

*Article*

## Deterioration in Sulfuric Acid of Cement Pastes incorporating High CaO and Low CaO Fly Ashes

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**Abstract.** This research studies the deterioration in sulfuric acid solution (pH 1) of cement pastes with fly ash. Effects of three major factors affecting the acid attack behavior are described. First, for the water to binder ratio, it was found that cement pastes with a higher water to binder ratio (w/b of 0.40) have a lower mass loss in sulfuric acid solution than those with a lower water to binder ratio (w/b of 0.25). In addition to the known mechanism of higher porosity in higher w/b pastes which makes the higher w/b pastes to be able to accommodate more gypsum, another mechanism was described based on the different abilities of calcium ion and sulfate ion to diffuse out of and into the pastes, respectively. Second, the type and content of binder provide a great influence on the degradation of cement pastes. The test of cement pastes with 30% and 50% fly ash replacement demonstrated that the fly ashes decrease the deterioration of pastes in sulfuric acid solution. In addition, it was observed that fly ash with low calcium oxide provided better resistance to sulfuric acid attack than fly ash with high calcium oxide did. Finally, the characteristics of the deterioration of paste specimens due to sulfuric acid attack was found to correlate well with CaO/SiO<sub>2</sub> ratio.

**Keywords:** Sulfuric acid attack, calcium silicate hydrate (C-S-H), fly ash, concrete, cement paste.

**ENGINEERING JOURNAL** Volume 25 Issue 2

Received 13 July 2020

Accepted 29 December 2020

Published 28 February 2021

Online at <https://engj.org/>

DOI:10.4186/ej.2021.25.2.71

## 1. Introduction

Nowadays, there are many underground sewage systems in many countries. However, one of the major problems for this type of concrete structure is the deterioration of the structure due to aggressive substances, such as sulfuric acid, which are produced in a sewage water environment. Therefore, the current practice which mainly focuses on the strength of the concrete may be not adequate for these structures. Another important factor that should be considered is the durability of concrete to withstand aggressive environments such as exposure to acids. In case of wastewater system, bacteria in the system can generate aggressive aqueous solutions which is generally known as biogenic sulfuric acid (BSA). BSA might damage these structures, reducing their service life and resulting in high maintenance cost each year. The mechanism of BSA corrosion of concrete can be explained as follows. In an anaerobic condition of a sewage system, sulfate ion ( $\text{SO}_4^{2-}$ ) in wastewater is harmful to submerged concrete structures. It can also react with a reducing agent by sulfate-reducing bacteria (SRB) to form hydrogen sulfide gas ( $\text{H}_2\text{S}$ ). Then, in aerobic condition, hydrogen sulfide can react with an oxidizer by sulfur-oxidizing bacteria (SOB) to form sulfuric acid ( $\text{H}_2\text{SO}_4$ ). Sulfuric acid causes erosion of the concrete in the sewage system because of formation of expansive secondary mineral products such as gypsum and ettringite. The mechanisms of deterioration of sulfates and acids in sewers are different. Sulfuric acid can cause more damage than basic sulfates [1, 2].

At present, supplementary cementitious materials (SCMs) that can be used to improve concrete performances in fresh and hardened states, especially the performance in aggressive environments are popularly applied in concrete [3-6]. Many studies have focused on improving the resistance of concrete in sulfate ion environment by partially replacing cement with SCMs such as fly ash, silica fume, and slag. These SCMs decrease the amount of calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) which is the main component to react with sulfuric acid to cause deterioration [7-11]. Fly ash usually contains a high silica content and so can react with  $\text{Ca}(\text{OH})_2$  to produce calcium silicate hydrate (C-S-H). This reaction is well known as the pozzolanic reaction. The C-S-H produced by pozzolanic reaction has a higher binding capacity to resist acid attack than that of the cement hydration [12-15].

It is necessary to understand the mechanism of the reaction with acid of concrete with SCMs. Well-understood mechanisms are useful for predicting the service life of concrete structures in acidic environments and for developing concrete mixtures which can slow down or decrease the rate of deterioration.

In addition, fly ashes can be used for improving concrete performances in aggressive environments. Another way to improve concrete so that it can resist sulfuric acid attack is to increase the water to binder (w/b) ratio of concrete. As reported in the literature, the deterioration of concrete at a high acid concentration

decreases with a decrease in the cement content (high w/c ratio). There is a lower weight loss of concrete with a higher water to cement ratio (w/c) when compared to concrete with a low water to cement ratio [16]. Concrete with a higher water to binder ratio has larger and more pores than that of concrete with a lower water to binder ratio. These pores decrease the expansion pressure caused by the produced gypsum. The inner pressure caused by expansive products can exceed the tensile strength of the paste structure which leads to cracking in concretes [17-19].

The above-mentioned mechanism may not be the only mechanism causing a lower sulfuric acid resistance in lower w/b mixtures. The effects of the types of fly ashes, especially for those with different chemical compositions, are still not clear. In this research, another mechanism is presented for the effect of water to binder ratio and the effects of types and contents of fly ashes, especially fly ashes with low CaO and high CaO content.

## 2. Experiment

### 2.1. Materials

Ordinary Portland cement (type I) according to ASTM C150 [20] and TIS15 [21] was used as the main binding material. In case of cement replacing materials, two types of fly ash were used for the tests. One was from Mae Moh power plant of the Electricity Generating Authority of Thailand in Lampang province, northern Thailand, that produces fly ash with high CaO content (FAM). The other one was from BLC Power Co., Ltd. in Rayong province, east of Thailand, that produces fly ash with low CaO content (FAR). All of the fly ashes followed Thai Industrial Standard (TIS 2135-2545) [22]. Chemical compositions and physical properties of all binders are given in Table 1.

### 2.2. Specimen Preparation

Table 2 lists the mix proportions of the cement paste specimens used in this study, with water to binder ratios of 0.25 and 0.40. The percentages of cement replacing materials (CRMs) in binary binders were 30% and 50% for each type of fly ash (FAM or FAR). Five cement paste specimens for each mix were cast, three specimens for weight change of cement paste from acid attack, one specimen for precipitate measurement of cement paste specimen in sulfuric acid solution, and one specimen for the analysis of compounds on the specimen surface after the acid attack. The cubic cement paste specimens were cast with a size of 50 mm x 50 mm x 50 mm for the acid corrosion test. Each test specimen was removed from the mold one day after casting and cured in lime water until 28 days of age. The specimens were exposed to a sulfuric acid solution with a pH of 1 after the 28 days of curing. The acid solution was prepared using sulfuric acid (95-97%, EMSURE of Merck) dissolved in reverse osmosis water to obtain a solution with a pH of 1. The prepared

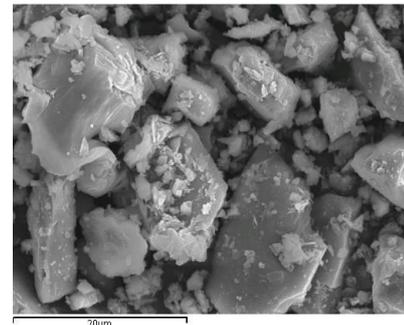
cement paste specimens with different mix proportions were immersed in the sulfuric acid solutions. The pH of the acid solutions was measured daily by a pH meter (Mettler Toledo, FiveGo™ pH portable meter, FG2, accuracy + 1). A pH of 1 was maintained by addition of acid throughout the test period.

