

Effect of Ground Granulated Blast Furnace Slag, Pulverized Fuel Ash, Silica Fume on Sulfuric Acid Corrosion Resistance of Cement Matrix

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Abstract: In this study, the effect of supplementary materials (GGBS, PFA, SF) on sulfuric acid corrosion resistance was assessed by measuring the compressive strength, corroded depth and weight change at 7, 28, 56, 91, 180 and 250 days of immersion in sulfuric acid solution with the pH of 0.5, 1.0, 2.0 and 3.0. Then, it was found that an increase in the duration of immersion and a decrease in the pH, as expected, resulted in a more severe corrosion irrespective of binders: increased corroded depth and weight change, and lowered the compressive strength. 60% GGBS mortar specimen was the most resistant to acid corrosion in terms of the corroded depth, weight change and compressive strength, due to the latent hydraulic characteristics and lower portion of calcium hydroxide. The order of resistance to acid was 60% GGBS > 20% PFA > 10% SF > OPC. In a microscopic examination, it was found that acid corrosion of cement matrix produced gypsum, as a result of decomposition of hydration products, which may loose the structure of cement matrix, thereby leading to a remarkable decrease of concrete properties.

Keywords: acid corrosion, compressive strength, weight change, corroded depth, supplementary materials.

1. Introduction

The durability of concrete structures subjected to waste treatment, hot spring, or chemical industry is susceptible to chemical attack. It is well known that in particular, concrete exposed to a sewer system may be subjected to acid corrosion,^{1,2} which is induced from sulfate-reducing bacteria, generating hydrogen sulfide to form sulfuric acid on the surface of concrete structures.^{3,4}

D. desulfuricans as these bacteria reduces sulfate ions,⁵ as being much influenced by the temperature and pH, of which optimized conditions for an active reduction reaction are at 30-35°C of the temperature⁶ and at 2.5 in the pH,⁷ respectively. Then hydrogen sulfide generated in the reduction reacts with water to form sulfuric acid. Alternatively, sulfate ions may also produce hydrogen sulfide by a combined reaction with water and other bacteria.⁸

It was found from a previous researches that acid corrosion depends on free water/cement ratio⁹ and type of acid,¹⁰ and sulfuric acid corrosion led to a more severe damage of concrete than

sulfate attack.¹¹ To minimize the acid corrosion, supplementary materials, such as silica fume (SF), metakaolin, ground granulated blast furnace slag (GGBS) or pulverised fuel ash (PFA) were used,^{4,12-14} and the replacement was found to be effective in enhancing the resistance to acid corrosion, depending on type of supplementary materials, replacement ratio and type of acid.

As alternative methods against acid corrosion, polymer concrete and glass fiber matt were also suggested.¹⁵⁻¹⁷ However, a reduction of concrete properties through acid corrosion has been rarely investigated in a quantitative way to date, while chemistry of cement matrix to acid, in terms of acid neutralisation capacity, has been extensively studied.

The present study concerned the effect of supplementary materials on mitigating the acid corrosion using OPC, GGBS, PFA and SF mortar specimens. To assess the damage of acid corrosion, the compressive strength, weight change and corroded depth of specimens immersed in sulfuric acid solutions were measured at 7, 28, 56, 91, 180 and 250 days. Also was microscopically examined the corroded segment in XRD, SEM and EDXA to ensure the chemistry of acid corrosion.

2. Experimental work

2.1 Materials

As binders, ordinary portland cement (OPC), ground granulated blast furnace slag (GGBS), pulverized fuel ash (PFA), and silica fume (SF) were used to manufacture mortar specimens. The mix proportion for binder : water : sand was 1 : 0.45 : 2. For supplementary materials, the replacement ratio accounted for 60, 20 and 10% for GGBS, PFA and SF mortar specimens, respectively.

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Their oxide composition is given in Table 1.

After 28 days curing in water at $20 \pm 1^\circ\text{C}$, the specimens were immersed in a sulfuric acid solution for 250 days, whose pH ranged 0.5, 1.0, 2.0 and 3.0. The concentration and pH of the sulfuric acid solution were controlled using distilled water, so that the speed of testing could be accelerated, as the acidic condition with a relatively higher pH may take extremely long to get specimens corroded. The solution was replaced every 2 weeks to maintain the pH of solution.

