Deterioration of portland-metakaolin cement pastes and mortars exposed to magnesium sulfate solution

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Abstract: This paper describes the deterioration degree and chemical resistance of Portland-metakaolin cement pastes and mortars exposed to 4.24% magnesium sulfate solution. Both pastes and mortars, which were prepared using a water-binder ratio of 0.45, were exposed to magnesium sulfate attack. The main variable was the level of cement replacement (0 to 15% by mass) by metakaolin.

 Magnesium sulfate resistance was evaluated using visual examination, compressive strength loss, and expansion measurements. Microstructural analyses such as XRD and SEM/EDS were also carried out.

 From the test results, it can be concluded that mortars with a high replacement level of metakaolin showed lower resistance to magnesium sulfate attack up to the approximately 15% replacement level studied here. Furthermore, the microstructural findings performed on pastes also correlated well with the physical properties of mortar specimens exposed to magnesium sulfate solution. Conclusively, the degrees of deterioration of the paste and mortar by magnesium sulfate attack were dependent on the replacement levels of metakaolin.

1. Introduction

The advances of concrete technology show that the use of supplementary cementitious materials such as silica fume, blast-furnace slag and fly ash is necessary and essential for producing durable concrete [1]. Metakaolin (MK) is a largely amorphous dehydration product of kaolinite, which exhibits strong pozzolanic activity [2]. In particular, there has been a growing interest in the use of MK for the durable concrete [3-5]. Recent works have shown that MK is effective as a supplementary cementitious material on improving the durability of concrete, for example, alkali-silica reaction, and resistance to chloride ingress [6,7].
Concerning sulfate resistance of MK, Khatib and Wild [8] reported the superior resistance of MK against sodium sulfate attack. However, few studies have been reported on the resistance of MK to magnesium sulfate attack. In fact, magnesium sulfate is known to be particularly corrosive in

sulfate attacks, and magnesium ions are not uncommon in groundwater. Magnesium sulfate attack on the cement matrix is mainly related to the substitution of Mg^{2+} ions for Ca^{2+} ions in portlandite as well as the process of the disintegration of C-S-H gel to M-S-H gel, which is noncementitious material. Under magnesium sulfate environment, therefore, it is necessary to consider the C-S-H gel formed by pozzolanic reaction of MK, and to understand the detailed deterioration mechanism of MK under magnesium sulfate attack.

The main aim of this study, thus, is to investigate the resistance and deterioration mechanism of a range of cement-MK binders by magnesium sulfate attack.

2. Experimental Program

2.1 Materials
ASTM C 150 Type I Portland cement produced by S Cement Ltd. in South Korea was used in all the mortar and paste mixtures. The C_3S, C_2S, C_3A and C_4AF contents of the cement by Bogue calculation were 54.9%, 16.6%, 10.3% and 9.1%, respectively. MK, which was obtained from K Chemical Ltd. in South Korea, was used to replace cement in the paste and mortar. The chemical composition and physical properties of cement and MK used in this investigation are shown in Table 1.

River sand was used as the fine aggregate in the mortar mixtures. The fine aggregate was less than 5 mm. The specific gravity, absorption and fineness modulus of the fine aggregate used are 2.60, 0.80 and 2.80%, respectively. To obtain a suitable workability, a polycarbonic acid-based superplasticizing chemical admixture was used in all mortar mixtures. Magnesium sulfate solution concentration used was 4.24% (33,800 ppm of SO_4^{2-}). The sulfate solution was refreshed every 4 weeks for the first year and every 3 months for the following year. Tap water was used as a control for the comparison solution. The sulfate solution and tap water were maintained at 20 ±1C° during the test period.

2.2 Mixture proportions and specimen preparation
Cement was partially replaced with 0%, 5%, 10% and 15% of MK by mass. The water-cementitious materials ratio (w/cm) was fixed at 0.45 by mass, and the mass ratio of fine aggregate to cement was kept invariant at 2.0. All mortar specimens were demoulded after 24 hours of casting and then cured in tap water for an additional 6 days. Thereafter, some of the specimens were moved to magnesium sulfate solution and continuously immersed in the solution.