Table 1. Chemical compositions and physical properties of the tested cement and fly ashes.

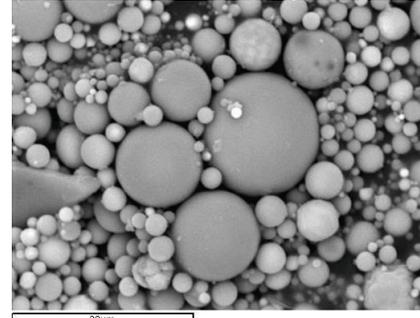
Chemical compositions (% by weight) /Physical properties	Cement (OPC Type I)	Fly ash	
		Mae Moh (FAM)	BLCP (FAR)
SiO <sub>2</sub>	19.70	40.93	61.91
Al <sub>2</sub> O <sub>3</sub>	5.19	22.42	20.35
Fe <sub>2</sub> O <sub>3</sub>	3.34	13.64	5.20
CaO	64.80	13.63	2.32
MgO	1.20	2.93	1.35
Na <sub>2</sub> O	0.16	0.89	0.79
K <sub>2</sub> O	0.44	2.39	1.36
SO <sub>3</sub>	2.54	1.93	0.28
Free lime content	0.87	0.22	0.19
Loss on ignition	2.10	0.46	5.68
Specific gravity	3.13	2.26	2.16
Blaine fineness (cm <sup>2</sup> /g)	3,660	2,460	3,400
Mean particle diameter (μm)	15.41	17.74	15.91

Table 2. Mix proportions of the tested pastes.

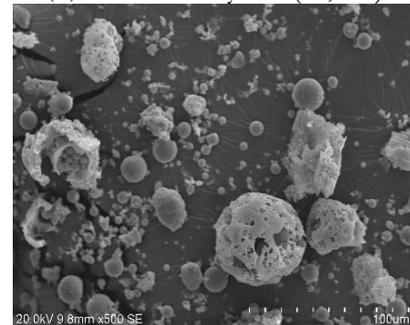
No.	Mix ID.	w/b	Proportion (ratio by weight)		
			OPC	FAM	FAR
1	C100	0.25	1.00	-	-
2	C70FAM30	0.25	0.70	0.30	-
3	C50FAM50	0.25	0.50	0.50	-
4	C70FAR30	0.25	0.70	-	0.30
5	C50FAR50	0.25	0.50	-	0.50
6	C100	0.40	1.00	-	-
7	C70FAM30	0.40	0.70	0.30	-
8	C50FAM50	0.40	0.50	0.50	-
9	C70FAR30	0.40	0.30	-	0.30
10	C50FAR50	0.40	0.50	-	0.50



(a) Portland cement type I (x2,500)



(b) Mae Moh fly ash (x2,500)



(c) BLCP fly ash (x500)

Fig.1. SEM images of cement and fly ashes used in this study.

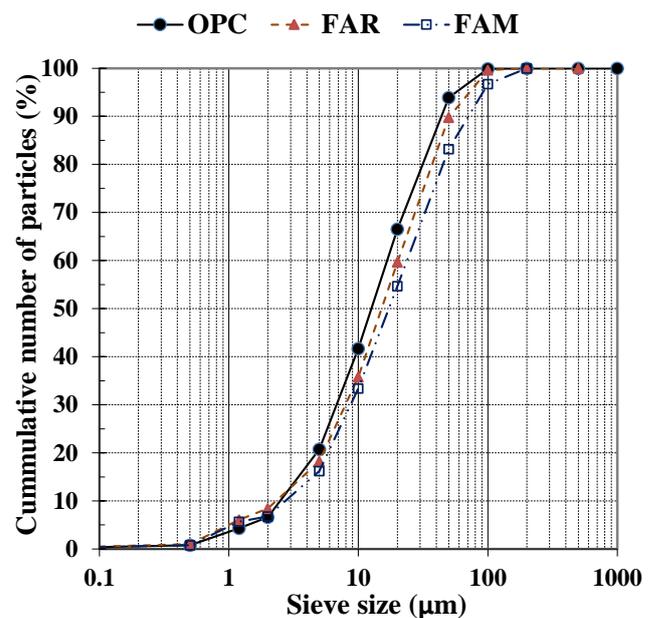


Fig. 2. Particles size distribution of cement and fly ashes used in this study.

The BLCF fly ash (FAR) contains low calcium oxide (CaO) content of 2.32%, which is classified as TIS 2135-2545 class 2a. On the other hand, the Mae Moh fly ash (FAM) contains high calcium oxide (CaO) content of 13.63%, and so is classified as TIS 2135-2545 class 2b. In case of physical properties, the Blaine fineness and mean particle size are 2,460 cm<sup>2</sup>/g and 17.74 microns for FAM and are 3,400 cm<sup>2</sup>/g and 15.91 microns for FAR, respectively. The shape and size distribution of the binders are shown in Figs. 1 and 2.

### 2.3. Acid Corrosion Test

#### 2.3.1. Weight change of cement paste specimens from acid attack

After curing the cement paste specimens in lime water until 28 days of age, the initial weight of each sample was measured. Then, the paste samples were put in the prepared acid solution. The paste samples were removed from the solution to measure their weight (every week), to obtain the change in weight. Before weighting, the cement paste specimens were washed using tap water and brushed with a soft brush to eliminate the unsound and disintegrated surfaces caused by the acid attack and were then dried with a clean towel. The weight change of each paste mixture was calculated from the average weight change of three specimens.

#### 2.3.2. Analysis of compounds on the specimen surface after acid attack

The surface structure of each cement paste sample was analyzed to find reaction products after having been immersed in sulfuric acid solution for 30 days. The specimens were washed with water, brushed, dried, and then left at room temperature for 24 hours. After that, the powders that were scraped from the specimen surface were dried at 60°C in an oven for 5 hours to eliminate moisture. The dried specimens were ground by a planetary ball mill to obtain a powder with a particle size range of 45-75 µm. The ground sample was mixed with corundum with a ground powder to corundum ratio by weight of 9:1. The prepared samples were characterized by using XRD (XRD, Bruker D4 Endeavor with Cu K $\alpha$ 1 radiation at 35 kV and 45 mA, 5° to 70° 2 theta, 0.02° step size, and 0.2 seconds). EVA software was used to identify the compounds in the sample, and Rietveld analysis of the XRD pattern of each sample was used to quantify the amount of each compound.