2.2 Mortar properties

After immersion of the specimens in sulfuric acid solutions for 7, 28, 56, 91, 180 and 250 days, the specimens were split and then 1% phenolphthalein solution was sprayed to detect the corroded depth. The corroded depth could be visually determined by whether or not color was changed by spraying, and measured with a ruler. Four measurements were carried out across the section of a specimen and the average value of these measurements was reported in the present study. The number of specimens accounted for 18 for the testing of compressive strength, 3 replications at each duration of immersion in acid. The weight of the specimens exposed to sulfuric acid solution was monitored at 7, 28, 56, 91, 180 and 250 days, and was compared to the weight of specimens cured in water for 28 days. The corroded part of the specimen was removed in measuring the weight. Then the percentage of weight change was calculated as follows:

$$W_c = \frac{W_s - W_w}{W_w} \times 100 \quad (1)$$

where, W_c : the percentage of weight change(%)

W_w : the weight of specimen cured in water for 28 days

W_s : the weight of specimen immersed in a sulfuric acid solution

The reduction of compressive strength of specimens immersed in a sulfuric acid solutions was also measured at 7, 28, 56, 91, 180 and 250 days, and compared the strength of specimens cured in water for 28 days.

2.3 Microstructural examination

Cement paste was used for X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDXA), assuming that aggregate has no impact on corrosion of concrete. The cement paste was, after 28 days curing in water, immersed in a sulfuric acid solution at 0.5 in the pH for 180 days, and then crushed and ground to obtain proper samples for the analysis. The instrumental parameters for XRD were: accelerating

voltage in Ni filter = 30 kV applied current = 20 mA; scanning speed = $5^\circ/\text{min}$; $2\theta = 5-40^\circ$. The paste sample was microscopically examined at $\times 4,000$ magnification, captured by XL30 ESEM (Philips) for SEM analysis, and then EDXA Falcon energy system 60SEM for EDXA, respectively.

3. Results

3.1 Corroded depth

It was seen, as shown in Fig. 1, that the corroded depth of mortar specimens was strongly dependent on the pH of sulfuric acid solution, duration of immersion in acid, and binder types. For all specimens and all pH values in acidic environments, an increase in the duration of immersion resulted in an increase in the corroded depth.

At an early age (7 days immersion), the corroded depth was very low, ranging below 0.75 mm from the mortar surface, irrespective of binder or pH of the solution, but at 250 days of immersion, the pH significantly affected the corroded depth. At 0.5 in the pH, the corroded depth ranged from 6.2 to 8.4 mm after 250 days immersion, while the corroded depth at 3.0 in the pH was below 1.6 mm for the corresponding duration of immersion.

It was also found that GGBS mortar specimen is likely to be the most resistant to penetration of acid at all pH values, whereas OPC is the least. The order of corroded depth for binders was $\text{OPC} > 10\% \text{ SF} > 20\% \text{ PFA} > 60\% \text{ GGBS}$.

3.2 Weight change

It was again observed that 60% GGBS mortar specimen was the most resistant to acid corrosion, while OPC mortar was less resistant (Fig. 2), in that the weight change of specimen immersed in sulfuric acid solutions reflects the degree of acidic deterioration.

At all levels of the pH and duration of immersion, the weight of GGBS mortar specimens was the least reduced, compared to the weight change of the other specimens, accounting for about 7.8%. For OPC, 20% PFA, and 10% SF mortar specimens, the weight change reached up to 25.7, 18.8 and 22.9% at 0.5 in the pH, respectively. The pH of sulfuric acid solution has also a strong impact on the weight change. At 0.5 and 1.0 in the pH, the weight change was significantly increased by immersion duration, ranging from 7 to 250 days, reaching 25.6 and 13.6% respectively, but at 2.0 and 3.0 of pH the weight change was below 5%. In addition, it is notable that the weight of specimens slightly increased at 7 days of immersion, regardless of the pH of sulfuric acid solutions.

3.3 Compressive strength

It was seen that the influence of the pH on the compressive strength of mortar specimens was significant, depending on binders (Fig. 3).

The reduction of compressive strength was lowered, as the pH of sulfuric acid solution increased. At 0.5 in the pH of the acidic solution, the compressive strength was reduced at 250 days by up to 92% for OPC, 68% for 60% GGBS, 76% for 20% PFA and 85% for 10% SF mortar specimens, respectively, while at 3.0 in the pH the compressive strength was decreased about 5.4~8.3%, compared to the compressive strength of mortar cured in water for 28 days.