2.3 Test techniques

Mortar cube specimens were used for monitoring compressive strength. The compressive strengths for the 5 mm cubes were measured prior to sulfate solution, and then after 180, 360 and 720 days of exposure. Companion cube mortar specimens cured in tap water for the same period were also tested. The compressive strength loss was evaluated as expressed in the following equation:

$$\text{Compressive strength loss, } \% = (f'_{cw} - f'_{cs}) / f'_{cw} \times 100$$

where, f'_{cw} is the average compressive strength of the specimens cured in tap water and f'_{cs} means the average compressive strength of the specimens exposed in magnesium sulfate solution.

After 6 days of initial curing after casting, expansion tests of the prism mortar specimens (25×25×285 mm), based on ASTM C 1012, were carried out. The expansion measurements were taken on three specimens, and the values averaged.

Paste samples exposed to sulfate solution for 360 days were used for XRD analysis and SEM observation. The upper side portions exposed to the sulfate attack were sliced 5-10mm in thickness for the microstructural investigations. For the XRD tests, $CuK\alpha$ radiation with a wavelength of 1.5405 $\overset{\text{o}}{A}$ at a voltage of 30 kV and current of 30 mA were used. The analysis was performed between 5° and 40° 2θ at a scanning speed of 2°/min. For the investigation by SEM and EDS, the sample was dried in a desiccator for 24 h., and subsequently gold coated.

Table 1. Chemical composition and physical properties of cement and MK

	Cement	MK
Chemical composition		
SiO_2, %	20.2	56.0
Al_2O_3, %	5.8	37.0
Fe_2O_3, %	3.0	2.4
CaO, %	63.3	2.4
MgO, %	3.4	0.3
SO_3, %	2.1	-
TiO_2, %	-	0.2
Na_2O, %	0.2	0.3
K_2O, %	0.3	0.6
Loss on ignition, %	1.2	0.6
Physical properties		
Specific gravity	3.13	2.63
Specific surface area, m^2/kg	312	12,000

3. Results and discussion

3.1 Visual appearance

All the mortar cubes were carefully examined at regular intervals to monitor for visible signs of cracking and damage suffered under magnesium sulfate attack. Fig. 1 shows the visual appearances of mortar cubes with different replacement levels of MK exposed to magnesium sulfate solution for 720 days. This makes it clear that the degree of deterioration was significantly different with the replacement level of MK. In particular, for the mortar cubes with 15% MK cement replacement by mass (Fig. 1 (d)), exhibited the worst performance with a great amount of cracking and spalling as well as delamination. In fact, the deterioration of the mortar cubes started at as early as 91 days. As the deterioration progressed, the mass loss of the specimens was severe and they completely disintegrated after 720 days as shown in Fig. 1.

To detail the progress of deterioration, the visual rating of mortar cubes based on the study by Al-Amoudi [9] was used and the results are shown in Fig. 2.

(a) 0% MK	(b) 5% MK
(c) 10% MK	(d) 15% MK

Fig. 1 Visual appearance of mortars exposed to sulfate attack
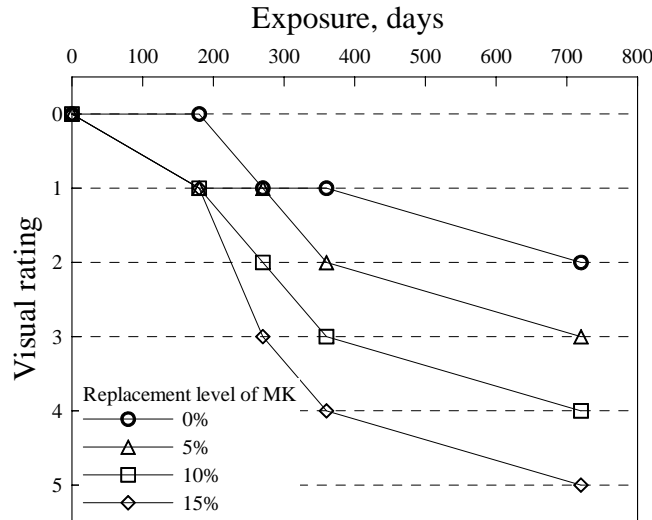
Exposure, days

