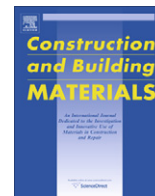




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## Long-term evolution of delayed ettringite and gypsum in Portland cement mortars under sulfate erosion

Jian-kang Chen <sup>a,\*</sup>, Min-qiang Jiang <sup>b</sup>

<sup>a</sup>Department of Mechanics and Engineering Science, Ningbo University, Ningbo 315211, China

<sup>b</sup>State Key Laboratory of Non-linear Mechanics (LNM), Institute of Mechanics, Chinese Academy of Sciences, Beijing 100871, China

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### ABSTRACT

The magnitude evolution of ettringite and gypsum in hydrated Portland cement mortars due to sulfate attack was detected by X-ray powder diffraction. The influences of sulfate concentration and water-to-cement ratio on the evolution of ettringite and gypsum were investigated. Experimental results show that the magnitude of ettringite formation in sodium sulfate solution follows a three-stage process, namely, the 'penetration period', 'enhance period of strength', and 'macro-crack period'. The cracking of concrete materials is mainly attributed to the effect of ettringite. The gypsum formations occurred in two stages, the 'latent period' and the 'accelerated period'. The gypsum formation including ettringite formation was relative to the linear expansion of mortars to some extent. Both water-to-cement ratio and sulfate concentration play important roles in the evolution of ettringite and gypsum.

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### 1. Introduction

Because the existence of a great number of deleterious ions in seawater or in groundwater, such as chlorine ion and sulphate radical ion, the durability of the concrete structures near coasting will be attenuated due to the erosion of those ions. Many efforts have been devoted to the erosion of chloride ions (for instance, Li and Page [1,2], Wang et al. [3,4], Onyejekwe and Reddy [5], and Samson et al. [6]). Sulfate attack, however, is an important issue in concrete durability and its serviceability. The general reactions involved in external sulfate attack have been described previously in 1988 by Cohen and Bentur [7]. Sulfate attack on cement mortars or concrete leads to the conversion of the hydration products of cement to ettringite, gypsum, and the possible phase exchanges. The formation of ettringite and gypsum is common in cementitious systems exposed to most types of sulfate solutions. The expansion and cracking resulting from sulfate attack are generally attributed to the formation of these two compounds, which is recognized by many researchers.

Because of the complexity of exposure surrounding, components and microstructure of concrete materials, sulfate attack has been traditionally studied by two methods; one is that ettringite and gypsum formation are reflected indirectly by measuring the macro-mechanics of concrete materials during external sulfate attack. Odler and Colán-Subauste [8] measured the expansion associ-

ated with ettringite formation on pastes made from an Al-bearing compound, gypsum, and tricalcium silicate and analyzed the effect of ettringite formation on expansion. In a study by Tian and Cohen [9], the effect of gypsum formation during sulfate attack on the resulting expansion of CS paste and mortar prisms was investigated. Measurements of expansion, dynamic elastic modulus, and weight gain of mortars prepared from laboratory cements blended from a set of six representative ground clinkers and Terra Alba gypsum were recorded at intervals of up to 900 days by Zhang et al. [10], and the influences of DEF on the macro-mechanics were analyzed. The other is that the quantities of expansion products and micro-structures are obtained directly by such micro-experimental methods as XRD, DTA, DSC, SEM and Micro CT or so. Fu et al. [11] reported the results of a kinetic study of delayed ettringite formation in hydrated Portland cement paste by XRD analysis over the temperature range 5–85 °C. Evju and Hansen [12] studied the hydration products formation of a paste consisting of 25 wt.% calcium aluminate cement, 12.5 wt.% Portland cement, 12.5 wt.% β-calcium sulfate hemihydrate and 50 wt.% water at 20 °C and 100% relative humidity using in situ synchrotron X-ray powder diffraction, isothermal conduction calorimetry and dilatometric measurements. According to Santhanam et al. [13], the quantity of gypsum and ettringite, as measured by differential scanning calorimetry, increased with the time of immersion in the sulfate solution. In a study by Naik et al. [14], X-ray microtomography (microCT) and spatially resolved energy dispersive X-ray diffraction (EDXRD) were used in combination to non-destructively monitor the physical and chemical manifestations of damage in

\* Corresponding author. Tel.: +86 574 87600075; fax: +86 574 87608358.  
E-mail address: [chenjiankang@nbu.edu.cn](mailto:chenjiankang@nbu.edu.cn) (J.-k. Chen).

