



# Influence of cation type on deterioration process of cement paste in sulfate environment



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## HIGHLIGHTS

- Influence of cation type on sulfate attack to cement paste is studied.
- Mechanical distribution based on Vickers hardness of cement paste is proposed.
- A model of compressive strength with the average Vickers hardness is established.
- The expansion of cement paste with exposure time for different sulfate is presented.
- The damage process of cement paste with attacked ratio is analyzed.

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## ABSTRACT

The objective of this study is to examine the influence of cation type on deterioration process of cement paste exposed to external sulfate attack. The experiment was carried out by micro-hardness test (Vickers hardness), compressive strength test and expansion test. Solutions respectively containing  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{MgSO}_4$  with sulfate concentration of 5.0 wt% were chosen as the sources of sulfate to attack the cement paste. The pH values of solutions containing different sulfate salts were measured to support the analysis. The deterioration process of the cement paste specimens immersed in different attacking solutions was analyzed. The results shown that, the reducing rate of Vickers hardness of cement paste samples immersed in solutions containing different sulfate salts were generally sequenced as  $\text{Na}_2\text{SO}_4 \approx \text{K}_2\text{SO}_4 > \text{MgSO}_4 > (\text{NH}_4)_2\text{SO}_4$ . With the addition of exposure time, the deterioration process exerted at different rate with the variation of sulfate salts. The expansion of specimens immersed in solutions containing  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{MgSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  occurred in two stages within a certain range of exposure time. Besides, compressive strength appeared to be well correlated with Vickers hardness for different kinds of sulfate salts.

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## 1. Introduction

Sulfate attack is one of the immediate causes of degradation of properties and shortening of service life of concrete structures [1–3]. When concrete is exposed to external sulfate-laden environments, however, sulfate ions will penetrate into the hardened concrete through pores. Then, the sulfate ions react with cement hydration, forming various chemical compounds (i.e., gypsum, ettringite etc.) with larger volume. As soon as the concentration exceeds a certain level in the pore solution, together with molecules of chemically linked water, the newly formed compounds deposit on the porous walls. This process develops in

time and causes the damage of structures. This is a complex physicochemical process and is affected mainly by two aspects. One is the feature of concrete itself, including binder type, water to binder ratio (W/B), the amount of cement, mineral admixtures and so on [4–7]. The other is the condition of the aggressive environment, such as the sulfate concentration in solutions, pH value, sulfate salt types, temperature of environment etc. [8–13].

$\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $(\text{NH}_4)^+$  are common cation types that exist in water and soil where concrete structures are serviced. In previous investigations, some efforts have been done on the mechanisms and deterioration process of concrete in sulfate solutions with cations of  $\text{Na}^+$  and  $\text{Mg}^{2+}$ . For instance, in solutions containing  $\text{Na}_2\text{SO}_4$ , sulfate attack is initiated by the reaction of  $\text{Na}_2\text{SO}_4$  with the  $\text{Ca}(\text{OH})_2$  produced by the hydration of cement. Then, the newly formed gypsum reacts with part of cement hydrates to produce

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“secondary” ettringite [14]. However, Magnesium sulfate attack starts by the reaction of  $\text{MgSO}_4$  with  $\text{Ca}(\text{OH})_2$  and then produces gypsum. In addition, Magnesium sulfate also react with C–S–H to produce M–S–H with no binding properties. Owing to the low solubility of  $\text{Mg}(\text{OH})_2$ , the pH value pore solutions will be decreased. Such a low pH destabilizes both ettringite and C–S–H [14,15]. Furthermore, the reduction in strength and expansion was measured to evaluate the degradation process of cement based materials in solutions containing  $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$ . Omar Saeed Baghabra et al. [8] studied the influence of  $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$  on the durability of cement with mineral admixtures. They have found that the loss of strength for 100 days of exposure in  $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$  were basically the same. Then the loss coefficient of compressive strength in  $\text{MgSO}_4$  was 1.6 times of that in  $\text{Na}_2\text{SO}_4$  with 360 days of exposure. Moreover, the expansion of specimens in  $\text{Na}_2\text{SO}_4$  was bigger than that of  $\text{MgSO}_4$ . It has been found that the expansion of samples in  $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$  environment occurs in two stages. In stage 1, there was little expansion. Then, a sudden and rapid increase in expansion followed in stage 2 [10,16]. Up to now, seldom investigations have reported the influence of  $\text{K}^+$  and  $\text{NH}_4^+$  on the deterioration process of concrete in sulfate environment. However, these two ions exist with a considerable content in agricultural water, municipal wastewater, industrial wastewater and alkali soil where many cementitious structures are serviced. Furthermore, owing to the low ionization degree of  $\text{NH}_3$  in water, the pH value of solutions with  $\text{NH}_4^+$  will be reduced significantly. Therefore, solutions with  $\text{NH}_4^+$  are often used to accelerate leaching process [9]. Thus, it is supposed to promote the sulfate attack into concrete in solutions with sulfate as well as  $\text{NH}_4^+$ . The  $\text{K}^+$ , with a large ionic radius, may have some effects on the cation exchange in the multiphase reaction of sulfate attack. Under these circumstances, it is necessary to investigate the influence of  $\text{K}^+$  and  $\text{NH}_4^+$  on deterioration process of cement paste in sulfate environment. In addition, clarifying the relations between the deterioration processes and attacked ratio as well as the exposure duration of cementitious materials exposed to external sulfate attack with different cation types is a good and exciting job.

