

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

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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 other 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.%  $\beta$ -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

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

Since the above research has played an important role on studying the sulfate attack problem, the reports about ettringite and gypsum formation during the whole process have been not seen in detail. The kinetic study of ettringite and gypsum formation is of great benefit to understanding which roles the two products play respectively during external sulfate attack on concrete materials and revealing the mechanism of sulfate attack. The research reported here focuses on the kinetic characteristics of ettringite and gypsum formation, as measured by X-ray powder diffraction, in hydrated Portland cement mortars at water-to-cement ratio = 0.40, 0.55, 0.70 exposed to sulfate sodium solution with sulfate concentration of 0, 20,250, 54,000, respectively, at intervals of up to 180 days. The influences of sulfate concentration and water cement ratio on ettringite and gypsum formation were also discussed.

## 2. Materials and specimens preparation

### 2.1. Materials

The samples used in the present experiments are the 425# common Portland cement consisting of 13.01 wt.%  $\text{Al}_2\text{O}_3$ , 2.63 wt.%  $\text{SO}_3$ , 2.63, and 2.91 wt.%  $\text{Fe}_2\text{O}_3$  made from Lvyang cement Ltd. Co, Yangzhou. The ISO standard sand used conformed to GB1717671 and was derived from Xiamen. AR-grade anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) was produced from chemistry reagent Co. Shanghai, Chinese medicine group, molecular weight is 142.04.

### 2.2. Specimens moulding and treatment

The proportions of mortar prisms ( $10 \times 10 \times 30$  mm) were 1.0 (cement): 2.5 (sand): 0.4 (water), 1.0 (cement): 2.5 (sand): 0.55(water), 1.0 (cement): 2.5 (sand): 0.70 (water), respectively, all by mass. After mixing, mortar specimens used in this experiment were procured in their molds that were stored at 20 °C and 90% relative humidity, and then removed from molds one day later.

Subsequently, the specimens were exposed to standard curing for 28 days.

## 3. Experiment

After the common initial curing regime as mentioned above, specimens were stored in three different solutions (shown in Fig. 1.) a controlled solution, a 3.00 mass% sodium solution, and an 8.00 mass% sodium solution (in other words, a  $\text{SO}_4^{2-}$  concentration of 0, 20,250 and 54,000 ppm, respectively). The mortar specimens were dried naturally after removal from the solutions. After 5 h, the specimens were ground to a fine powder using a mortar and pestle and passed through an 80  $\mu\text{m}$  opening sieve. XRD analysis at intervals of up to 180 days used M03XHF22 type of X-ray diffractometer manufactured Mac Science Co. Japan that had a curved Ge (1 1 1) monochromator yielding  $\text{Cu K}\alpha_1$  radiation (wavelength is 1.54056 Å, voltage is 40 KV, current is 40 mA). The fundamental of quantity analysis by XRD is [16] that the diffraction line intensity increases with content of the phase. Because the diffraction intensity is probability distribution, the intensity must be an area integral. For simplification, the integral is performed using an approximate method given by the following equation:

$$S = I_m B$$

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

## 4. Results and discussion

### 4.1. Evolution of ettringite

The solid phases in the specimens after different exposure periods were examined using XRD. 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 are

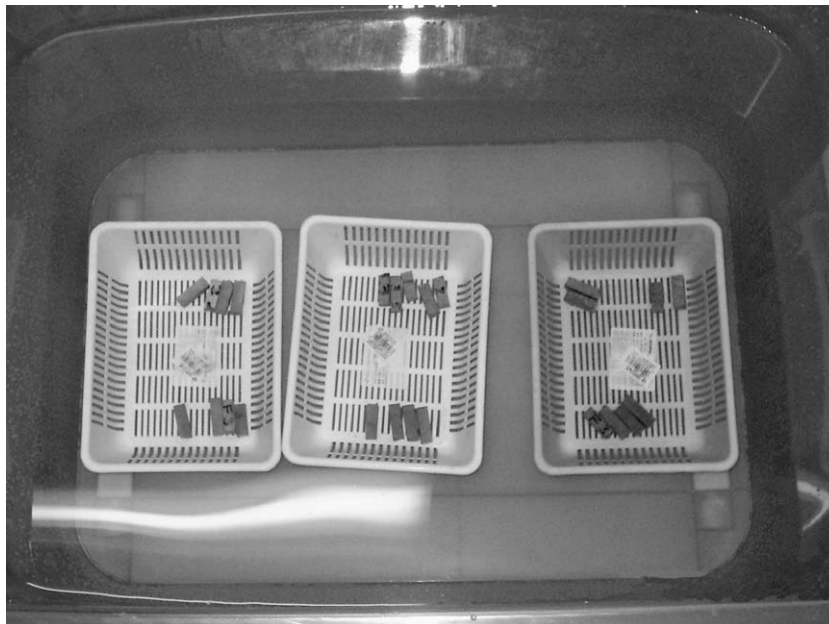


Fig. 1. The specimens stored in sodium sulfate solution.