87 Portland cement paste samples subjected to severe sodium sulfate  
88 attack. Another interesting work conducted by Bellmann et al. was  
89 the examination of the influence of sulfate solution concentration  
90 on the formation of gypsum [15].

91 Since the above research has played an important role on study-  
92 ing the sulfate attack problem, the reports about ettringite and  
93 gypsum formation during the whole process have been not seen  
94 in detail. The kinetic study of ettringite and gypsum formation is  
95 of great benefit to understanding which roles the two products  
96 play respectively during external sulfate attack on concrete mate-  
97 rials and revealing the mechanism of sulfate attack. The research  
98 reported here focuses on the kinetic characteristics of ettringite  
99 and gypsum formation, as measured by X-ray powder diffraction,  
100 in hydrated Portland cement mortars at water cement ratio = 0.40,  
101 0.55, 0.70 exposed to sulfate sodium solution with sulfate concen-  
102 tration of 0, 20,250, 54,000, respectively, at intervals of up to 180  
103 days. The influences of sulfate concentration and water cement ra-  
104 tio on ettringite and gypsum formation were also discussed.

## 105 2. Materials and specimens preparation

### 106 2.1. Materials

107 The samples used in the present experiments are the 425# com-  
108 mon Portland cement consisting of 13.01 wt.% Al<sub>2</sub>O<sub>3</sub>, 2.63 wt.% SO<sub>3</sub>  
109 2.63, and 2.91 wt.% Fe<sub>2</sub>O<sub>3</sub> made from Lvyang cement ltd. Co, Yangz-  
110 hou. The ISO standard sand used conformed to GB1717671 and  
111 was derived from Xiamen. AR-grade anhydrous sodium sulfate  
112 (Na<sub>2</sub>SO<sub>4</sub>) was produced from chemistry reagent Co. Shanghai, Chi-  
113 nese medicine group, molecular weight is 142.04.

### 114 2.2. Specimens moulding and treatment

115 The proportions of mortar prisms (10 × 10 × 30 mm) were 1.0  
116 (cement): 2.5 (sand): 0.4 (water), 1.0 (cement): 2.5 (sand):  
117 0.55(water), 1.0 (cement): 2.5 (sand): 0.70 (water), respectively, all  
118 by mass. After mixing, mortar specimens used in this experiment  
119 were procured in their molds that were stored at 20 °C and 90% re-  
120 lative humidity, and then removed from molds one day later. Subse-  
121 quently, the specimens were exposed to standard curing for 28 days.

## 122 3. Experiment

123 After the common initial curing regime as mentioned above,  
124 specimens were stored in three different solutions (shown in  
125 Fig. 1.) a controlled solution, a 3.00 mass% sodium solution, and  
126 an 8.00 mass% sodium solution (in other words, a SO<sub>4</sub><sup>2-</sup> concentra-  
127 tion of 0, 20,250 and 54,000 ppm, respectively). The mortar speci-  
128 mens were dried naturally after removal from the solutions. After  
129 5 h, the specimens were ground to a fine powder using a mortar  
130 and pestle and passed through an 80 μm opening sieve. XRD anal-  
131 ysis at intervals of up to 180 days used M03XHF22 type of X-ray  
132 diffractometer manufactured Mac Science Co. Japan that had a  
133 curved Ge (1 1 1) monochromator yielding Cu Kα<sub>1</sub> radiation (wave-  
134 length is 1.54056 Å, voltage is 40 KV, current is 40 mA). The funda-  
135 mental of quantity analysis by XRD is [16] that the diffraction line  
136 intensity increases with content of the phase. Because the diffrac-  
137 tion intensity is probability distribution, the intensity must be an  
138 area integral. For simplification, the integral is performed using  
139 an approximate method given by the following equation:

$$140 S = I_m B$$

141 where  $S$  is the integral intensity,  $I_m$  is the value of the intensity  
142 at the peak point,  $B$  is the diffraction line width corresponding to  
143 the intensity of  $I_m/2$ , as shown in Fig. 2. In this work, the quantity  
144 of ettringite and gypsum formed in various specimens were com-  
145 pared by the relative integral intensity of the corresponding XRD  
146 peaks, the strongest reflections at  $2\theta = 9.08^\circ$  for ettringite and  
147  $2\theta = 11.59^\circ$  for gypsum, respectively. 148