In this paper, the influences of  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{MgSO}_4$  on the deterioration process of cement paste under sulfate attack have been investigated by micro-hardness test, compressive strength test and expansion test. Besides, the pH values of solutions with different sulfate salts have been measured to support this investigation. Based on the experimental evidence, the relationship between the average Vickers hardness and compressive strength was obtained. In addition, the relation between compressive strength and attacked ratio was analyzed.

## 2. Experimental procedure

### 2.1. Mix designs and test parameter

The P. II 42.5 portland cement (GB 175-2007) was used in this study. Pure cement paste was prepared with water to cement ratio (W/C) of 0.4 and 91 days of standard curing prior. The composition of the cement is listed in Table 1. Experiments were conducted to measure the 2-D diffusion tests, micro-hardness properties and axial compressive strength of specimens exposed to external sulfate attack. To study the effects of cation types in sulfate solution on deterioration law, four categories of sulfate solution ( $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{MgSO}_4$ ) with sulfate concentration of 5.0% were used. Samples prepared were circular cylinder with a size of  $\phi$

50 mm  $\times$  100 mm and two end surfaces of the samples were coated with epoxy resin before exposure. The exposure times for testing were 30, 180, 360 and 540 days, and a group of samples were put in lime water as a contrast test.

After a certain time of exposure, the  $\phi$ 50 mm  $\times$  100 mm specimens were cut into small samples with two sizes of  $\phi$ 50 mm  $\times$  10 mm for micro-hardness and  $\phi$  50 mm  $\times$  50 mm for compressive tests, as shown in Fig. 1. To guarantee the accuracy of the experimental data, at each age of exposure to sulfate attack with one kind of cation type, three  $\phi$ 50 mm  $\times$  100 mm specimens were prepared for the Vickers hardness, compressive strength test and expansion test. At last, the mean values of each parameter of the three samples were used as the final data.

### 2.2. Micro-hardness

To measure the micro-hardness accurately, one end of the thin samples were polished with 200, 400, 800 and 1000 grit polishing papers and the cross sections were divided using a sharp tipped pencil into 80 regions as schematically shown in Fig. 2. Avoiding the influence of humidity on hardness of cement-based materials, the polished samples were placed in the oven at 60 °C for 24 h. Then, Vickers hardness was determined in each of the regions. For each region, three Vickers hardness values were measured. The average values of Vickers hardness on the regions with the same radius were used for the experimental data in relevant depth. Furthermore, the values of Vickers hardness near the external edge lines are measured as the surface Vickers hardness of samples. Vickers hardness test is a common method of evaluating the quality of materials, such as cement stone [9] and concrete [17,18]. Concretely, the experimental procedure is applying a certain load for a known period of time and measuring the area of indentation (Fig. 3). The Vickers hardness  $HV$  ( $\text{kgf}/\text{mm}^2$ ) is calculated by Eq. (1), in which  $P$  ( $\text{kgf}$ ) is the test force,  $A$  ( $\text{mm}^2$ ) is the area of indentation,  $l$  ( $\text{mm}$ ) is the average length of diagonals ( $l_1$  and  $l_2$ ) of the indentation [9,19]. In this study, the Vickers hardness test was carried out in HDX-1000TC Micro-hardness Tester and 0.1  $\text{kgf}$  force was applied on the samples for 10 s.

$$HV = \frac{P}{A} = \frac{2P \sin\left(\frac{136^\circ}{2}\right)}{l^2}, l = \frac{l_1 + l_2}{2} \quad (1)$$

### 2.3. Compressive strength and expansion

The  $\phi$ 50 mm  $\times$  50 mm were cut from the  $\phi$ 50 mm  $\times$  100 mm specimens (Fig. 1) for the uniaxial compressive strength test after 30, 180, 360 and 540 days of exposure. The loading rate of the compressive test controlled by displacement was 0.1 mm/min during the loading procedure.

For the expansion test, the diameter of circular cylinder was measured by a vernier caliper with a degree of accuracy of 0.02 mm before exposure. Then after that, the diameter of circular cylinder was measured every another month. The expansion was calculated by the following equation:

$$P_t = \frac{\frac{1}{4} \cdot L \cdot (d_t^2 - d_0^2)}{\frac{1}{4} \cdot L \cdot d_0^2} \times 100\% = \left[ \left( \frac{d_t}{d_0} \right)^2 - 1 \right] \times 100\% \quad (2)$$

where  $P_t$  (%) is the expansion of  $t$  (days),  $L$  (mm) is the length of circular cylinder specimens,  $d_0$  (mm) is the initial diameter of circular cylinder specimens and  $d_t$  (mm) is diameter of circular cylinder specimens of  $t$ .

## 3. Experimental results and discussion

### 3.1. Micro-hardness

Cation plays an important role in the attacking process of sulfate into concrete. In early period before expansion and cracking, the influence of cation on sulfate attack is mainly in two aspects. One is that the weak hydrolytic function of cation in water changes the pH value of attacking solution [20,21], the other is that cation reacts with cement hydrates directly and changes the pore structure of concrete [22,23]. Therefore, for elucidating the influence of  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{MgSO}_4$  on the deterioration process of paste under sulfate attack, it is essential to clarify the distribution of pH value in different sulfate ( $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{MgSO}_4$ ) solutions.

**Table 1**  
Composition of cement (wt%).

Compn.	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	CaO	MgO	$\text{SO}_3$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{TiO}_2$	MnO	$\text{P}_2\text{O}_5$
Content	21.74	6.32	4.32	62.62	1.02	2.18	0.41	0.97	0.13	0.11	0.08

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