#### 2.3.3. Precipitate measurement of cement paste in sulfuric acid solution

After immersion of the specimens with a w/b of 0.25 and a w/b of 0.40 in the sulfuric acid solution for 30 days, the specimens were removed from the acid solution. The differences of turbidity in the acid solution used for submerging pastes with different water to binder ratios

were compared by diluting the solution with de-ionized water at a 1:1 ratio before the turbidity measurement. Then, the acid solutions were centrifuged with a speed of 6000 rpm for 30 minutes to recover precipitates. The precipitates of the solutions were kept at room temperature for 24 hours and were dried at 60°C in an oven for 5 hours to eliminate moisture before the analysis of the precipitates by X-Ray Diffraction (XRD).

### 2.4. Pore Size Distribution Test

Pore size distributions of paste specimens C100 and C70FAM30 with a w/b of 0.25 were determined by Mercury Intrusion Porosimetry (MIP). A Micromeritics AutoPore V 9600 (U.S.A.) with a maximum 414 MPa intrusion pressure was used. This MIP instrument is able to detect the pores with the diameter ranging from 3 nm to 500 µm. The cube samples with dimensions of 10 mm × 10 mm × 10 mm were cut out using a diamond saw from the mid-portion of the paste specimens after curing in lime water until 28 days of age. After that, the small cube samples were submerged in acetone for 24 h and subsequently dried in an oven at 50 °C for 24 h to stop the hydration. Two samples were used for each MIP test.

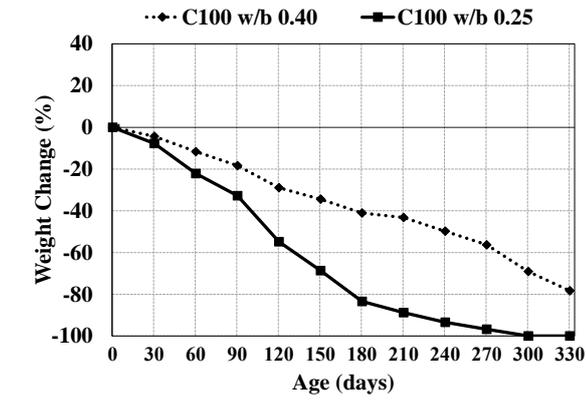
## 3. Results and Discussion

### 3.1. Effect of Water to Binder Ratio on Weight Change of Cement Paste Specimens in Sulfuric Acid Solution

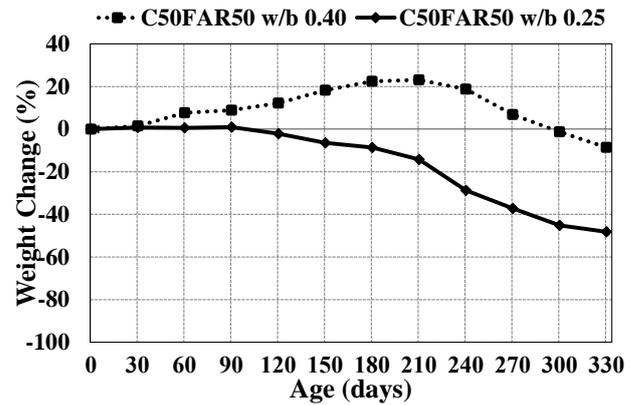
Figure 3 shows weight change of cement paste specimens exposed to sulfuric acid solution for 330 days. The weight change of specimens with a w/b of 0.40 is lower than that of the specimens with a w/b of 0.25.

The effect of water to binder ratio on weight change in our study is similar to many previous researches which reported the effect of the w/c ratio of cement pastes on resistance to sulfuric acid attack. It was reported that specimens with a lower w/c ratio showed higher degradation with a sulfuric acid attack than those with a higher w/c ratio. This was reported to be due to the larger pore sizes and the higher amount of pores in the paste with a higher water to binder ratio, providing more spaces to accommodate the expansion product, which is mainly gypsum [16-18].

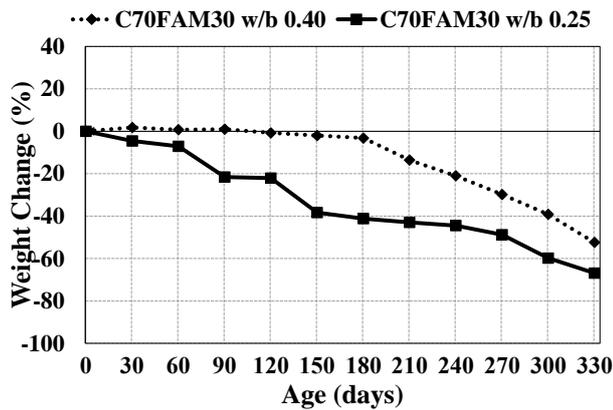
In addition to the mechanism explained in the previous paragraph, another phenomenon, which is the effect of w/b on acid corrosion behavior, found in this study is the dissolving and diffusion of calcium ions from cement pastes to react with sulfate ions in the sulfuric acid solution, as discussed in the following precipitate analysis section.



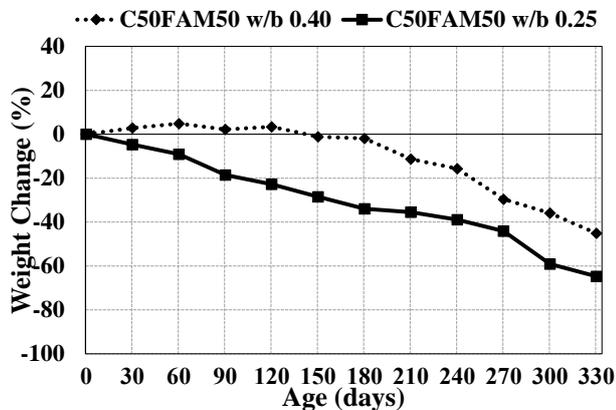
(a) Cement paste



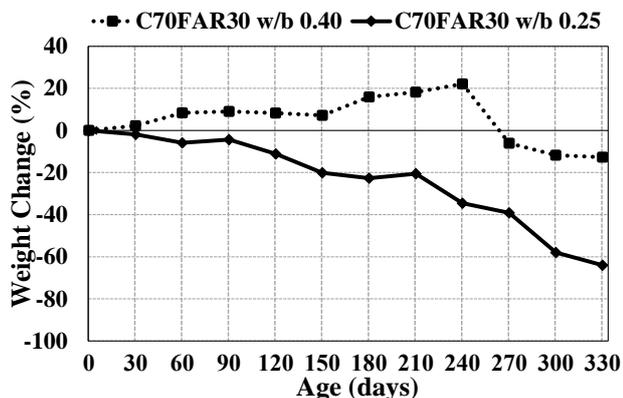
(e) Paste with 50% FAR



(b) Paste with 30% FAM



(c) Paste with 50% FAM



(d) Paste with 30% FAR

Fig. 3. Weight change of cement pastes with w/b of 0.25 and w/b of 0.40 exposed to sulfuric acid solution with constant pH 1 for 330 days.