## 149 4. Results and discussion

### 150 4.1. Evolution of ettringite

151 The solid phases in the specimens after different exposure peri-  
152 ods were examined using XRD. Evolution of the strongest XRD  
153 peak intensities of ettringite in cement mortar ( $w/c = 0.70$ ) exposed  
154 to sulfate concentration of 54,000 ppm in sodium sulfate are  
155 shown in Fig. 3a and formation of ettringite in three types of ce-  
156 ment mortars at  $w/c = 0.40, 0.55, 0.70$ , exposed to sulfate sodium

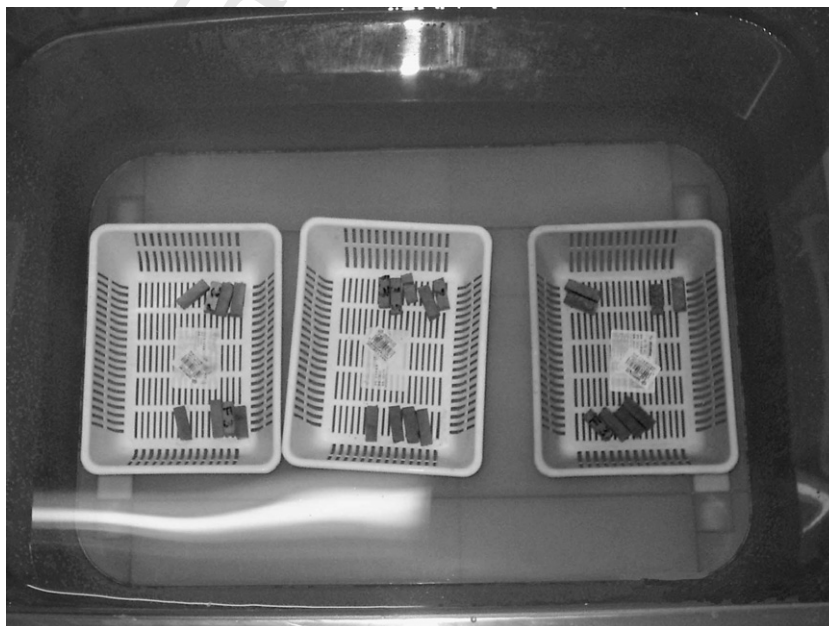


Fig. 1. The specimens stored in sodium sulfate solution.

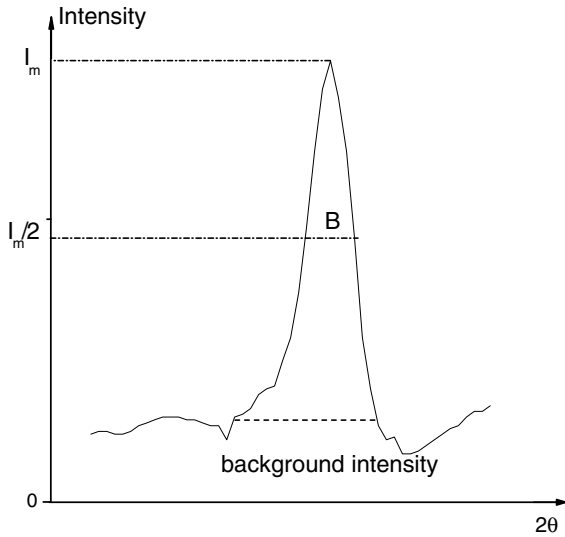
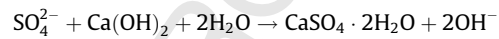


Fig. 2. Integral intensity of diffraction line.

to the strongest peak of ettringite has a small offset, which is due to the influence of impurities in specimens. In general, the ettringite strongest peak intensity grows with the exposure period of 180 days, but the grow rate varies, which indicates the rate at which ettringite was formed differed significantly in different periods.

Fig. 3b–d shows the kinetics of ettringite formation in the specimens at  $w/c = 0.40, 0.55, 0.70$ , exposed to sulfate sodium with sulfate concentrations of 0 ppm, 20,250 ppm, and 54,000 ppm, respectively. The quantities of ettringite in the specimens exposed to water are almost unchangeable in 180 days. The ettringite formation in sodium sulfate solution follows a three-stage process. In stage 1, the ettringite grows suddenly because of sulfate ions' penetration. On the 14th day or so, this is followed by a rapid decrease, which shows the end of the stage 1 that can be called the 'penetration period'.

