

## Sulfate Attack and the Role of Cement Compositions

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### ABSTRACT

This paper presents an experimental study of the sulfate resistance of mortars and pastes exposed to sodium sulfate solutions up to one year. In order to check deterioration modes due to sulfate attack, the sodium sulfate solution was varied at three concentration steps (3,380, 10,140 and 33,800 ppm of  $\text{SO}_4^{2-}$  ions), and maintained at ambient temperature. The tests include a visual examination, expansion and compressive strength loss measurements as well as x-ray diffraction tests. The experimental data indicated that the use of cement with a low  $\text{C}_3\text{A}$  content and low silicate ratio has a beneficial effect on the sulfate attack of mortars. In contrast, the mortars with a high  $\text{C}_3\text{A}$  content and high silicate ratio became severely degraded due to the formation of ettringite, gypsum and/or thaumasite in the cement matrix.

**Key words:** Sulfate attack, Cement compositions, Ettringite, Gypsum, Thaumasite

### 1. Introduction

It has been commonly accepted that sulfate attack occurs in concrete when concrete is in contact with a source of sulfate ions, which can be present in groundwater, soil, or seawater. Sulfate attack usually manifests itself by the cracking and spalling of concrete accompanied by expansion, mass loss and strength reduction. Thus, the deterioration of concrete exposed to sulfate-bearing environments has been a big concern for concrete engineers and scientists. Furthermore, a number of hypotheses have been proposed to describe the mechanisms responsible for sulfate deterioration of cement matrix.<sup>1,2)</sup>

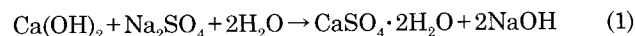
Clearly, the role of cement compositions in sulfate attack is of significance. More recently, laboratory studies on sulfate attack have shown that the expansive and softening types of deterioration forming ettringite and gypsum are related to  $\text{C}_3\text{A}$  and calcium hydroxide (CH) content.<sup>3,4)</sup>

In terms of the cement compositions, it is generally agreed that there is a correlation between the  $\text{C}_3\text{A}$  content and sulfate resistance. However, it is clear that the  $\text{C}_3\text{A}$  content is not the only factor influencing concrete durability in sulfate-bearing environments. Another factor that may determine sulfate resistance is the silicate ratio ( $\text{C}_3\text{S}/\text{C}_2\text{S}$ ). It is well known that the silicate ratio controls the quantity of CH in hydrated cement paste, and controls the rate of early age hydration and strength development when the content of the two aluminates ( $\text{C}_3\text{A}$  and  $\text{C}_4\text{AF}$ ) is relatively constant.

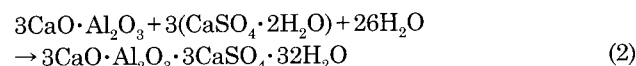
According to Mehta,<sup>5)</sup> stoichiometric calculations show that the hydration of  $\text{C}_3\text{S}$  would produce 61%  $\text{C}_3\text{S}_2\text{H}_3$  and 39% CH, whereas the hydration of  $\text{C}_2\text{S}$  would produce 82%  $\text{C}_3\text{S}_2\text{H}_3$  and 18% CH. If the durability of a hardened cement paste to sulfates is reduced due to the presence of CH, it can be expected that cement containing a higher proportion of  $\text{C}_2\text{S}$  will be more durable in such environments compared to cement containing a higher proportion of  $\text{C}_3\text{S}$ .

Type V cement with a low  $\text{C}_3\text{A}$  is generally recommended in concrete structures placed in sulfate environments. However, significant changes in cement chemistry have resulted in cement with a lower silicate ratio for sulfate environments. Cement with a higher silicate ratio leads to the increased CH content in the hardened cement matrix, thereby enhancing the susceptibility to softening type of sulfate attack.<sup>6)</sup>

Generally, sulfate ions from external sources penetrate into the cement matrix to react with CH. One of the main products formed from this reaction is gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), as shown in Eq. (1). This reaction will proceed according to the quantity of CH and the supply of sulfate ions in the environment. During the process of the reaction, the formation of soluble NaOH ensures the high alkalinity of the cement paste.