Fig. 2 Visual rating of mortar cubes

3.2 Compressive strength loss and expansion of mortar specimens

The compressive strengths of the test mortar specimens were determined from 50 mm cube specimens. Tables 2 and 3 summarize these results for a w/cm of 0.45 at the ages of 180, 360 and 720 days of immersion in tap water and magnesium sulfate solutions, respectively.

The compressive strength loss of mortars with and without MK immersed in magnesium sulfate solution was compared with those cured in tap water is shown in Fig. 3. The results indicate that the compressive strength loss of mortar specimens with increasing replacement level of MK increased after 360 days of exposure. The overall strength loss is associated with the replacement levels of MK. In particular, mortar specimens with a higher replacement level of MK displayed poor performance with respect to compressive strength. After 720 days of exposure in magnesium sulfate solution, the compressive strength losses of mortar specimens with replacement levels of 0, 5, 10 and 15% were 67.3%, 70.0%, 82.7% and 90.2%, respectively.

The expansion-exposure time relationship of mortar bars obtained in accordance with ASTM C 1012 test method is given in Fig. 4. The expansion of mortar specimens with 15% MK was 0.556% after 360 days of exposure, compared with a value of 0.244% noted in mortar specimen without MK. It should be noted that the mortar specimens containing 10 and 15% MK had disintegrated after 420 days of exposure, although the mortar specimen without MK expanded only 0.418% after that exposure period, but was disintegrated after 540 days of exposure. It was obvious that the higher replacement level of MK led to the higher expansion in mortar mixture. This trend is in agreement with the visual appearance ratings shown in Fig. 1.

The results of compressive strength loss and expansion confirm that special care should be taken when using MK under magnesium sulfate attack.

Table 2. Compressive strength of mortar specimens cured in tap water

Replacement level of MK	Compressive strength, MPa		
	180d.*	360d.	720d.
0%	54.8	58.0	62.3
5%	56.6	59.2	64.3
10%	57.9	61.0	62.5
15%	63.2	65.5	66.4

* Curing period of mortar specimens after a pre-curing of 7 days

Table 3. Compressive strength of mortar specimens exposed to magnesium sulfate solution

Replacement level of MK	Compressive strength, MPa		
	180d.*	360d.	720d.
0%	41.0	37.5	20.4
5%	43.6	35.9	19.3
10%	46.6	33.5	10.8
15%	42.0	30.1	6.5

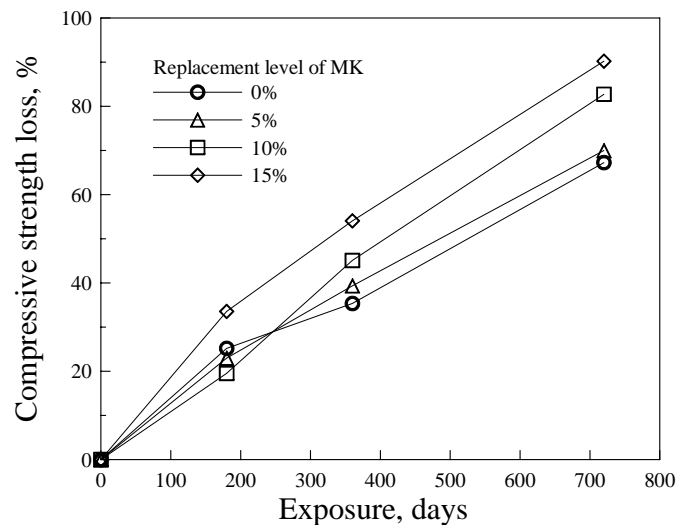* Exposure period of mortar specimens after a pre-curing of 7 days