The benefit of GGBS from a higher resistance to a reduction of

Table 1 Oxide composition of OPC, GGBS, PFA and SF.

Oxide	OPC	GGBS	PFA	SF
CaO (%)	63.3	41.7	3.4	0.7
SiO ₂ (%)	20.2	31.7	57.6	91.2
Al ₂ O ₃ (%)	5.8	14.5	25.5	1.3
Fe ₂ O ₃ (%)	3.0	0.7	6.1	0.8
MgO (%)	3.4	5.4	0.9	0.3
SO ₃ (%)	2.1	2.1	-	-
Density (g/cm ³)	3.15	2.92	2.39	2.20
Fineness (cm ² /g)	3,120	4,450	3,590	204,700

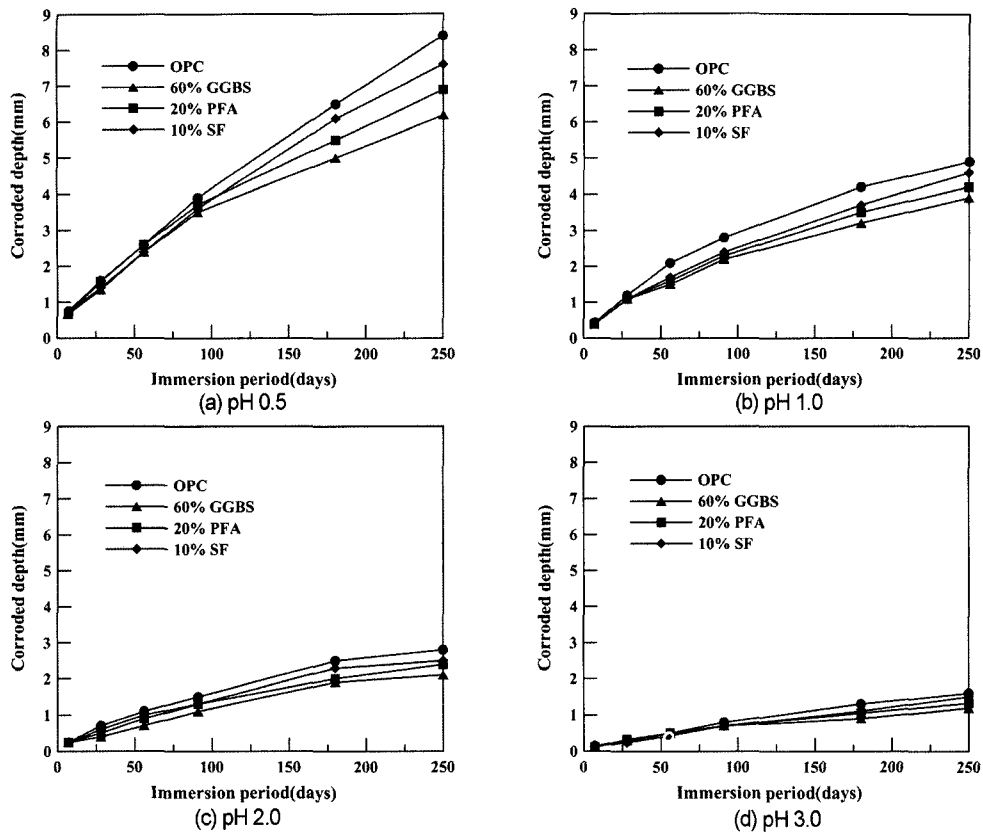


Fig. 1 Corroded depth of OPC, 60% GGBS, 20% PFA and 10% SF mortar specimens immersed in a sulfuric acid solution at (a) 0.5, (b) 1.0, (c) 2.0 and (d) 3.0 in the pH for 250 days.