In stage 2, the pH of the surrounding solution changes to 11–12 after the specimens are introduced because of the following reaction:



Because water surrounding the specimens is stagnant, the pH will remain in the range of 11–12, which insures that ettringite can exit stably. At  $w/c = 0.40$ , the quantities of ettringite leveled off for about 135 days; at  $w/c = 0.55$  and 0.70, the ettringite forms rapidly, but the increase of the former was more rapid than that of the latter. Macro-experiments show that the ettringite formation can increase the value of the cement mortars' dynamic modulus [17]. Hence, this stage is named as the 'enhance period of strength'.

with sulfate concentration of 0, 20,250, 54,000 ppm, respectively, are shown in Fig. 3b–d, respectively.

Fig. 3a displays the increase of the ettringite strongest peak intensity with exposure periods. The specimens is at  $w/c = 0.70$  and exposed to sulfate concentration of 54,000 ppm. In the exposure period of 180 days, the diffraction angle ( $2\theta$ ) corresponding

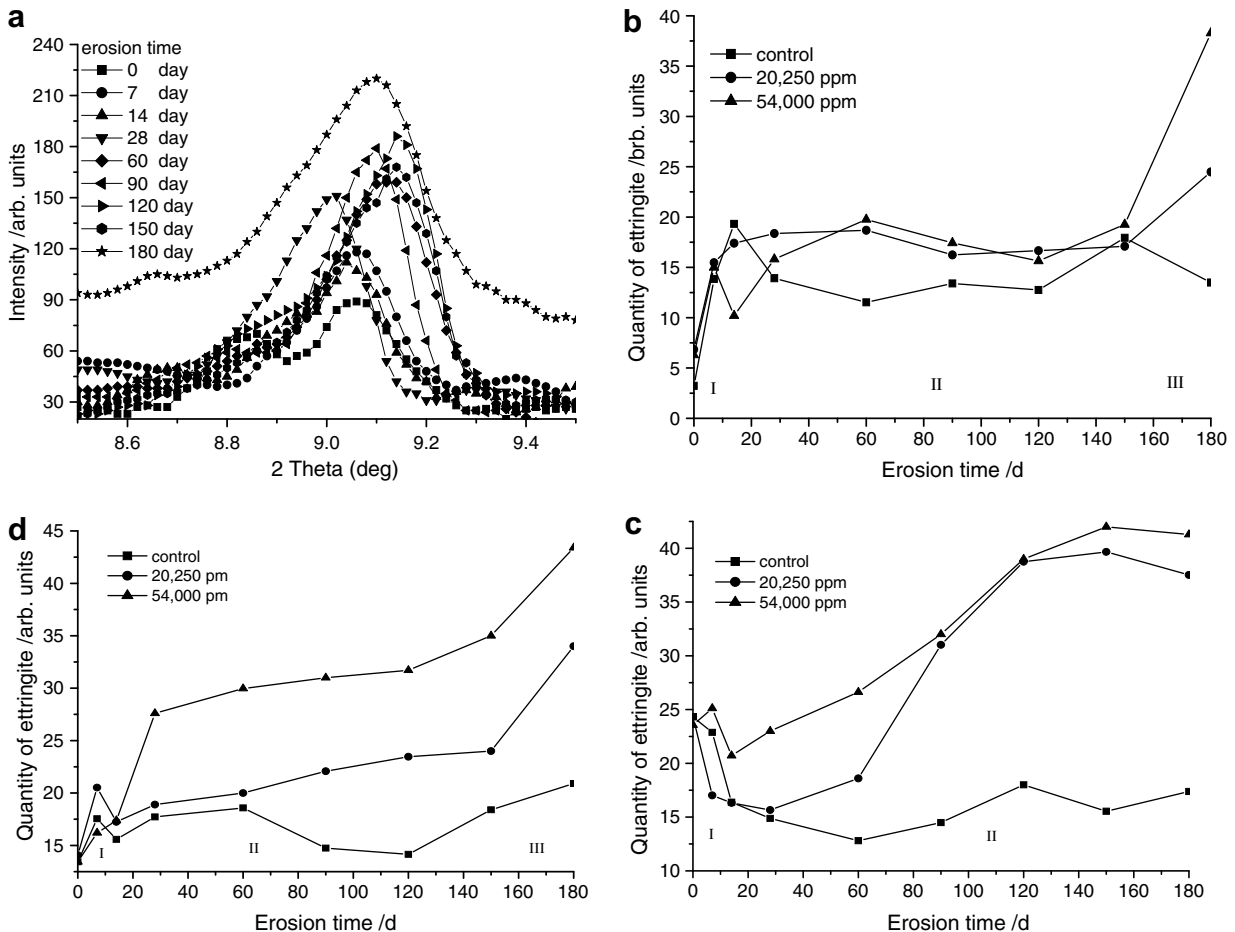


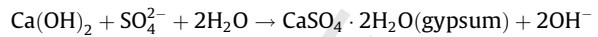
Fig. 3. (a) Evolution of the strongest XRD peak intensities of ettringite in cement mortar ( $w/c = 0.70$ ) exposed to sulfate concentration of 54,000 ppm in sodium sulfate; Formation of ettringite in different mortars: (b)  $w/c = 0.40$ , (c)  $w/c = 0.55$ , (d)  $w/c = 0.70$ , exposed to sulfate sodium with sulfate concentration of 0, 20,250, 54,000 ppm.

At the end of stage 2, the ettringite formation appears different in different cases. At that time, the ettringite formation depended on the quantities of  $C_3AH_6$ , because the sulfate ions were redundant. If there is an excess of  $C_3AH_6$ , the  $C_3AH_6$  can react with sulfate ions and form the ettringite more rapidly, as was shown in the specimens at  $w/c = 0.40$  (Fig. 3b) and at  $w/c = 0.70$  (Fig. 3d), which indicated that there appeared a few of macro-cracks in the two type of specimens. This stage has been marked 'macro-crack period'. If the  $C_3AH_6$  was consumed in stage 2, the quantities of ettringite would keep constant, as is shown in the specimens at  $w/c = 0.55$ , (Fig. 3c), which means that the type of specimens will not crack due to the ettringite formation under this experimental condition.