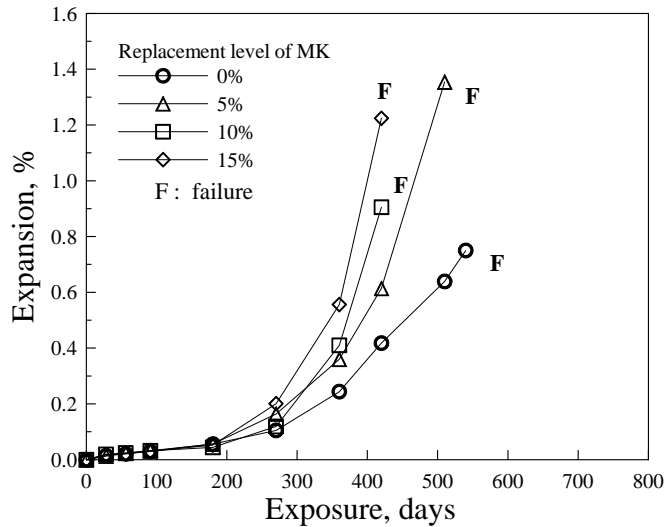Fig. 3 Compressive strength loss of mortar specimens

Fig. 4 Expansion of ASTM C 1012 mortar specimens

3.3 XRD

The XRD study indicates the main cause of deterioration with the replacement levels of MK under magnesium sulfate attack. In this study, powdered paste samples with different replacement levels of MK were examined by XRD after 360 days of exposure to 4.24% magnesium sulfate solution.

Fig. 5 shows that the mineralogical phases are somewhat different with the replacement levels of MK. From the XRD analysis, the presence of ettringite (E), thaumaiste (T), gypsum (G), portlandite (P), calcite (c) and brucite (B), which are the expected products formed by hydration and magnesium sulfate attack was investigated. As expected, the peaks for portlandite were weak due to the significant comsumption of calcium hydroxide in the process of sulfate reaction or pozzolanic reaction of MK.

More importantly, under severe magnesium sulfate attack, the XRD pattern for the paste sample with higher MK replacement levels showed higher intensity peaks for thaumasite, compared with that of the paste sample without MK. It should be noted that thaumasite can be detected in the paste specimens exposed at ambient conditions, although the formation is frequently regarded as a low-temperature phenomenon [10, 11].

However, it was confirmed that the peaks for gypsum around 11.7° and 20.7° 2θ were very strong in intensity, regardless of the replacement levels of MK.