Subsequently, gypsum formed will react with the aluminate phases of cement to form the high-sulfate product (ettringite), as shown in the following Eq. (2).



The aims of this study are to investigate the role of the cement compositions on sulfate attack, and to assess the

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**Table 1.** Chemical Composition, Mineralogical Compound and Physical Properties of Cements

Chemical composition	PC1	PC2	PC3
SiO <sub>2</sub> , %	20.2	25.7	22.7
Al <sub>2</sub> O <sub>3</sub> , %	5.8	3.2	3.7
Fe <sub>2</sub> O <sub>3</sub> , %	3.0	3.2	3.5
CaO, %	63.3	62.5	63.1
MgO, %	3.4	2.1	3.2
SO <sub>3</sub> , %	2.1	2.1	1.8
Loss on ignition, %	1.2	0.6	1.6
Mineralogical compound			
C <sub>2</sub> S, %	16.6	53.1	28.1
C <sub>3</sub> S, %	54.9	27.3	49.2
C <sub>3</sub> A, %	10.3	3.1	3.9
C <sub>4</sub> AF, %	9.1	9.7	10.6
C <sub>3</sub> S/C <sub>2</sub> S	3.31	0.51	1.75
Physical properties			
Specific gravity	3.15	3.17	3.18
Specific surface area, m <sup>2</sup> /kg	312	367	328

sulfate resistance of a cement matrix prepared using Portland cements with different C<sub>3</sub>A contents and silicate ratios. In order to achieve these aims, the expansion characteristics and compressive strength of mortars exposed to sodium sulfate solution were regularly monitored. Additionally, x-ray diffraction was performed to identify the sulfate products formed in paste samples made with the same cements.

## 2. Experimental

### 2.1. Materials

Three types of Portland cements having different C<sub>3</sub>A contents and silicate ratios (C<sub>3</sub>S/C<sub>2</sub>S) were used to make mortars and pastes. The chemical compositions, mineralogical compound, and physical properties of the Portland cements are shown in Table 1. The three types of cements were designated as PC1, PC2 and PC3, respectively. River sand with a maximum size of 5 mm was used as fine aggregate. The superplasticizer used to produce the mortars was a polycarboxonic acid-based chemical admixture.

### 2.2. Preparation of mortars and pastes

Mortars and pastes were prepared with a water-to-cement ratio of 0.45 and a cement-to-fine aggregate ratio of 1:2 by mass. The mortars and pastes were initially cured in air for one day and then in tap water for six days. After a seven-day pre-curing period, some mortars and pastes were moved to sodium sulfate solutions. The samples were continuously immersed in the test solutions for 360 days.

### 2.3. Test solutions

The exposure solutions used to simulate the sodium sul-

fate attack with the test samples were made by dissolving reagent grade chemical in tap water. The three solution concentration used contained 3,380 ppm, 10,140 ppm and 33,800 ppm of SO<sub>4</sub><sup>2-</sup> ions, respectively. These test solutions were refreshed every month. No acid titration was made to change the pH of the sulfate solutions. Tap water was used as a control for a comparison solution. All solutions were maintained at 20 ± 1°C during the test period.

### 2.4. Test techniques

The mortars were periodically retrieved from test solutions and visually inspected to characterize the deterioration. Spalling, cracking, delamination and visible expansion of the mortars were checked after predetermined periods of exposure.

Based on ASTM C 1012, the expansion of mortars, with 25 × 25 × 285 mm, exposed to the sulfate solutions was measured at each exposure period.

Compressive strength measurements were performed on 50 mm cube mortars at 0, 28, 91, 180, 270 and 360 days of exposure. Companion specimens cured in tap water were tested along with the specimens immersed in sodium sulfate solutions.