### 3.2. Precipitate Analysis of the Sulfuric Acid Solution after Sample Submersion

After immersing the cement paste samples in the sulfuric acid solution for 30 days, the turbidity of the sulfuric acid solution was observed. The results obtained by a turbidity meter indicated that the solutions of cement pastes with a water to binder ratio of 0.25 had a higher turbidity when compared to those of the pastes with a water to binder ratio of 0.40. The results show that the turbidity, after the immersion of the cement pastes with water to binder ratios of 0.25 and 0.40, were 87.80 and 32.50 units, respectively.

Moreover, the components of the precipitate in the acid solution were analyzed by using XRD, with the results shown in Fig. 4. The results of the precipitate analysis showed mainly the existence of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). Therefore, the amount of gypsum in the solution is related to the turbidity of the solution. This means that more gypsum was formed in the acid solution outside the samples with w/b of 0.25 when compared to the samples with w/b of 0.40 due to the results of the more calcium ion ( $\text{Ca}^{2+}$ ) diffusing out of the samples with w/b of 0.25 [23]. There are 2 reasons for more calcium ion ( $\text{Ca}^{2+}$ ) diffusing out of the samples with lower w/b. One is because more  $\text{Ca}(\text{OH})_2$  produced in lower w/b pastes as a result of higher cement content [24]. Second is because of more major hydrated products like C-S-H in the pastes with lower w/b to be decalcified by the acid [25, 26].

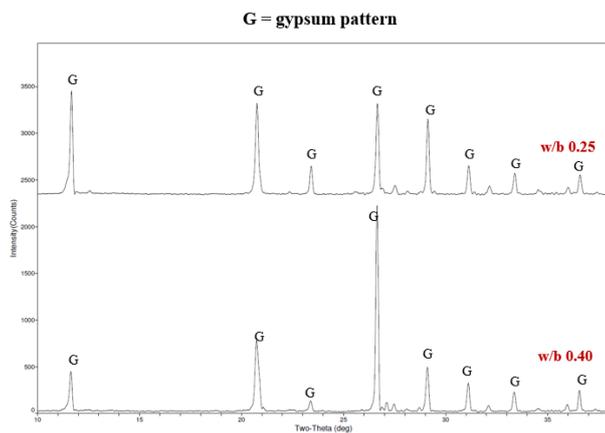


Fig. 4. XRD patterns of the precipitates in sulfuric acid solutions of C100 with w/b 0.25 and w/b 0.40.

These results can be explained by the size of the sulfate ion ( $\text{SO}_4^{2-}$ ) which is larger than that of the calcium ion ( $\text{Ca}^{2+}$ ) [27]. Cement pastes with a lower water to binder ratio (w/b of 0.25) have a denser paste structure. Therefore, it is more difficult for sulfate ions ( $\text{SO}_4^{2-}$ ) from the sulfuric acid solution to penetrate into the specimens with low w/b. However, calcium ions ( $\text{Ca}^{2+}$ ) can easily diffuse out into the solution, thereby reacting with sulfate ions ( $\text{SO}_4^{2-}$ ) in the acid solution outside the pastes and form a precipitate in the acid solution. Cement pastes with a higher water to binder ratio (w/b of 0.40) have higher porosity and a larger pore size, making it easier for the sulfate ions to diffuse into the specimen and form gypsum inside the pores. This explains the behavior of weight increase in the pastes with w/b of 0.40 at the first 270 days (see Fig. 3) but no weight gain was seen in the pastes with w/b of 0.25.

For more support of the above hypothesis, the change of pH values with time of the solutions used for immersing the specimens (with a w/b of 0.25 and a w/b of 0.40) was measured, with the results shown in Fig. 5. Note that the pH of the solutions in this series was not kept constant during the 120 min of the measurement. The measured results indicated that the pH value of the sulfuric acid solution in which the specimens with a w/b of 0.25 were immersed was higher than that of the solution of the specimens with a w/b of 0.40. The rate of pH increase is almost double for the case of w/b of 0.25 when compared to that of w/b of 0.40 for the first 10 min. This means that more  $\text{Ca}^{2+}$  and  $\text{OH}^-$  were dissolved from the specimen with a w/b of 0.25 than from the specimen with a w/b of 0.40, even though the specimen with a w/b of 0.25 was lower in porosity or had a lower diffusion coefficient.

The observed results indicate that in addition to the effects of porosity, dissolved calcium ions ( $\text{Ca}^{2+}$ ) can diffuse away from cement pastes to react with sulfate ions ( $\text{SO}_4^{2-}$ ) in the sulfuric acid solution, influencing the deterioration of the paste specimens.

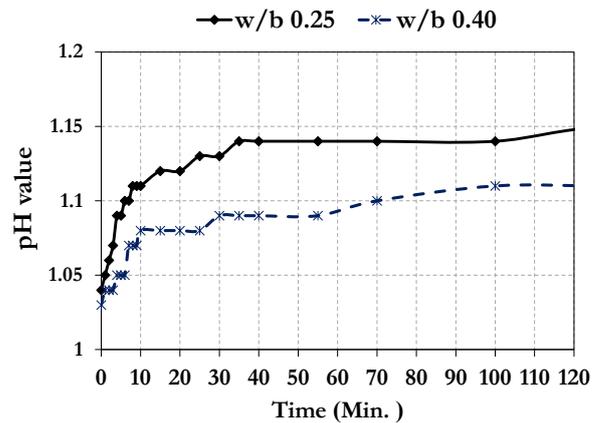


Fig. 5. Change of pH of the solutions in which the pastes with w/b of 0.25 and 0.40 were immersed.

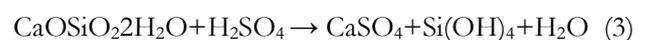
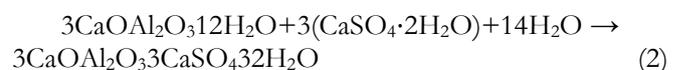
### 3.3. Effect of Fly Ashes on Weight Change of Paste Specimens in Sulfuric Acid Solution

Both fly ashes, FAM and FAR, can reduce the weight change in sulfuric acid of the paste specimens, as shown in Fig. 6.

The weight change results of pastes in Fig. 6 (a) and Fig. 6 (b) show small differences in the first 30 days of exposure. Nonetheless, more differences were noticed after that. The control cement-only paste specimen demonstrated the greatest weight change after 330 days in the sulfuric acid solution. Moreover, the control (cement-only) specimens with a w/b of 0.25 were completely destroyed at 300 days of immersion. On the contrary, the sulfuric acid resistance was enhanced when fly ashes were used. The paste mixture with 50% FAR demonstrated the smallest weight change, followed by the 30% FAR mixture. The mixes with 30% and 50% FAM showed lower weight changes than that of the control paste specimens, but higher weight changes than those of the mixes with 30% and 50% FAR.

These results confirmed that the use of fly ash can improve the resistance of cement pastes to sulfuric acid attack. This is because of the ability of fly ash to reduce the amount of calcium hydroxide, which is vulnerable to sulfuric acid attack.