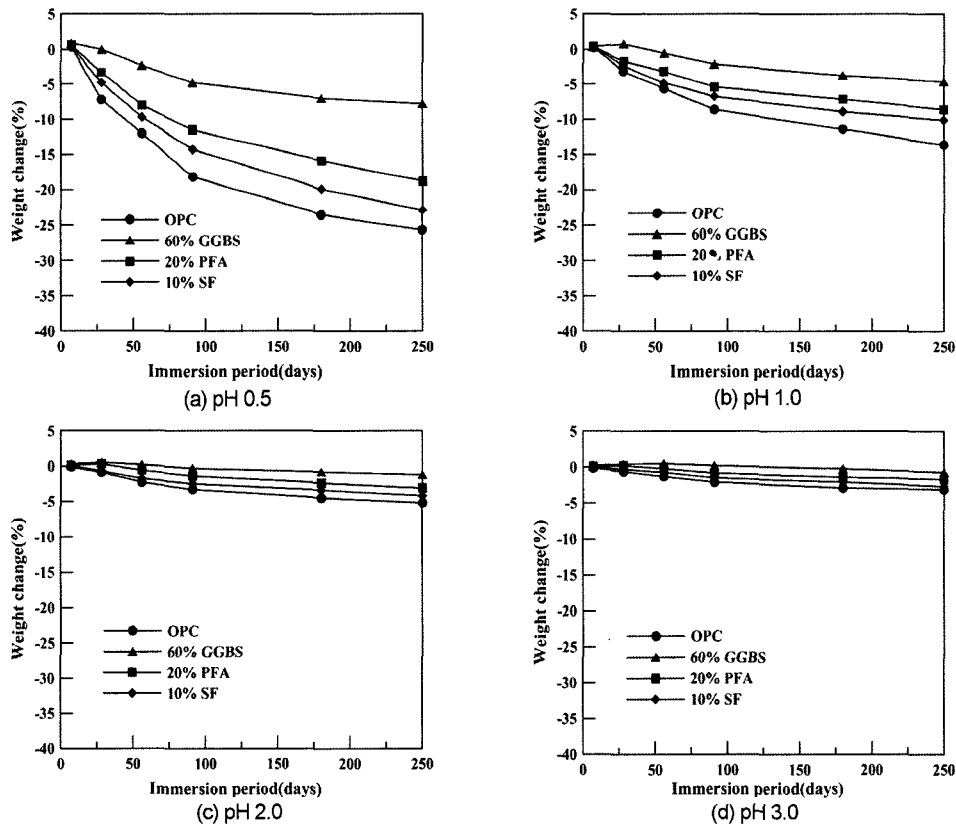


Fig. 2 Weight change of OPC, 60% GGBS, 20% PFA and 10% SF mortar specimens as a function of immersed duration in a sulfuric acid solution at (a) 0.5, (b) 1.0, (c) 2.0 and (d) 3.0 in the pH, comparing the weight of mortars cured in water for 28 days, with images of the corroded specimens.