The strength deterioration of the cube mortar specimens was investigated by measuring the compressive strength loss, which was determined using following equation.

$$\text{Compressive strength loss} = [(A - B) / A] \times 100(\%)$$

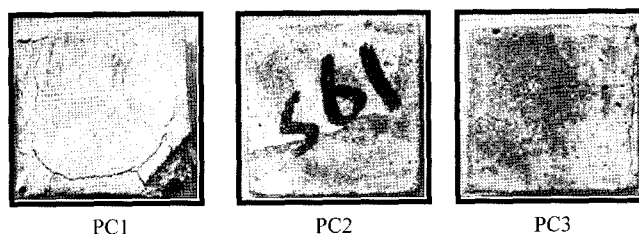
where, A is the average compressive strength of the mortars cured in tap water, and B is the average compressive strength of mortars immersed in the test solutions.

In order to determine the solid phases formed in the pastes qualitatively, x-ray diffraction (XRD) analysis technique was used. The source of radiation is Cuka with a wavelength of 1.54 Å at a voltage of 30 kV. The 2θ angle range covered for each pastes is from 5° to 40°. The scanning speed is 2°/min.

## 3. Results and Discussion

### 3.1. Visual examination

The visual appearances of the PC1, PC2 and PC3 mortars made with different types of cement exposed to sodium sulfate solutions with 33,800 ppm of SO<sub>4</sub><sup>2-</sup> ions for 360 days are



**Fig. 1.** Cube mortars exposed to 33,800 ppm sodium sulfate solution for 360 days.

**Table 2.** Visual Deterioration Rating of Mortars

Exposure duration, days	PC1	PC2	PC3
91	1	0	0
180	2	0	0
270	3	0	1
360	4	1	2

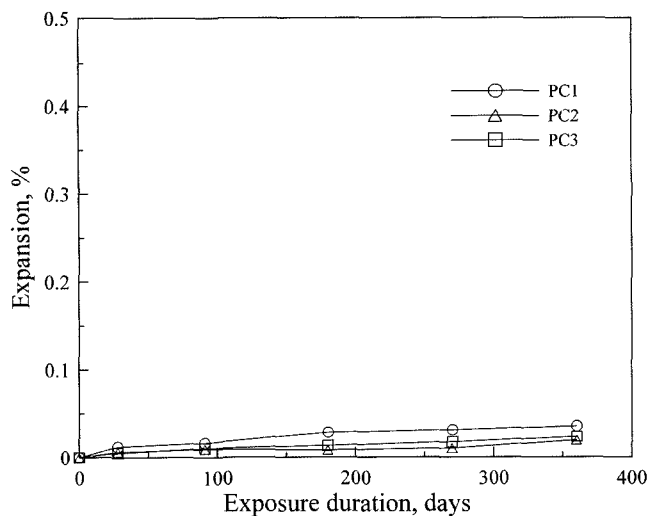
shown in Fig. 1. It was clearly confirmed that PC1 mortar with a higher  $C_3A$  content and higher silica ratio (SR:  $C_3S/C_2S$ ) were severely damaged by sulfate attack, showing a significant loss of mass (approximately 3%) in addition to wide cracks along the edges of the mortar. In contrast, the visible deterioration was negligible for the PC2 mortar with lower  $C_3A$  content and lower SR, although it was exposed to the same sulfate solution for 360 days. The PC3 mortar exhibited some cracks at the corners and edges.

Based on the study by Al-Amoudi et al.,<sup>7</sup> the deterioration was classified on a six-point scale ranging from 0 to 5. In this rating scale, a rating of 0 indicates no deterioration and a rating of 5 denoted complete disintegration of the mortar sample. Table 2 systematically summarizes the visual deterioration rating of the mortars exposed to the sodium sulfate solution with the concentration of 33,800 ppm  $SO_4^{2-}$  ions.