4.2. Gypsum formation

At the same time that the evolution of ettringite peak intensity in cement mortar were obtained by XRD, the evolution of XRD peak intensities of gypsum was also gained. For example, as is shown in Fig. 4a that the gypsum strongest peak intensity increase with exposure periods in cement mortar ( $w/c = 0.55$ ) exposed to sulfate concentration of 54,000 ppm in sodium sulfate. For the same reason, the diffraction angle corresponding to the strongest peak of gypsum has the similar offset as the ettringite. From Fig. 4a, we can also see the grow rate of peaks is not even with the exposure periods.

Fig. 4b-d presents the quantity grow rate of gypsum for the specimens at  $w/c = 0.40, 0.55, 0.70$  stored in sodium sulfate solutions with sulfate concentrations of 0, 20,250, 54,000 ppm, respectively. A gradual increase of the gypsum quantities in the specimens exposed to sulfate sodium were observed in the exposure period, but gypsum formed very slowly in the specimens stored in controlled solutions, which indicates that sulfate ions supply was necessary for gypsum formation because of the following reaction:



The gypsum formations for the specimens exposed to sodium sulfate solutions, as shown in Fig. 4b-d, occurred in two stages. The shapes of curves were similar to the results of linear expansion study by Tian et al. [9], and Santhanam et al. [12,18], which implied that the gypsum formation was relative to the linear expansion of mortars to some extent. After a latent period extending approximately 28 days at  $w/c = 0.40$ , 14 days at  $w/c = 0.55$ , and less than 7 days at  $w/c = 0.70$ , respectively, into the exposure, the gypsum formed more rapidly (marked 'accelerated period') as compared to the previous stage (called the 'latent period'). Water cement ratio and sulfate concentration played important roles in the formation of gypsum. The latent period lasted longer and the quantities of gypsum increased more rapidly with the increase of water cement ratio from 0.40 to 0.70. Higher concentration of sulfate sodium solutions speeded up the gypsum formation. For whichever