Conclusively, it seems that the degree of deterioration by magnesium sulfate attack as previously presented in the results of visual appearance, compressive strength loss and expansion is associated with thaumasite formation.
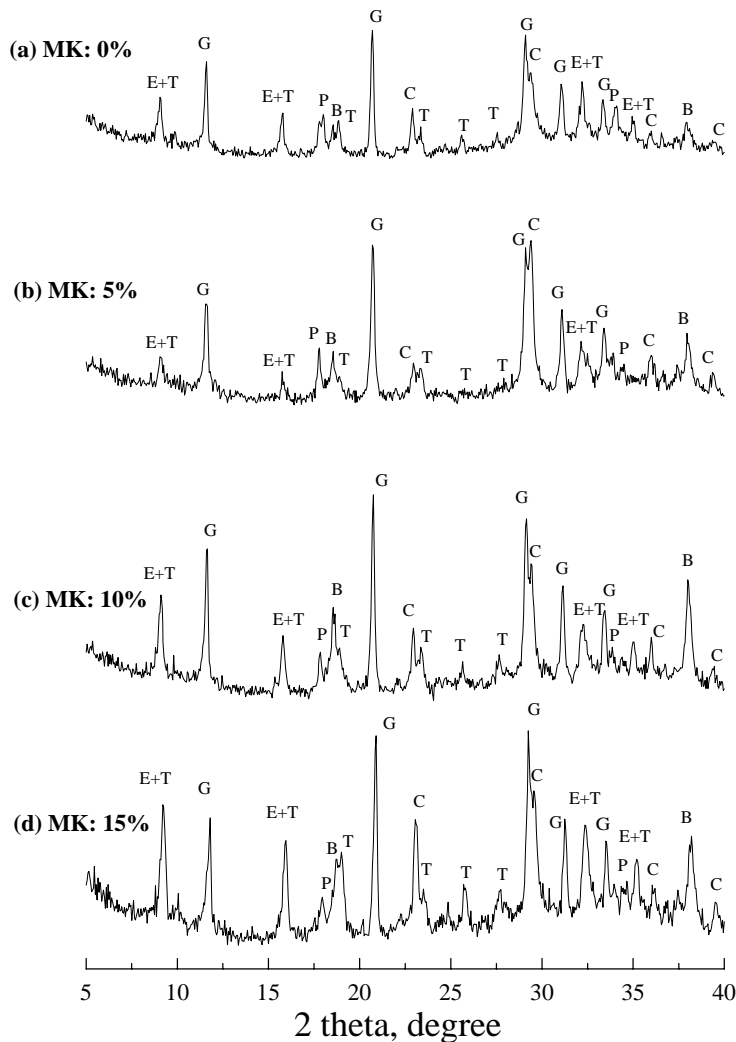
Fig. 5 XRD patterns of paste specimens exposed to magnesium sulfate solution

3.4 SEM

The microstructural features of the paste samples continuously immersed in the magnesium sulfate solution for 360 days were observed using SEM. To determine the reaction compounds formed in the paste samples due to magnesium sulfate attack, EDS analysis was also used. Because the mortar specimen containing 15% MK showed the most deterioration from the results of visual appearance, the microstructural observations for SEM and EDS analysis were focused on only the paste samples with 15% MK. Fig. 6 shows an SEM image on the surface of the paste sample with 15% MK which had deteriorated due to the magnesium sulfate attack. A great amount of reed-type products was observed in the right-hand side of the image. EDS analysis on these products (point A in Fig. 6) showed the

formation of thaumasite indicated by the presence of the calcium, sulfur, silicon and oxygen as well as a small amount of carbon as shown in Fig. 7 (a). Although there was a small amount of aluminum in the spectra, the product appeared to be thaumasite rather than ettringite. Fig. 7 (b) shows the EDS profile for the point B in Fig. 6. The presence of M-C-S-H (or Mg-rich C-S-H) due to the magnesium sulfate attack was confirmed through the EDS analysis. In fact, the product was not detected by XRD, because of its poor crystallinity.

A different SEM image from the same sample is shown in Fig. 8. This image indicates the presence of subhedral gypsum in the deteriorated part of the paste sample.

It seems that the primary cause of the severe deterioration of mortar specimen with MK is the formation of thaumasite and gypsum, but not the formation of ettringite.
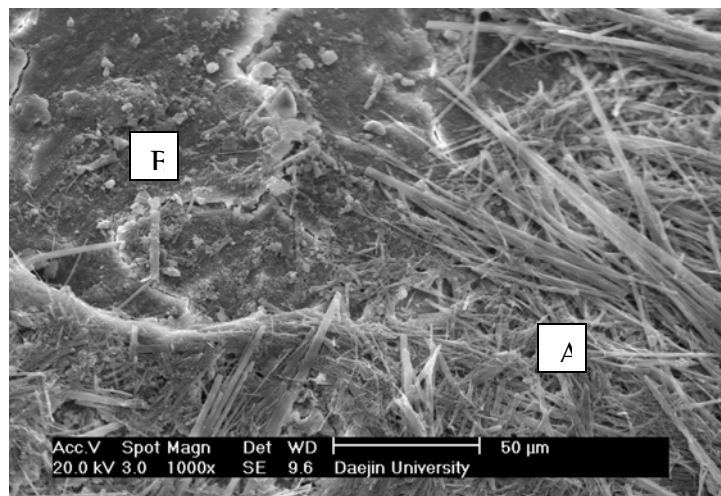