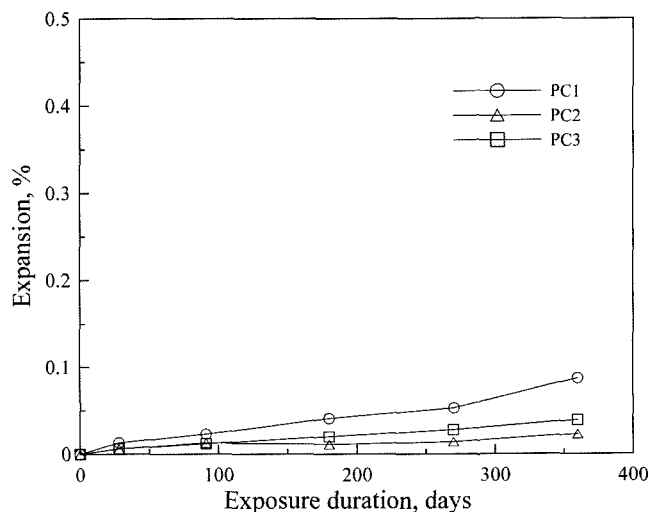
**3.2. Expansion**

The expansion data of mortars exposed to sodium sulfate solutions with different concentrations is presented in Figs. 2 to 4.

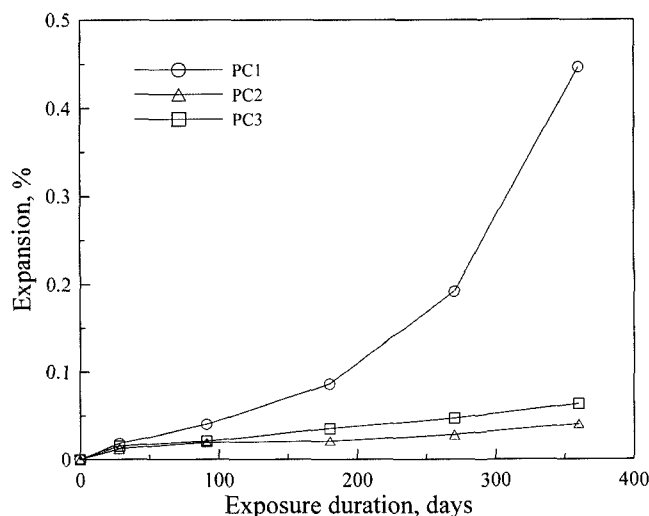
Fig. 2 shows the expansion of mortars stored in sodium sulfate solution with a concentration of 3,380 ppm. This figure indicates that the mortars exhibited very low values of expansion up to 360 days regardless of the cement type. Essentially, any remarkable deterioration was not visibly detected even in the PC1 mortar with a higher  $C_3A$  content and a higher SR in the solution. The expansion results of



**Fig. 2.** Expansion of mortars exposed to sodium sulfate solution (3,380 ppm).



**Fig. 3.** Expansion of mortars exposed to sodium sulfate solution (10,140 ppm).



**Fig. 4.** Expansion of mortars exposed to sodium sulfate solution (33,800 ppm).

mortars with different cement compositions exposed to 10,140 ppm sodium sulfate solution are presented in Fig. 3. From the results, a trend was observed that indicated the effect of the cement compositions on the expansion of mortars. In comparison, a general trend is shown in Fig. 5. It shows considerable expansion in the PC1 mortars exposed to 33,800 ppm sodium sulfate solution. After 510 days of exposure, the PC 1 mortars expanded significantly by as much as about 0.44%, while the expansion was approximately 0.04% and 0.06% for the PC2 and PC3 mortars, respectively. It was confirmed that higher  $C_3A$  and SR values have a negative effect on the sulfate expansion of Portland cement mortars. A similar finding was published by Moon and Lee.<sup>8</sup>