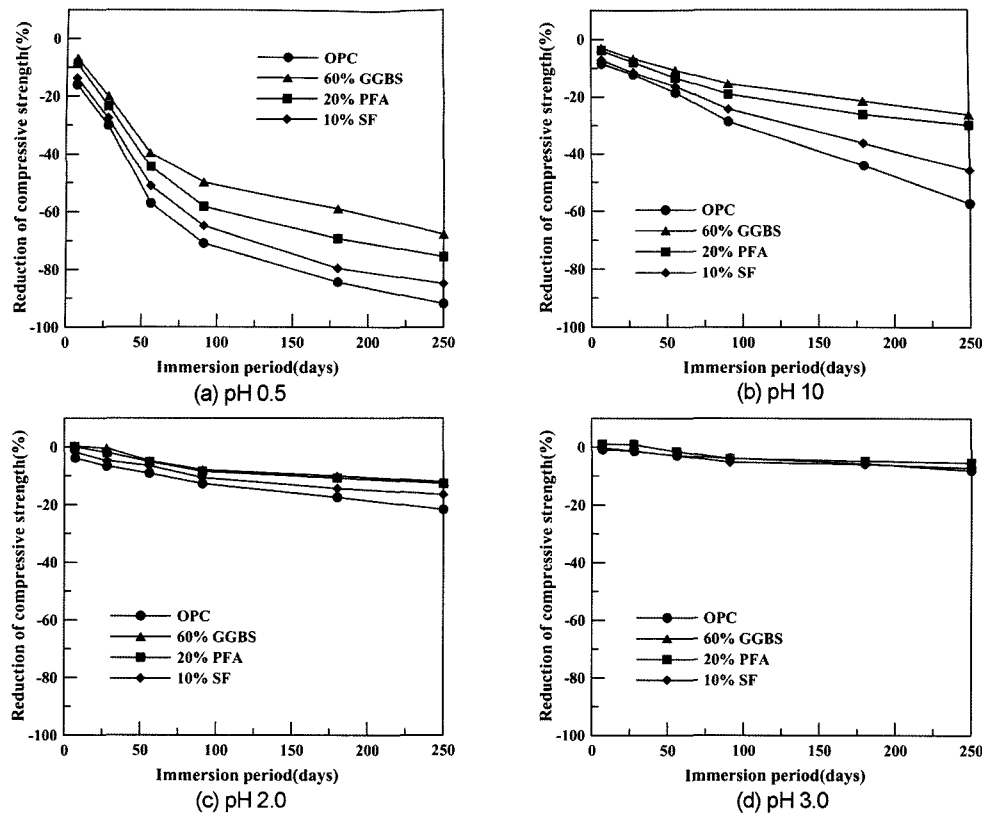


Fig. 3 Compressive strength change of OPC, 60% GGBS, 20% PFA and 10% SF mortar specimens as a function of immersed duration in a sulfuric acid solution at (a) 0.5, (b) 1.0, (c) 2.0 and (d) 3.0 in the pH, comparing the strength of mortars cured in water for 28 days.

compressive strength was observed at all pH values, whereas the compressive strength for OPC more significantly decreased than for other mortar specimens.

3.4 Microstructure

Fig. 4 gives the XRD results of cement pastes immersed in a sulfuric acid solution at 0.5 in the pH for 180 days. It was seen that the peaks for uncorroded samples in the cement paste generally were for calcium hydroxide (i.e. portlandite) in the XRD analysis, regardless of binders, while the peaks from corroded parts of cement paste were for gypsum. In particular, the intensity of peaks for calcium hydroxide was the greatest, compared to the peaks for SF, PFA, or GGBS cement pastes.

Fig. 5 gives SEM images of deteriorated segment of cement paste after immersion in a sulfuric acid solution at 0.5 in the pH for 180 days, and a result of EDXA analysis is given, corresponding to the part in the circle. It was seen that regardless of binders, the great peaks for calcium, Ca and sulfur, S were observed. It may suggest that the acid corrosion resulted in a formation of gypsum.

4. Discussion

4.1 Acid corrosion

The concentration of sulfate ions in a sewer system ranges from 20 to 100 mg/l, which forms the hydrogen sulfide by sulfate-reducing bacteria such as *D. desulfuricans*.⁵ Then, the hydrogen sulfide reacts with oxygen and then is dissolved in water to form sulfuric acid on the concrete surface in the sewer system, whose pH ranges from 1 to 2. The chemical reaction for generating sulfu-

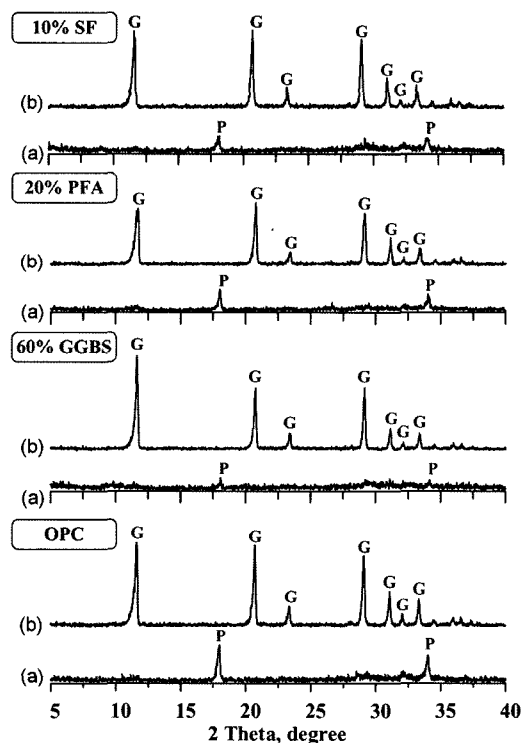
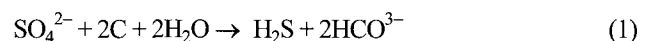


Fig. 4 XRD analysis of OPC, 60% GGBS, 20% PFA and 10% SF pastes (a) cured in water and (b) immersed in a sulfuric acid solution at 0.5 in the pH for 180 days (G : Gypsum, P : Portlandite).

ric acid from sulfate ions is as follows.