Fig. 6 SEM image of paste specimen with 15% MK exposed to magnesium sulfate solution for 360 days

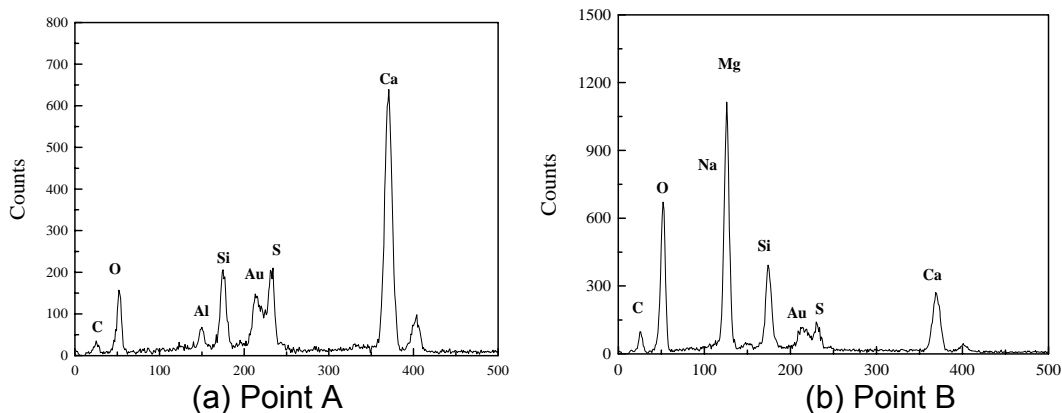(a) Point A   (b) Point B

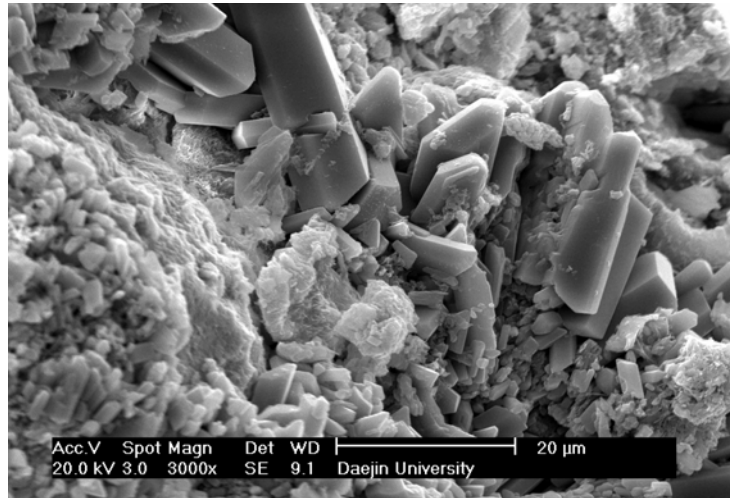Fig. 7. EDS profiles of Points A and B shown in Fig. 6

Fig. 8 Different SEM image of the 15% MK paste specimen exposed to magnesium sulfate solution for 360 days

4. Conclusions

(1) The mortar specimens with a higher replacement level of MK showed a significant compressive strength loss and expansion compared with mortar specimen without MK in magnesium sulfate environment. This is in agreement with the results of visual rating.

(2) The formation of thaumasite, M-C-S-H and gypsum played a key role in causing a significant deterioration due to the magnesium sulfate attack. This was found using XRD and SEM techniques.

(3) From the test results, it was confirmed that special care should be taken when using MK under magnesium sulfate attack.

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