**3.3. Compressive strength loss**

Figs. 5 to 7 show data on the compressive strength loss of

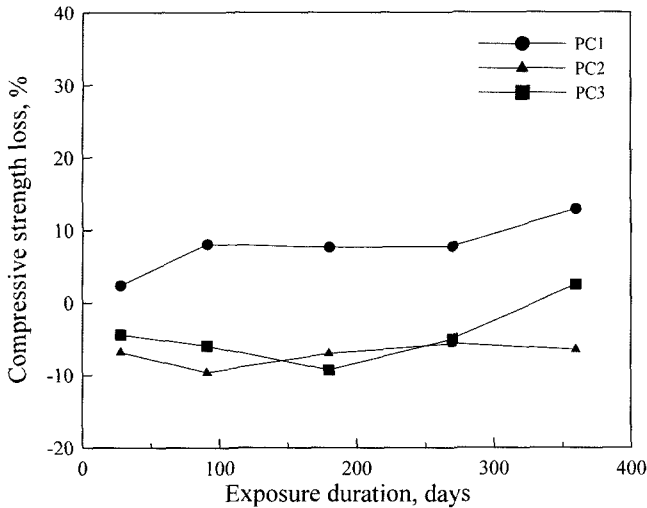


Fig. 5. Compressive strength loss of mortars exposed to sodium sulfate solution (3,380 ppm).

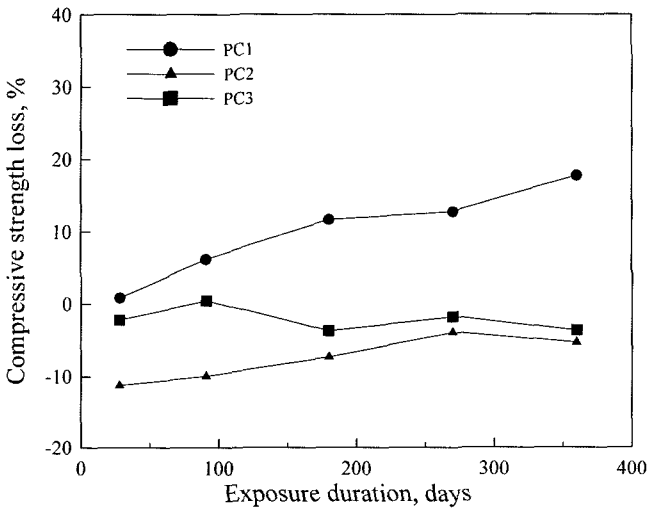


Fig. 6. Compressive strength loss of mortars exposed to sodium sulfate solution (10,140 ppm).

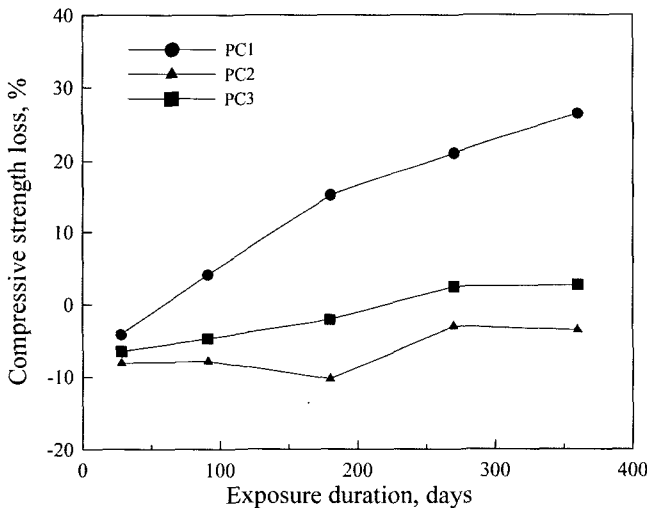


Fig. 7. Compressive strength loss of mortars exposed to sodium sulfate solution (33,800 ppm).

mortars immersed in sodium sulfate solutions with various concentrations. Fig. 5 is of a sodium sulfate solution containing 3,380 ppm of  $\text{SO}_4^{2-}$  ions, and indicates that the strength loss of the PC1 mortars was more remarkable compared to that of the PC2 and PC3 mortars. However, the compressive strength loss in the PC1 mortars was slightly stable up to 360 days. More importantly, as the concentrations of the solution increased, the ultimate compressive strength losses of the PC1 mortars also increased. The data in Fig. 7 suggest a higher rate of progressive deterioration of the mortars upon further exposure.