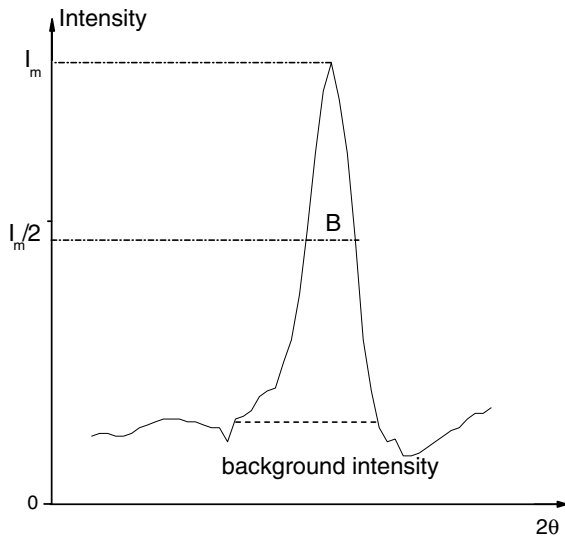


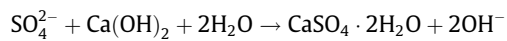
Fig. 2. Integral intensity of diffraction line.

shown in Fig. 3a and formation of ettringite in three types of cement mortars at  $w/c = 0.40, 0.55, 0.70$ , exposed to sulfate sodium 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 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