Degradation by sulfuric acid attack begins when the sulfate ions react with calcium ions to form gypsum and ettringite by further reactions, causing expansion. The mechanism of sulfuric acid attack in paste specimens is shown by the following chemical reactions [28].



The sulfuric acid starts to react with  $\text{Ca}(\text{OH})_2$  in the paste, resulting in gypsum as the product of the reaction.

The formed gypsum has a volume of about 1.2-2.2 times that of its original products. After that, gypsum reacts with calcium aluminate hydrate (C<sub>3</sub>A) to form ettringite. The formed ettringite has a much larger volume than that of the original products. Therefore, the formed gypsum and ettringite are the main cause of the large volume expansion which increases the internal pressure and leads to cracking in the paste specimens. Concurrently, calcium silicate hydrate (C-S-H) can be decomposed by sulfuric acid to form calcium sulfate compounds and silica gel. This reaction results in mass loss and cracking in pastes, and finally collapsing the paste structure.

From the above mechanism, fly ash can decrease the weight loss of cement paste specimens in sulfuric acid solution by decreasing the amount of calcium hydroxide. However, in addition to the benefits of fly ash to decrease calcium hydroxide (Ca(OH)<sub>2</sub>), it also produces a stronger calcium silicate structure against the acid attack. This was confirmed by a previous research [12] which mentioned that a C-S-H product which is produced by pozzolanic reactions has a different structure and calcium to silicate ratio (CaO/SiO<sub>2</sub> of about 1.0) from that of the conventional C-S-H (CaO/SiO<sub>2</sub> of about 3.0) produced by hydration reaction of ordinary Portland cement. Decomposition of C-S-H (release of Ca<sup>2+</sup>) starts at a pH below 9.0.

While decalcification of C-S-H with a high CaO/SiO<sub>2</sub> is preferential and produces a structure vulnerable to acid attack while dissolution of C-S-H with a low CaO/SiO<sub>2</sub> takes place at a slower rate and produces a dense silico-aluminous gel. It is generally known that the use of fly ash decreases the amount of Ca(OH)<sub>2</sub> in the mixtures due to the effects of cement dilution and pozzolanic reaction. The more fly ash used in the mixtures, the lower the amount of Ca(OH)<sub>2</sub>. Low CaO fly ash mixtures exhibit a lower pH, meaning also a lower amount of Ca(OH)<sub>2</sub>, than the high CaO fly ash mixtures as shown in Fig. 7.

Figure 7 compares the amount of calcium hydroxide in the mortars incorporating FA1 (low CaO fly ash, CaO = 8%) and FA2 (high CaO fly ash, CaO = 15%) at the age of 28 days, tested by thermo gravimetric analysis. The results show that at the same fly ash content, the amount of calcium hydroxide in the FA2 mortars is generally higher than that of the FA1 mortars [29].

The effect of the calcium to silicate ratio of the mixture is also demonstrated here. The relationship between the CaO/SiO<sub>2</sub> ratio, which is determined from the chemical compositions of all binders in the mixtures by using Eq. (4), and the weight change after 300 days of immersion, is shown in Fig. 8.

$$\frac{\text{CaO}}{\text{SiO}_2} = \frac{(\text{CaO}_c \times W_c) + (\text{CaO}_f \times W_f)}{(\text{SiO}_{2c} \times W_c) + (\text{SiO}_{2f} \times W_f)} \quad (4)$$

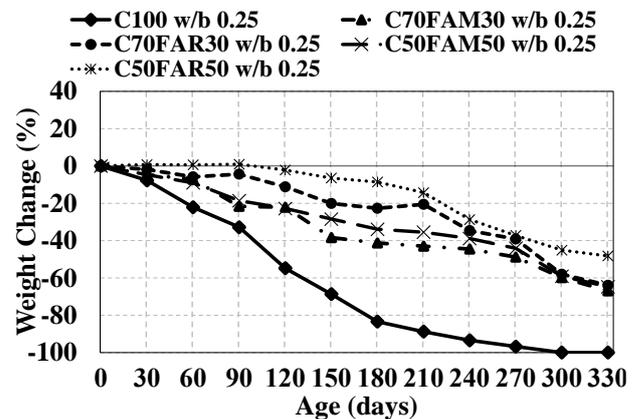
where CaO<sub>c</sub> = Percentage of CaO in the cement (%)  
 CaO<sub>f</sub> = Percentage of CaO in the fly ash (%)  
 SiO<sub>2c</sub> = Percentage of SiO<sub>2</sub> in the cement (%)  
 SiO<sub>2f</sub> = Percentage of SiO<sub>2</sub> in the fly ash (%)

W<sub>c</sub> = Cement content in the mixture (kg/m<sup>3</sup>)

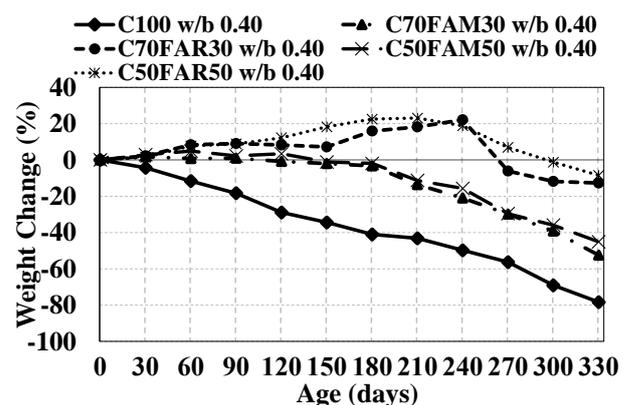
W<sub>f</sub> = Fly ash content in the mixture (kg/m<sup>3</sup>)

Though the CaO/SiO<sub>2</sub> ratio computed from Eq. (4) is different from the CaO/SiO<sub>2</sub> ratio of the C-S-H in the respective mixture, they are correlated. It was observed that the incorporation of FAR and FAM in the pastes results in lower CaO/SiO<sub>2</sub> ratios when compared to the ratio of the control mixture (see Fig. 8). From Fig. 8, the CaO/SiO<sub>2</sub> ratio of the C100 mixture is 3.29. The fly ash replacement decreases the CaO/SiO<sub>2</sub> ratio to 1.90 for C70FAM30, 1.29 for C50FAM50, 1.42 for C70FAR30, and 0.82 for C50FAR50.

Regarding CaO/SiO<sub>2</sub> ratios, Fig. 8 shows that generally a mix with a lower CaO/SiO<sub>2</sub> ratio has a lower weight change than that with a higher CaO/SiO<sub>2</sub> ratio. For the mixtures with fly ashes, fly ashes improve the bonding capacity of the C-S-H structure in long term. Moreover, low calcium oxide (CaO) and high silicon dioxide (SiO<sub>2</sub>) contents in fly ashes can contribute to a higher acid resistance of paste specimens [12, 30, 31].