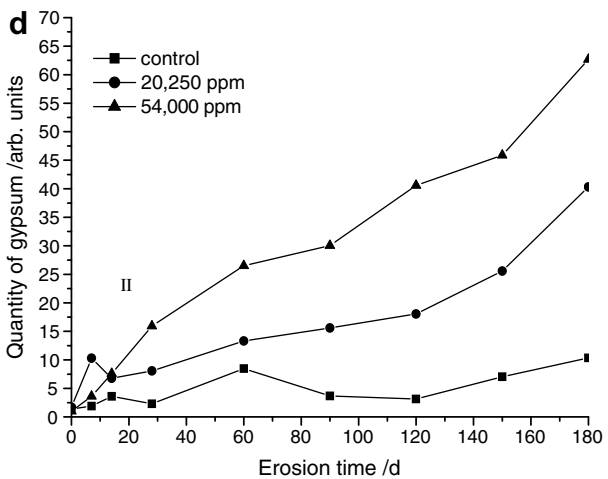
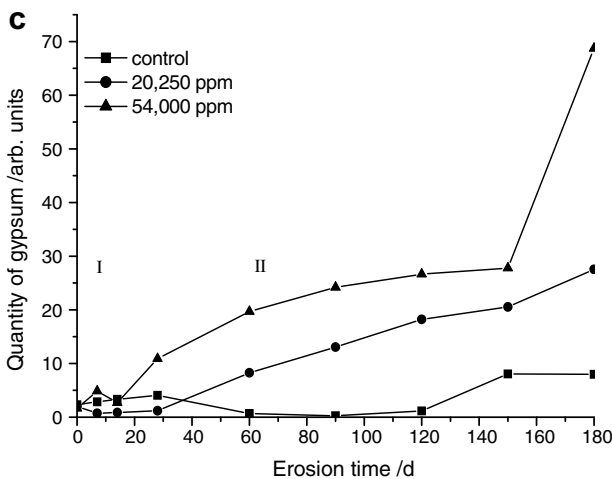
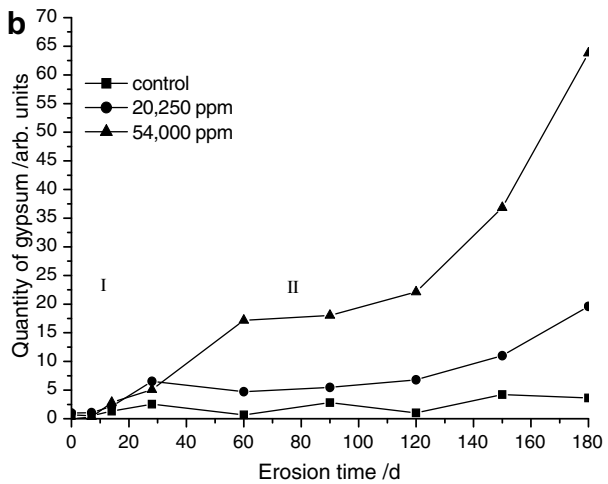
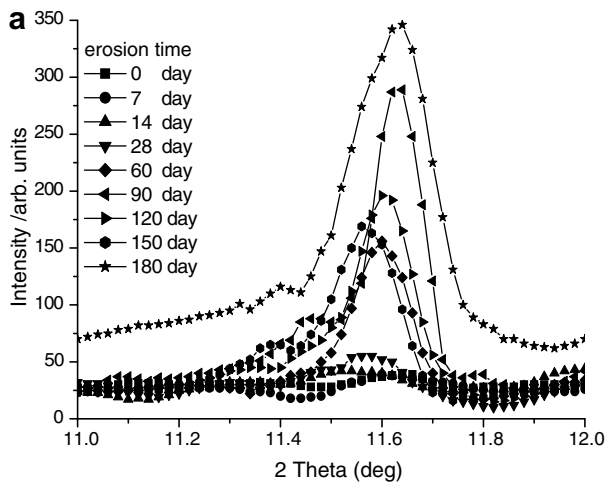


Fig. 4. (a) Evolution of the XRD peak intensities of gypsum in cement mortar ( $w/c = 0.70$ ) exposed to sulfate concentration of 54,000 ppm in sodium sulfate; Formation of gypsum in different mortars: (b)  $w/c = 0.40$ , (c)  $w/c = 0.55$ , (d)  $w/c = 0.70$ , exposed to sulfate sodium with sulfate concentration of 0, 20,250, 54,000 ppm, respectively.

specimens, the amount of gypsum formation in the sulfate sodium solution with sulfate concentration of 54,000 ppm was much more than ones in 20,250 ppm solutions.

## 5. Conclusions

From the experiments, the following conclusions can be drawn.

- (1) The ettringite formation in sodium sulfate solution follows a three-stage process, which are 'penetration period', 'enhance period of strength', and 'macro-crack period', respectively. The cracking of the concrete materials is mainly attributed to the effect of ettringite.
- (2) The gypsum formations occurred in two stages, the 'latent period' and 'accelerated period'. The gypsum formation including ettringite formation was relative to the linear expansion of mortars to some extent.
- (3) Both water cement ratio and sulfate concentration play important roles in the formation of ettringite and gypsum.

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