ attack was higher than that of FAGC in standard curing condition with the same age. Bakharev [6] also found that, in the magnesium sulfate solution, water absorption was stronger than that of OPCC. Further, the mass increase might be that water was still in the OPCC samples under 32-cycle MgSO₄ attack, which indicated that fly ash geopolymeric concrete suffered strength loss in the magnesium sulfate attack.

The deterioration of heating group samples was explained by the compression strength loss ratio $R^H$, which was calculated using

$$R^H = \frac{f_{c32} - f_{ch}}{f_{ch}} \times 100\%$$  \hspace{1cm} (1)

where $R^H$ is the compression strength loss ratio of heating group samples (%), $f_{c32}$ is the compression strength of the experiment group specimens after 32 cycles, and $f_{ch}$ is the compression strength of the heating group specimens.

By calculation, $R^H$ of OPCC (17.8%) was higher than that of FAGC (12.7%). From the result, it was clear that FAGC had better magnesium sulfate resistance than OPCC, because the cross-linked aluminosilicate polymer structure of FAGC was firmer than the C-S-H gel of OPCC, which could be confirmed by the microstructure analysis results below.

### 3.3. Mass Change

The mass of both OPCC and FAGC specimens rose after the sulfate attack, as presented in Figure 6. The increase of OPCC specimens was 0.8% compared to the initial mass after 32-cycle drying-wetting and heating-cooling sulfate penetration. The mass growth rate of FAGC specimens was 4.05% after the same experiment period. The reason for the mass increase might be that water was still in the OPCC or FAGC specimens even after 10-hour heating and cooling. The results demonstrated that the water absorptivity of FAGC was stronger than that of OPCC.

### 3.4. Microstructure Analysis

#### 3.4.1. XRD Analysis

The XRD patterns of OPCC in the 60-day standard curing condition, heating condition, and the 32-cycle MgSO₄ attack environment are presented in Figure 7. When OPCC specimens were exposed to MgSO₄ solution, quartz, calcium hydroxide, C-S-H gel, and gypsum could be observed in the peaks. The quartz, calcium hydroxide, and C-S-H could be the main hydration products, as their peaks are strong. Gypsum could be observed at around 32.14° (2θ), which demonstrated that gypsum was a corrosion product. Similar results were also suggested by Jiang and Niu [17] and Qi et al. [23]. Moreover, the peak of C-S-H in the specimen under 32-cycle MgSO₄ attack environment disappeared at about 27.57° (2θ), which meant that C-S-H reacted with MgSO₄ and the number of C-S-H gels decreased. The XRD analytical results agreed with the compressive strength of OPCC.

As shown in Figure 8, the main phases that could be detected were quartz and N-A-S-H gel. Traces of M-A-S-H gel could be observed at 8.60° (2θ) in the XRD spectrum of the 32-cycle MgSO₄ attack group, which illustrated that MgSO₄ reacted with N-A-S-H gel and produced M-A-S-H gel [12]. It was observed that the concentration of N-A-S-H gel in the
3.4.2. **FTIR Analysis.** The FTIR spectra of OPCC samples under 60-day standard curing, heating, and 32-cycle MgSO$_4$ attack conditions are shown in Figure 9. The bands at about 874 and 1420 cm$^{-1}$ meant existence of CO$_3^{2-}$, which indicated that the specimens had already attracted CO$_2$ molecules from the atmosphere before immersion into MgSO$_4$ solution [24].

60-day standard curing group was lower than that of N-A-S-H gel in the heating and 32-cycle MgSO$_4$ attack group, which coincided with the compressive strength behavior of FAGC under magnesium sulfate attack.
The band of approximately 995 cm$^{-1}$ came from asymmetric stretching vibration of silicon-oxygen bond in the hydrated calcium silicate gel [25]. It could be observed clearly from Figure 10 that the strength of the band at around 995 cm$^{-1}$ in the 32-cycle MgSO$_4$ sample was lower than that in the samples under 60-day standard curing and heating conditions. This probably resulted from the degradation of hydrated calcium silicate gel caused by MgSO$_4$ attack. The band of approximately 3643 cm$^{-1}$ was due to the stretching vibration of hydroxy bond in calcium hydroxide [6]. The bending vibration and stretching vibration of hydroxy bond in hydration products induced the changes in the bands at around 1630 and 3435 cm$^{-1}$, respectively [6]. The aluminum oxygen bond vibrations of [Al(OH)$_6$]$_3^{3-}$ resulted in the bands at around 463 cm$^{-1}$ [26, 27].

As could be observed from Figure 10, there was no noticeable difference in the sample under the 60-day standard curing condition, heating condition, and 32-cycle MgSO$_4$ attack environment. In geopolymers based on fly ash, the band at about 1038 cm$^{-1}$ came from asymmetric stretching vibration of Si-O-Al, demonstrating that alkaline activation caused the constitution of an alkaline aluminosilicate (N-A-S-H or M-A-S-H) gel with amorphous nature [28]. The feature located at 770 cm$^{-1}$ was characterized as symmetric stretching vibration of Si-O-Si [29]. The vibrations attributed to bending and stretching of hydrogen bonds were investigated in about 1635 and 3435 cm$^{-1}$, respectively. The FAGC samples subjected to MgSO$_4$ attack under 32 drying-wetting and heating-cooling cycles still maintained the original structure, which indicated that the FAGC samples were durable to magnesium sulfate attack.