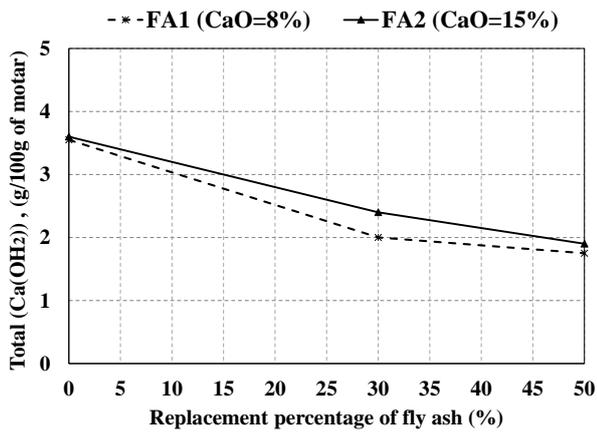
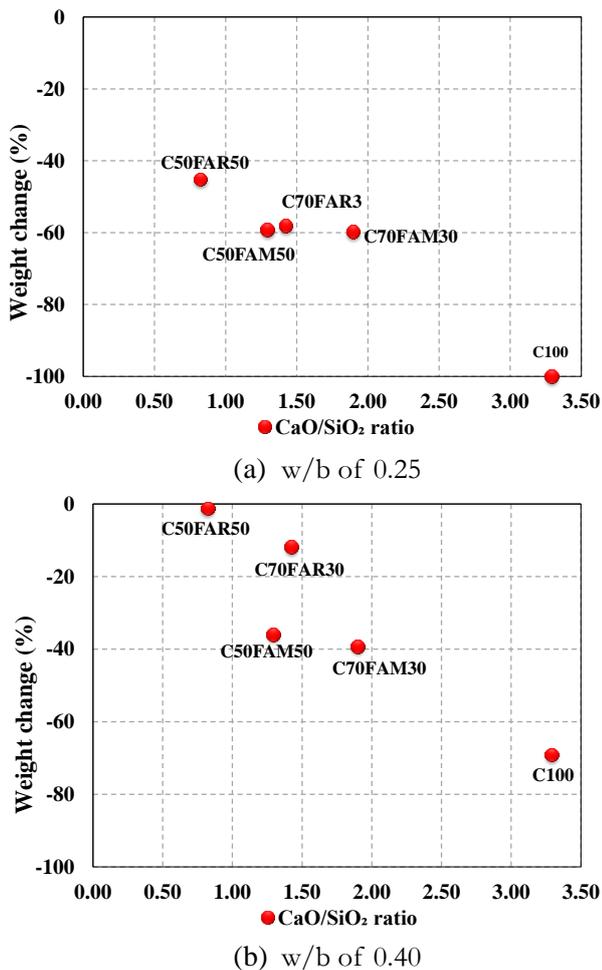


(a) Weight change of pastes (w/b = 0.25)



(b) Weight change of pastes (w/b = 0.40)

Fig. 6. Weight change of pastes with w/b of 0.25 and 0.40 in sulfuric acid with constant pH 1 after 330 days of exposure.

Fig. 7. Total Ca(OH)<sub>2</sub> in mortar specimens [29].Fig. 8. Relationship of CaO/SiO<sub>2</sub> ratios and weight change of paste specimens with w/b of 0.25 and 0.40 at 300 days of immersion.

### 3.4. Characteristics of the Deterioration of Specimen in Sulfuric Acid Solution

Figure 9 (a) shows that C100 specimens disintegrate into clay-like materials. For fly ash replaced specimens, the deterioration of the paste surface was in the form of a hard layer as shown in Fig. 9 (b) to Fig. 9 (e). To analyze the products of reactions of the cement pastes with the

sulfuric acid, the unsound portions (both the clay-like material and the hard layer on the surfaces of the specimens in Fig. 9) were removed. After that, the specimen surfaces were scraped to obtain samples for XRD analysis.

The XRD results show that the surface of cement pastes reacts with the sulfuric acid and mainly forms gypsum, as shown in Fig. 10. The test results from Fig. 10 show mainly gypsum, which is the same as the product found in the sulfuric acid solution outside the specimens. The test results correlate well with the reactions in Eq. (1) and Eq. (3), which indicate the reactions of sulfuric acid and hydrated products to mainly produce gypsum. Ettringite was not detected in the XRD results because ettringite can be converted to calcium sulfate and aluminum hydroxide (Al(OH)<sub>3</sub>) by sulfuric acid. The latter, Al(OH)<sub>3</sub>, could not be detected by XRD because of its amorphous nature. The reaction between ettringite and sulfuric acid is illustrated in Eq. (5) [32]. This reaction is then followed by the attack on the aluminum hydroxide if the pH of the acidic solution is below 4, as shown in Eq. (6).

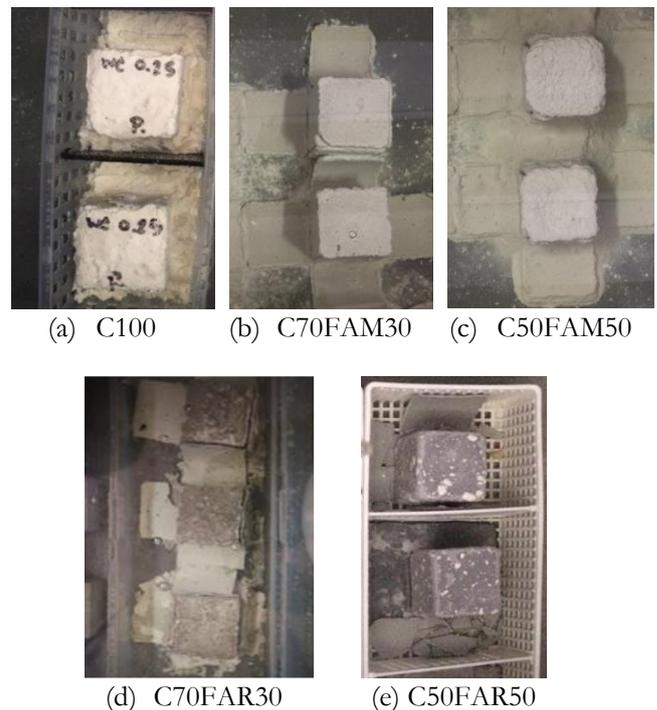
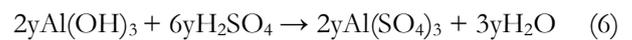
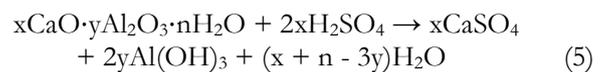


Fig.9. Deterioration of cement paste specimens at 30 days.