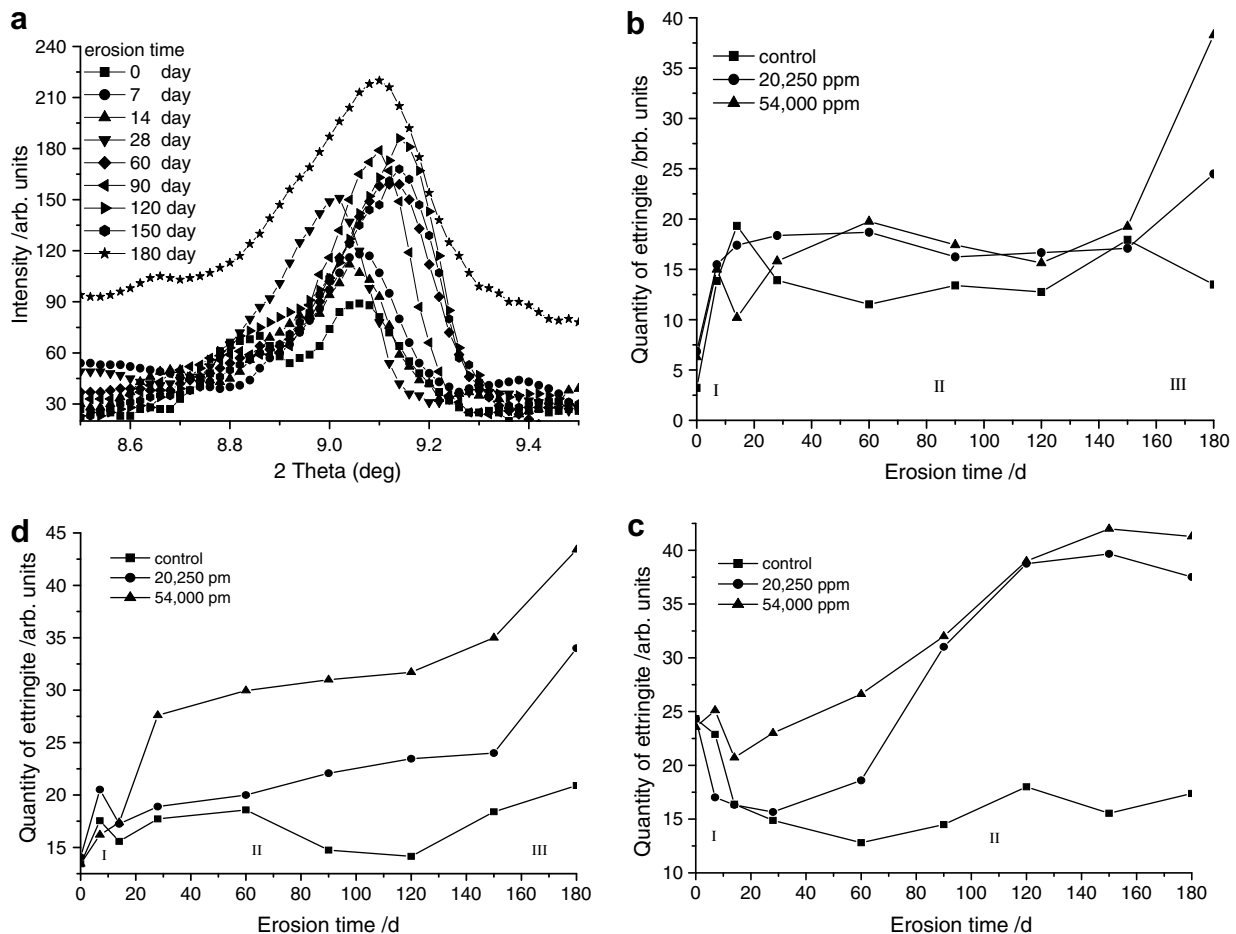


Fig. 3. (a) Evolution of the strongest XRD peak intensities of ettringite in cement mortar ( $w/c = 0.70$ ) exposed to sulfate concentration of 54,000 ppm in sodium sulfate; Formation of ettringite in different mortars: (b)  $w/c = 0.40$ , (c)  $w/c = 0.55$ , (d)  $w/c = 0.70$ , exposed to sulfate sodium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

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 may be named as the 'enhance period of strength'.

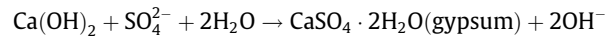
At the end of stage 2, the ettringite formation appears different in different cases. At that time, the ettringite formation depended on the quantities of  $C_3AH_6$ , because the sulfate ions were redundant. If there is an excess of  $C_3AH_6$ , the  $C_3AH_6$  can react with sulfate ions and form the 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-to-cement