It should be noted that the PC2 mortars with lower  $\text{C}_3\text{A}$  and SR values showed negative values in terms of compressive strength loss during the test period irrespective of the solution concentrations. As previously reported in the literature,<sup>9</sup> this is attributed to the filling up of the pore space by the expansive products, which made the mortars more dense.

### 3.4. X-ray diffraction

XRD analyses of the paste samples placed in sodium sulfate solution with a higher concentration (33,800 ppm of  $\text{SO}_4^{2-}$  ions) for 360 days are presented in this section. The XRD analyses were conducted on the deteriorated parts of the samples. The results are shown in Fig. 8.

The XRD patterns show that the main products consist of ettringite, gypsum thaumasite, calcite and portlandite. It should be noted that there were peaks for the presence of thaumasite at approximately 9.1, 16.0 and 19.5° 2θ, although the samples were continuously exposed to sulfate solution with ambient temperature.

Compared to the patterns for the PC2 and PC3 pastes, the XRD trace of the PC1 paste indicates the relatively high

E: ettringite, T: thaumasite, G: gypsum, CH: portlandite, C: calcite

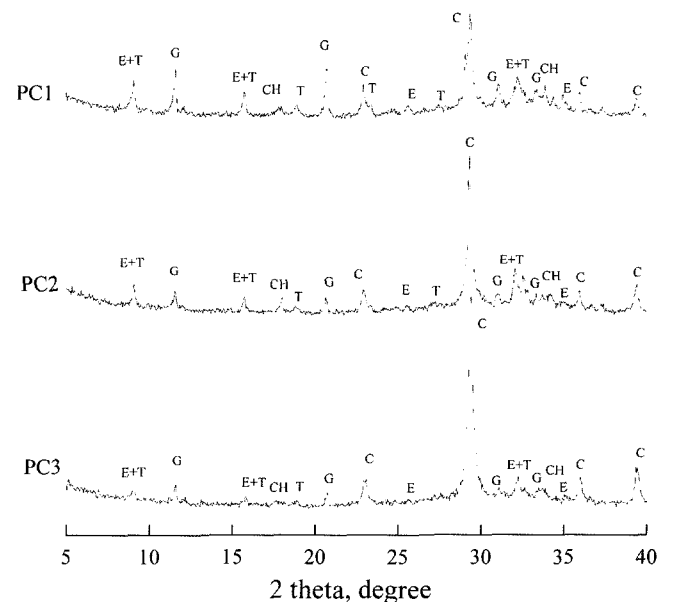


Fig. 8. XRD patterns of paste samples exposed to sodium sulfate solution (33,800 ppm) for 360 days.

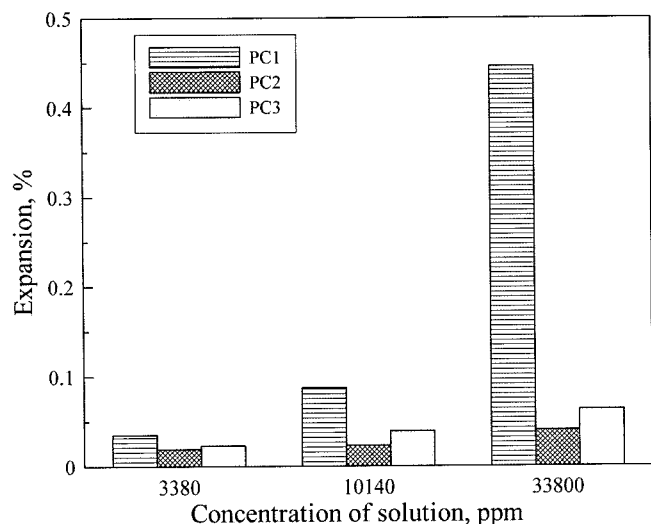


Fig. 9. Comparison of expansion in mortars exposed to varying concentrations of sodium sulfate solution for 360 days