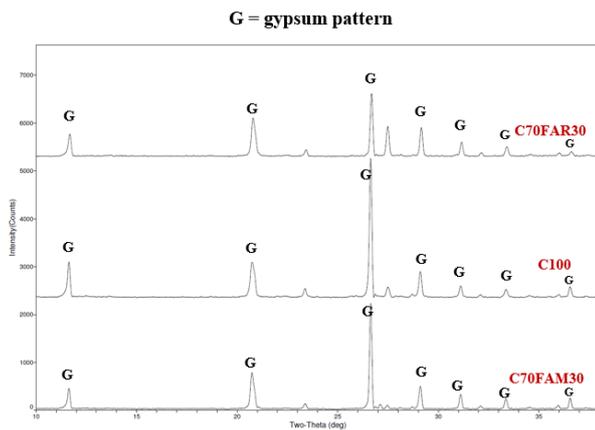


Fig. 10. XRD patterns of surface of specimens at 30 days of immersion.

It was observed from the experiments that the removal of the attacked specimen surfaces by acid, defined as unsound portion in this study, could be seen in 2 patterns, i.e. clay-like materials and hard layer patterns. The two patterns of deterioration of specimen surfaces can be explained by the effect of pore structures and CaO/SiO<sub>2</sub> ratios of the specimens. Before sulfuric acid attack, the hardened cement paste (C100) has larger pore size than the cement pastes with FAM30 and FAR30 due to pore refinery effect by pozzolanic reaction of the fly ashes as shown in Fig. 11. Figure 11 shows that the paste with 30% FAM replacement has more fine pores than the cement-only paste. So, when acid attacks, the gypsum formed in C100 can scatter throughout the hardened cement matrix as it has larger pore size and higher volume of capillary pores that are easier to be penetrated to the inside by the gypsum crystals formed. Hence, the gypsum crystals are present in the form of veins running along the matrix in the attacked zone leading to micro cracking [33]. Eventually, this is followed by mass loss induced by the damaging effect of sulfuric acid on the hydrated cement matrix leading to decalcification of C-S-H that has a higher Ca/SiO<sub>2</sub> ratio. Therefore, the paste matrix becomes weakened together with the mentioned gypsum formation pattern in the C100 paste, the paste near the specimen surfaces deteriorated as the clay-like materials as shown in Fig. 9(a). On the other hand, C-S-H produced by pozzolanic reaction, having a lower CaO/SiO<sub>2</sub> ratio, has a stronger resistance to acid. The densification of the pore structure by pozzolanic reaction makes it more difficult for gypsum formation deep inside. With the denser pore structure and stronger C-S-H to acid of the pastes with fly ash, the formation of gypsum deep inside the fly ash pastes are more difficult. The C-S-H matrix is also stronger and more difficult to be weakened by the acid. However, finally the expansion caused by gypsum will increase until the binding capacity of C-S-H structure cannot resist which results in disintegration and deterioration as hard layers as shown in Fig. 9 (b) to Fig. 9 (e). The schematic deterioration patterns of cement paste specimens are shown in Fig. 12.

To support the explanation in the above paragraph, a quantitative analysis to obtain the amount of gypsum on the surface of paste specimens (after removing the unsound portion) with a w/b of 0.25, after immersion in sulfuric acid pH of 1 for 30 days, was conducted, and the results are shown in Fig. 13. It was found that the amount of gypsum of the mixture C70FAR30 is the lowest at 58.67%, followed by C70FAM30 at 67.12%, while C100 has the highest content at 73.88%. The amounts of gypsum of fly ash replacing mixtures are lower than that of the control specimen due to dilution and pozzolanic reaction effects. More gypsum formed in C100 can contribute to a higher expansive pressure on the weaker C-S-H matrix structure, which is likely to cause the clay-like pattern of the surface deterioration.

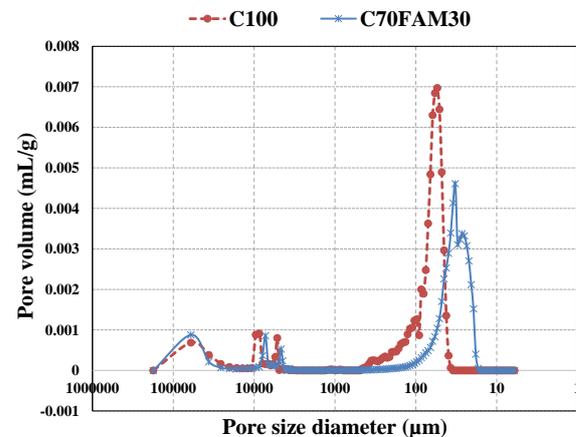


Fig. 11. Pore size distributions of the tested specimens w/b of 0.25 at age 28 days before immersion in sulfuric acid.

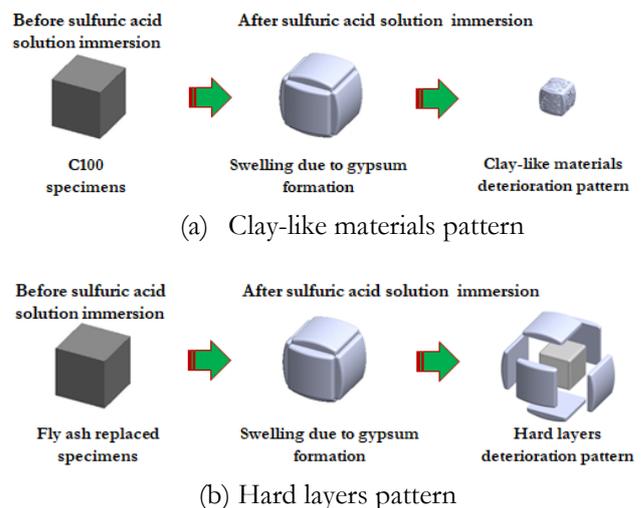


Fig. 12. Schematic deterioration patterns of cement paste specimens in sulfuric acid solution.

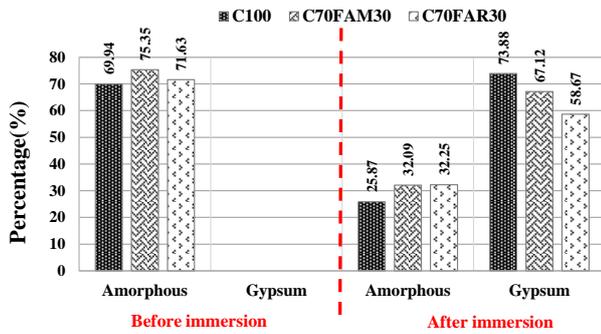


Fig.13. Quantitative analysis of gypsum and amorphous contents on surface of paste specimens before and at 30 days of immersion of specimen with w/b of 0.25.

Table 3 show the amount of gypsum on the surface of C100 at 73.88% and the amount of amorphous component (mainly C-S-H) dropped from 69.94% to 25.87% (dropped 63.01% from the amount before immersion) because C-S-H with a higher CaO/SiO<sub>2</sub> ratio in cement-only matrix was more easily decalcified by sulfuric acid attack. However, C70FAM30 and C70FAR30 pastes show the amounts of gypsum of 67.12% and 58.67%, respectively, and the amount of amorphous component (mainly C-S-H) dropped only 57.41% and 54.98%, respectively. From the results of the dropped percentages of the amorphous component, supposed to be mainly C-S-H, it can be somewhat confirmed that the C-S-H structure of the fly ash mixtures is stronger than that of the cement-only paste.