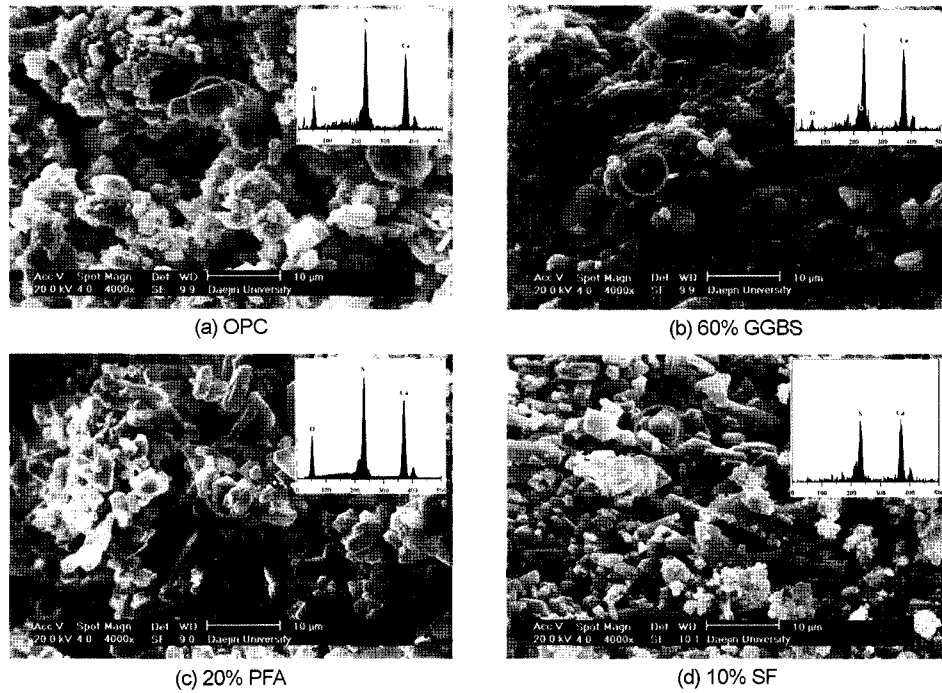
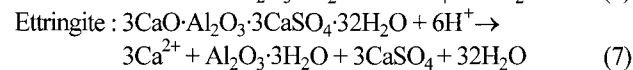
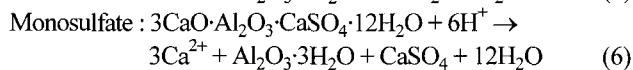
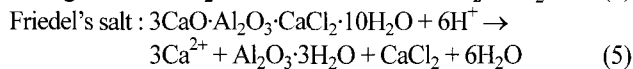
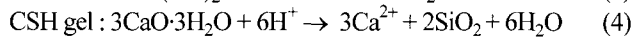
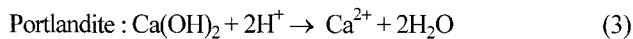


Fig. 5 SEM and EDXA analysis of (a) OPC, (b) 60% GGBS, (c) 20% PFA and (d) 10% SF pastes immersed in a sulfuric acid solution at 0.5 in the pH for 180 days.



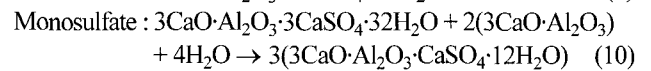
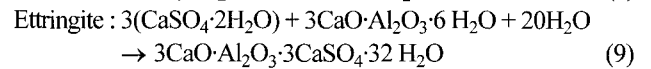
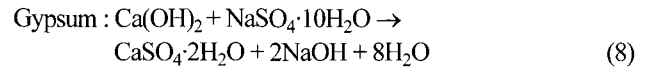
When concrete is exposed to sulfuric acid solution, hydrogen ions (H^+) and sulfate ions (SO_4^{2-}) deteriorate the concrete properties by reacting with hydration products to make cement matrix more porous or/and expansive.