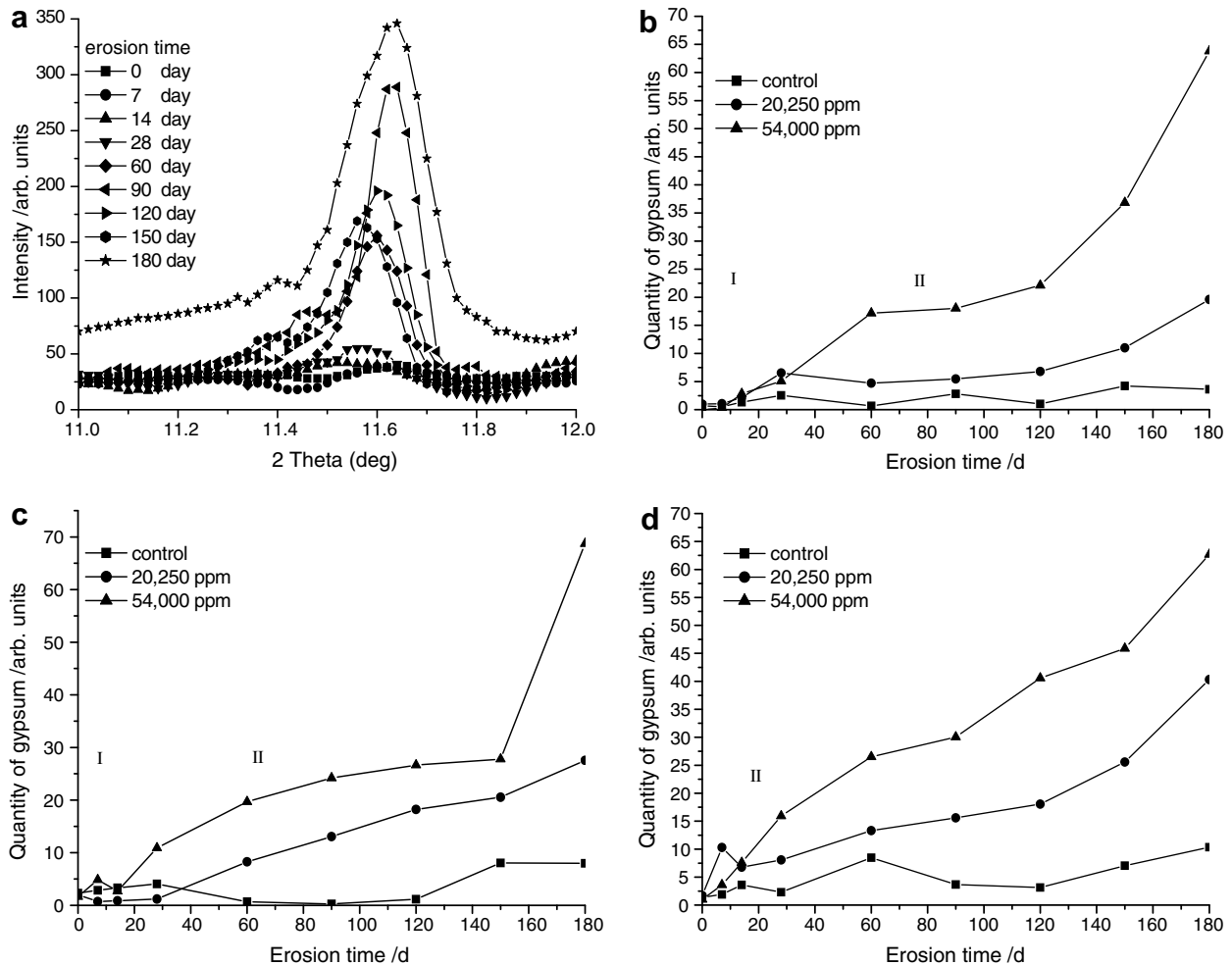


Fig. 4. (a) Evolution of the XRD peak intensities of gypsum in cement mortar ( $w/c = 0.70$ ) exposed to sulfate concentration of 54,000 ppm in sodium sulfate; Formation of gypsum in different mortars: (b)  $w/c = 0.40$ , (c)  $w/c = 0.55$ , (d)  $w/c = 0.70$ , exposed to sulfate sodium with sulfate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

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-to-cement ratio from 0.40 to 0.70. Higher concentration of sulfate sodium solutions speeded up the gypsum formation. For which-ever 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-to-cement ratio and sulfate concentration play important roles in the formation of ettringite and gypsum.

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## References

- [1] Li LY, Page CL. Finite element modelling of chloride removal from concrete by an electrochemical method. *Corr Sci* 2000;42(12):2145–65.
- [2] Li LY, Page CL. Modelling of electrochemical chloride extraction from concrete: influence of ionic activity coefficients. *Comput Mater Sci* 1998;9(3–4):303–8.
- [3] Wang Y, Li LY, Page CL. Modelling of chloride ingress into concrete from a saline environment. *Build Environ* 2005;40(12):1573–82.
- [4] Wang Y, Li LY, Page CL. A two-dimensional model of electrochemical chloride removal from concrete. *Comput Mater Sci* 2001;20(2):196–212.
- [5] Onyejekwe OO, Reddy N. A numerical approach to the study of chloride ion penetration into concrete. *Mag Concrete Res* 2000;52(4):243–50.
- [6] Samson E, Marchand J, Beaudoin JJ. Describing ion diffusion mechanism in cement-based materials using the homogenization technique. *Cement Concrete Res* 1999;29(10):1341–5.
- [7] Cohen MD, Bentur A. Durability of Portland cement-silica fume pastes in magnesium sulfated and sodium sulfate solutions. *ACI Mater* 1998;85(3):148–57.
- [8] Odler I, Colán-Subauste J. Investigation on cement expansion associated with ettringite formation. *Cement Concrete Res* 1999;29:731–5.
- [9] Tian Bing, Cohen Menashi D. Does gypsum formation during sulfate attack on concrete lead to expansion. *Cement Concrete Res* 2000;30:117–32.
- [10] Zhang Zhaozhou, Olek Jan, Diamond Sidney. Studies on delayed ettringite formation in early-age, heat-cured mortars I. Expansion measurements, changes in dynamic modulus of elasticity and weight gains. *Cement Concrete Res* 2002;32:1729–36.
- [11] Fu Yan, Gu Ping, Xie Ping, Beaudoin JJ. A kinetic study of delayed ettringite formation in hydrated Portland cement paste. *Cement Concrete Res* 1995;25:63–70.
- [12] Evju Cecilie, Hansen Staffan. Expansive properties of ettringite in a mixture of calcium aluminate cement, Portland cement and  $\beta$ -calcium sulfate hemihydrate. *Cement Concrete Res* 2001;31:157–261.
- [13] Santhanam Manu, Cohen Menashi D, Olek Jan. Effects of gypsum formation on the performance of cement mortars during external sulfate attack. *Cement Concrete Res* 2003;33:325–32.
- [14] Naik NN, Jupe AC, Stock SR, et al. Sulfate attack monitored by microCT and EDXRD: influence of cement type, water-to-cement ratio, and aggregate. *Cement Concrete Res* 2006;36:144–59.
- [15] Bellmann Frank, Moser Bernd, Stark Jochen. Influence of sulfate solution concentration on the formation of gypsum in sulfate resistance test specimen. *Cement Concrete Res* 2006;36:358–63.
- [16] Yu Zhou. Materials analysis method. Beijing: China Machine Press; 2004.
- [17] Minqiang Jiang, Jiankang Chen, Dingyi Yang. Dynamic modulus of cement mortar in sulphate erosion measured by ultrasonic checking. *J Chinese Ceram Soc* 2005;33:126–32.
- [18] Santhanam Manu, Cohen Menashi D, Olek Jan. Mechanism of sulfate attack: a fresh look. Part 2: proposed mechanisms. *Cement Concrete Res* 2002;32:341–6.