### 3.4.3. Thermogravimetric Analysis

The TGA results presented in Figure 11 showed that the mass loss observed was a little higher in FAGC specimens after exposure to MgSO$_4$, when compared with the standard curing FAGC samples. However, the mass loss of OPC specimens was much lower than that of OPC sulfate attack samples. The DTG results in Figure 12 indicated that, as for OPC specimens, the peak near 100°C was mainly attributed to the dehydration of C-S-H gel. Compared to OPC 60-day standard curing samples, sample OPC 32-cycle sulfate attack had a weak strength of the peak for C-S-H gel, which was consistent with the XRD and FTIR results. In the FAGC samples, an endothermic peak was observed between 50°C and 70°C, which was attributed to the loss of evaporable water in the sample, and the water was combined in the aluminosilicates [30].

### 3.4.4. SEM and EDS Analysis

Specimens were adopted from the failed concrete of compression tests. Before being exposed to magnesium sulfate solution, typical reaction products of OPC, such as crystalline Ca(OH)$_2$, floc, and fibrous hydrated calcium silicate gel, could be seen in Figure 13. From the EDS analysis, the major chemical product in the paste is C-S-H gel, in which Si and Ca took up the 32.30% and 8.94% weighting, respectively.
As for the FAGC group specimens with 60-day standard curing, numerous unreacted fly ash particles were discovered in the binder as shown in Figure 14. This suggested that fly ash fine particles did not react with the solution which led to the low 60-day compressive strength on the macroscale [31]. The amorphous N-A-S-H gel could be found, which was validated by the EDS result with 5% weight of Na, supporting XRD finding in Figure 8 and FTIR finding in Figure 10.

After 32 wetting-drying and heating-cooling cycles, many CaSO$_4$·2H$_2$O crystals could be discovered in the OPCC as shown in Figure 15. This suggested that decalcification or decomposition of hydrated calcium silicate and calcium hydroxide phase in the OPCC supplied the calcium required for the formation of gypsum. Gypsum was expansive and this expansion resulted in the development of internal stresses that could damage the concrete and lead to a reduction in strength [32]. Besides, only a small number of floc C-S-H gels were observed. Ettringite was unstable and could be decomposed when temperature exceeded 60–70°C [33], so it did not appear in the specimens in the 32-cycle MgSO$_4$ attack environment, which were exposed to heating-cooling environments.

The amorphous aluminosilicate gels in the FAGC group subjected to 32-cycle MgSO$_4$ attack were much denser in Figure 16 than those in the FAGC 60-day standard curing group in Figure 14. Therefore, the compression strength of the former was much higher than that of the latter. The results in the EDS analysis illustrated that amorphous aluminosilicate gels included the low strength magnesium aluminosilicate hydrate (M-A-S-H) gel [34], which gave an explanation on the decrease of compressive strength in comparison to the heating group. Compared with the FAGC 60-day standard
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Figure 16: SEM and EDS results of FAGC in the 32-cycle MgSO₄ attack environment.

Figure 17: SEM and EDS results of OPCC in the heating group.

Figure 18: SEM and EDS results of FAGC in the heating group.

curing group, the weight of Na in the 32-cycle MgSO₄ attack group decreased from 5.2% to 1.28%, which gave a clarification that a few of N-A-S-H gels were decomposed.

The number of hydrated sodium silicate gels in the OPCC heating group samples in Figure 17 was a little more than that of hydrated sodium silicate gels in the OPCC 60-day standard curing group samples. Thus, the compressive strength in the OPCC heating group was slightly higher than that in the OPCC 60-day standard curing group.

The sodium aluminum silicate hydrate gels in the heating group in Figure 18 were a bit denser than those in the 32-cycle MgSO₄ attack group and no microcrack could be found compared with the 32-cycle MgSO₄ attack group samples. This might explain that the compression strength of heating specimens was a little higher than that of 32-cycle MgSO₄ attack specimens.

4. Conclusions

Based on the observation and analysis in the deterioration of FAGC subjected to magnesium sulfate solution with wetting-drying and heating-cooling cycles, some important parameters such as the compressive strength and microstructure characteristics were studied and analyzed using various analysis tools. Here, the main findings could be concluded as follows.

(i) Laboratorial outcomes demonstrated that the compressive strength loss ratio of OPCC and FAGC heating group specimens was 17.8% and 12.7%, respectively, after 32 wetting-drying and heating-cooling cycles. FAGC had better magnesium sulfate resistance than OPCC as the cross-linked aluminosilicate
polymer structure was more stable than hydrated calcium silicate gel after MgSO₄ attack.

(ii) Based on the consequences of XRD, FTIR, SEM, EDS, and TGA/DTG, the magnesium sulfate attack mechanism of OPCC could be explained as follows: MgSO₄ reacts with C-S-H and creates expansive and low strength gypsum with the decomposition of C-S-H. Besides, ettringite did not exist in the heating-cooling environment.

(iii) The heating-cooling regime enhanced the compressive strength of FAGC samples since polymerization reactions were highly temperature-dependent. The deterioration of FAGC under magnesium sulfate attack after 32 drying-wetting and heating-cooling cycles was due to N-A-S-H gels reacting with MgSO₄, which produced low strength M-A-S-H gels based on the microstructure analysis.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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