Table 3. Amorphous content and amount of gypsum of mixtures on surface of specimens.

Mixtures	Amorphous content (%)			Amount of gypsum (%)		
	Before	After	% Drop	Before	After	% Increase
C100	69.94	25.87	63.01	0.00	73.88	73.88
C70FAM30	75.35	32.09	57.41	0.00	67.12	67.12
C70FAR30	71.63	32.25	54.98	0.00	58.67	58.67

In addition, the amounts of gypsum in the samples that were disintegrated from the specimens' surfaces (unsound portion) were analyzed. The results show the same trend as that of the specimens' surfaces after removing the unsound portion. The mixture of C100 shows large amount of gypsum, 68.16%, and the amorphous content dropped 58.48% while the amount of gypsum of C70FAM30 and C70FAR30 are 62.66% and 60.43%, respectively, and the amount of amorphous content mainly (C-S-H) of C70FAM30 and C70FAR30 dropped only 55.71% and 54.45% respectively, as shown in Fig. 14 and Table 4.

This verifies that comparing with pastes with fly ash, more gypsum is produced by the acid attack and more C-S-H is destroyed by the acid in cement-only mixture, therefore the deteriorated surface of cement-only paste becomes clay-like materials, differently from the pattern of the fly ash pastes.

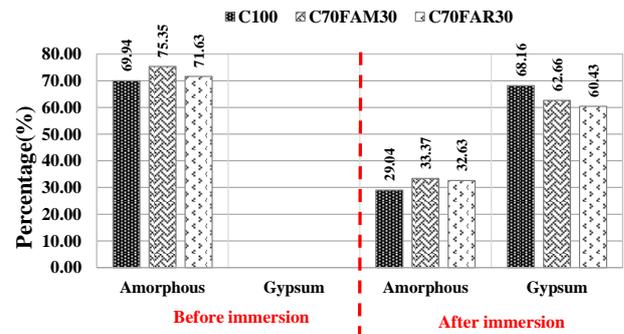


Fig.14. Quantitative analysis of gypsum and amorphous contents in unsound portion of paste specimens before and at 30 days of immersion of specimen with w/b of 0.25.

Table 4. Amorphous content and amount of gypsum of mixtures on unsound portion of specimens.

Mixtures	Amorphous content (%)			Amount of gypsum (%)		
	Before	After	% Drop	Before	After	% Increase
C100	69.94	29.04	58.48	0.00	68.16	68.16
C70FAM30	75.35	33.37	55.71	0.00	62.66	62.66
C70FAR30	71.63	32.63	54.45	0.00	60.43	60.43

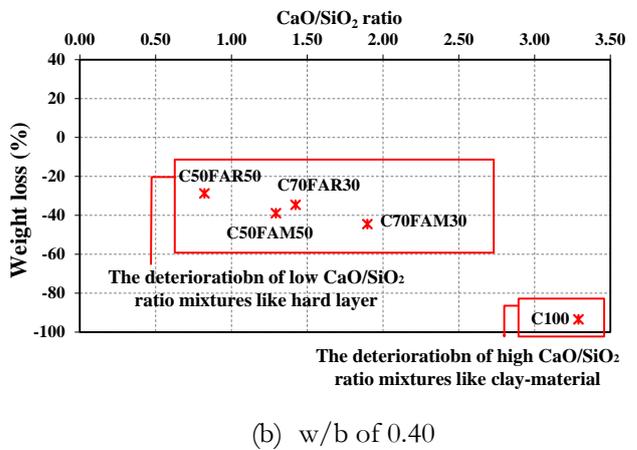
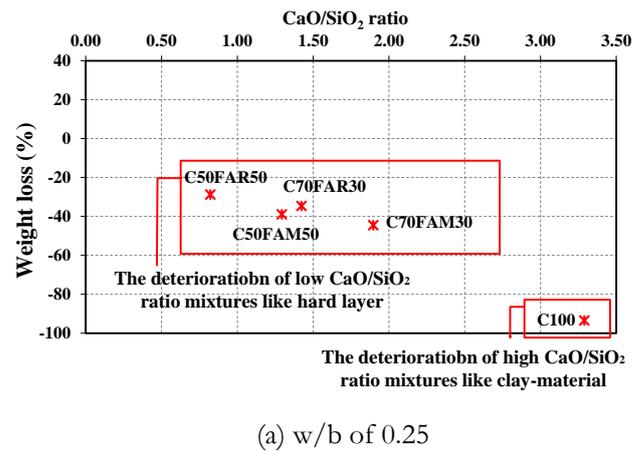


Fig.15. Relationship between weight loss and CaO/SiO<sub>2</sub> ratio.

Figure 15 shows that the pattern of deterioration, into clay-like materials or hard layers are clearly separated by the CaO/SiO<sub>2</sub> ratio, where high CaO/SiO<sub>2</sub> ratio pastes show a clay-like material pattern while low CaO/SiO<sub>2</sub> ratio pastes show a hard layer pattern of surface deterioration.

#### 4. Conclusions

The deterioration in sulfuric acid of cement pastes incorporating high CaO and low CaO fly ashes was investigated. From the test results, the following conclusions can be drawn:

- 1) Paste specimens with a higher w/b had lower weight change in sulfuric acid solution than those with a lower w/b. This is due to higher porosity in a higher w/b paste, providing more spaces to accommodate the expansion product, which is mainly gypsum.
- 2) In addition to the effects of porosity, dissolved calcium ions (Ca<sup>2+</sup>) can diffuse away from cement pastes to react with sulfate ions in the sulfuric acid solution, influencing a high degree of deterioration of the paste specimens with the lower w/b.
- 3) The use of fly ash can enhance the resistance of the pastes against sulfuric acid attack. This is mainly caused by a decrease in the amount of calcium hydroxide. Moreover, fly ash replacement can refine pore size and improve the CaO/SiO<sub>2</sub> ratio to produce a C-S-H structure with a higher resistance against sulfuric acid, leading to less gypsum.
- 4) The tested low CaO fly ash is more effective for enhancing the sulfuric acid resistance of cement pastes than the high CaO fly ash.
- 5) The deterioration of paste specimens due to sulfuric acid attack was found to correlate well with CaO/SiO<sub>2</sub> ratio. The high CaO/SiO<sub>2</sub> pastes showed a clay-like material pattern while the low CaO/SiO<sub>2</sub> pastes show a hard layer pattern of surface deterioration.

#### Acknowledgments

The authors would like to acknowledge the research support from the National Research Council of Thailand; the Center of Excellence in Material Science, Construction and Maintenance Technology, Thammasat University; the Chair Professor Program (P-19-52302), the National Science and Technology Development Agency (NSTDA), Thailand; and the scholarship provided to the first author from Pibulsongkram Rajabhat University.

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