Concrete is chemically stable in an alkaline environment, but unstable in a neutral or acidic environment. Hydrogen ions in sulfuric acid usually react with calcium ions in cement matrix then to decompose the hydration products as seen in following chemical equations. It is known that all hydration products can be corroded by acid at different rates and degrees, depending on types of acid, temperature, dry/wet cycles, abrasion, and freeze and thaw.¹⁸



Sulfate ions penetrated into concrete in general react with calcium hydroxide of cement matrix to form gypsum (i.e. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), which softens the inner concrete structure and decreases the concrete properties, as given in eq. (8). The gypsum generated from a reaction with calcium hydroxide may again react with hydrated C_3A to form ettringite (see eq. (9)), which induces expansion of cement matrix, and thus creates cracks and deterioration of concrete.¹⁹ The ettringite then reacts with C_3A to form monosulfate, which however does severely harm neither cement matrix nor concrete properties. eq. (10) gives the chemical equation for the generation of monosulfate. The sulfate attack can be severe,

only when the sulfate concentration in soil is quite high, compared to acid corrosion by hydrogen ions. Hence, a standard suggests 4 levels of water soluble sulfate and their expected damage: the sulfate attack can be prevented by sulfate resistant portland cement or/and pozzolanic materials against up to 2% sulfate ions.²⁰



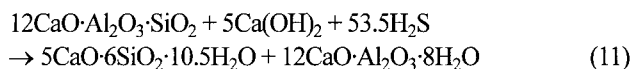
4.2 Supplementary materials

Mortar specimens of OPC, 60% GGBS, 20% PFA and 10% SF exposed to sulfuric acid solutions were deteriorated as time processed from 7 to 250 days: carbonation, weight change, and a decrease of compressive strength. The reduction of the concrete properties is mainly attributed to a generation of gypsum, resulting from a reaction between cement hydration products and sulfuric acid. The gypsum in cement matrix softens concrete and decomposes hydration products and thus the weight and strength of the mortar specimens was reduced (Figs. 2 and 3).

It was observed in the present study that the degree of deterioration was dependent on binder type. It is likely to be attributed to different hydration products and the rate of hydration. The most severe acid corrosion was observed from OPC mortars, which have the greatest portion of calcium hydroxide in hydration products, compared to the other mortar specimens (see Fig. 4). The higher amount of calcium hydroxide may imply the higher probability of formation of gypsum in cement matrix. Thus, a high level of the decomposition of hydration products seemed to lead to a catastrophic failure in the physical properties of concrete.

In contrast, 60% GGBS mortar specimens was less damaged,

presumably due to its latent hydraulic characteristics. Calcium oxide (CaO) and siliceous oxide (SiO₂) in GGBS react with water to form CSH hydrate in an alkaline environment and alumina (Al₂O₃) in GGBS also latently forms C-A-H hydrate. The latent hydraulic characteristics of GGBS result from a reaction between gehlenite (2CaO·Al₂O₃·SiO₂) and calcium hydroxide in hydrates as below.



This hydration process consumes calcium hydroxide, thereby less probability of reacting between sulfuric acid. Hence, 60% GGBS mortar specimens in the present study was the most beneficent in delaying the acid corrosion of specimen. Moreover, the hydrates generated from GGBS reduced the porosity of mortar, which allowed sulfuric acid to penetrate the specimens at a lower rate. 10% SF mortar also formed a denser pore structure in hydrates by filling up the pores (i.e. micro filler effect), but the C-S-H gel hydrated in SF mortar is relatively unstable. Hence, the resistance to acid corrosion, such as carbonation, weight change and a reduction of compressive strength, was less effective.

5. Conclusions

The present study investigated the resistance of OPC, 60% GGBS, 20% PFA and 10% SF mortar specimens against sulfuric acid corrosion. Then it was found that the corrosion resistance of mortar specimens were dependent on binder, duration of immersion and the pH of sulfuric acid solutions. An increase in the immersed duration and a decrease in the pH resulted in a significant increase in the acid corrosion of specimens. For binders, the order of degree of acid corrosion was 60% GGBS < 20% PFA < 10% SF < OPC.

In this study, it was ensured by XRD and SEM analysis that the main mechanism of acid corrosion is responsible for a formation of gypsum, resulting from a reaction between calcium hydroxide and sulfuric acid, which softens and looses the structure of cement matrix, thereby leading to a remarkable decrease of strength and weight change. The least level of the resistance of OPC mortar to acid corrosion was due to a higher amount of calcium hydroxide in hydrates, which implies a higher level of gypsum formation. In contrast, 60% GGBS mortar was the most effective in delaying acid corrosion, due to its latent hydraulic characteristics, which means that calcium hydroxide was consumed in the reaction between gehlenite and hydrates, and that GGBS formed the denser pore structure. 10% SF mortar was not much resistant to acid corrosion despite the dense pore structure, which was attributed to the unstable C-S-H gel.

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