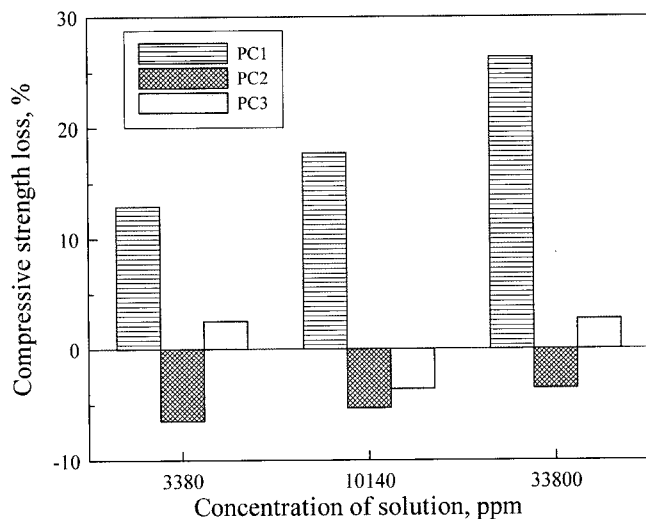


Fig. 10. Comparison of compressive strength loss in mortars exposed to varying concentrations of sodium sulfate solution for 360 days

intensities of gypsum and ettringite peaks that cause sulfate damage in the paste. These products forming in the PC1 paste can be associated with considerable expansion (Fig. 4) and compressive strength loss (Fig. 7) in the PC1 mortar system.

### 3.5. Effect of the cement compositions on sulfate attack

There has been great interest in the effect of the binder type on the sulfate resistance of cement. Several studies<sup>3,10</sup> has been carried out in an effort to investigate dominant role of cement compositions on sulfate attack. In order to classify the effect of the main components, particularly  $C_3A$  and silicates, used in this study, a comparison of the mechanical properties of the mortars exposed to sodium sulfate

solution for 360 days is presented in Figs. 9 and 10.

The highest expansion and compressive strength loss due to sulfate attack was found in PC1 mortars exposed to sodium sulfate solution at higher concentrations compared to the PC2 and PC3 mortars. From the comparison, the trend for the expansion and compressive strength loss was different. In other words, for PC1 mortars with a high  $C_3A$  content, the expansion in solution with a higher concentration was more pronounced compared to that in solution with a lower concentration. However, the difference in the loss of compressive strength in PC1 mortars with an increased solution concentration was not significant. This implies the presence of the different deterioration modes by sodium sulfate attack. Clearly, the  $C_3A$  content plays a critical role in expansion of mortars. It appears that the gypsum and/or thaumasite formations are closely associated with the compressive strength loss of mortars. The relationship between the silicates and gypsum in terms of the sulfate reaction was mentioned earlier. However, the effect of thaumasite formation on expansion remains unclear.

## 4. Conclusions

The experimental results obtained from this study confirm that the role of the cement composition on the degree of sodium sulfate attack is of importance. Through one-year exposure tests, significant deterioration was noted in the PC1 mortars with a high  $C_3A$  content and high silicate ratio, while it was relatively less in PC2 and PC3 mortars. The progressive deterioration of the PC1 mortars is attributed to the formation of sulfate products such as ettringite, gypsum and/or thaumasite due to sulfate attack. Additionally, it was found that the effectiveness of the evaluation parameters is most likely dependent on the deterioration mode by the sulfate attack.

It can be concluded that the use of cement with potentially low calcium hydroxide in addition to a low  $C_3A$  content will improve concrete durability in the event of sodium sulfate attack. However, further studies using more finely demarcated cement compositions are required.

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