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A new chemo-mechanical model of damage in concrete under sulfate attack

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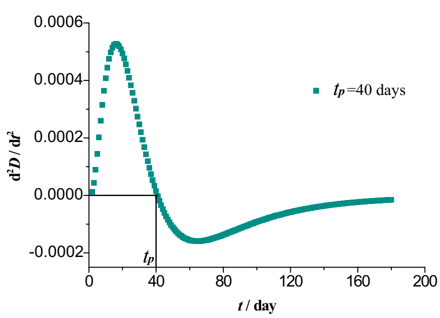
HIGHLIGHTS

- Damage evolution in concrete under sulfate attack is derived considering chemical reaction rate.
- The characteristic time of chemical reaction represents inflection point of damage evolution.
- Damage nucleation is due to tensile failure at the surface of pores by delayed ettringite.

GRAPHICAL ABSTRACT

The characteristic time t_p related chemical reaction rate approximately is the inflection point of damage evolution.



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ABSTRACT

Damage evolution is detected via the degradation of modulus of concrete immersed in sulfate solution. The mechanism of the damage is investigated by using SEM method, and it is proved that the internal expansion stress induced by delayed ettringite leads to the nucleation of micro-cracks. The criterion of damage nucleation is proposed in terms of the tension strength of concrete. The differential equation with respect to the internal expansion stress is derived by virtue of chemical reaction rate on delayed ettringite formation, and a new chemo-mechanical model of corrosion damage in concrete under sulfate attack is then proposed.

1. Introduction

In the environment of ocean or salt lake, the mechanical properties of concrete structures strongly degrade by attack of harmful ions, such as chloride ions, sulfate ions, magnesian ions, and so on [1,2]. It is well known that chloride ions dominantly attack reinforcing steel and induce it to corrosion, and magnesian ions react with C-S-H gel, and lead to calcium leaching. The mechanism for the sulfate attack on concrete matrix, however, is so complicated that it is still unclear till now. For instance, Tixier and Mobasher [3] and Ikumi et al. [4] thought that a series of chemical reactions take place between sulfate ions and the unreacted hydration compounds of the cement paste, and all those reactions lead to degradation of concrete. Therefore, this challenge problem attracts many

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researchers' close attention. In fact, people early realized the degradation effect of sulfate in the second half of the nineteenth century, and found sulfate ions diffused in porous of concrete react with pore solution to induce delayed ettringite formation (DEF). DEF leads to the damage evolution under the condition that concrete dose not experience an elevated temperature (e.g. [5,6]). Related studies on concrete under sulfate attack dominantly focus on the mechanism of degradation of mechanical properties and material design on sulfate resistance.

Because the degradation mechanism of mechanical properties relates to the delayed ettringite, some of studies focus on the mechanism of DEF [7,8] and crystal structure [9,10]. The internal expansion forces are produced under the action of delayed ettringite, and the expansion in concrete occurs due to the internal expansion forces. Barbarulo et al. [11] studied the expansion of concrete during DEF under high temperature and thermal cycle, and found that the expansion strain reaches 3%. Pavoine et al. [12] further considered the effect of wetting and drying on the expansion of concrete due to DEF, and indicated that the expansion occurs earlier than that in the concrete without wetting and drying condition. Zhang et al. [13] studied the expansion of concrete due to attack of sulfate and sulfate–chloride ions. It was found that the expansion caused by attack of sulfate–chloride ions is much less than that induced only by sulfate attack. The mechanism of such a phenomenon is that DEF in the former situation is much less than that in the latter situation.

Under sulfate attack, the corrosion damage leads to the degradation of stiffness and strength of concrete. Planel et al. [14] studied the long-term behavior of cement mortar, and analyzed size-effect on the degradation of mechanical properties of the material. Chen et al. [15] investigated the damage evolution in concrete due to sulfate attack, and suggested an empirical formula of the damage evolution. Rozière et al. [16] not only experimentally analyzed the variation of mass and deformation of concrete exposed to leaching and external sulfate attacks, but also showed some pictures of cracks growth in micro-scale. Because the filling effect of delayed ettringite in pores of concrete, the pore structure is changed. Pipilikaki et al. [17] examined the variation of microstructure of concrete under sulfate attack, meanwhile they also inspected the changes of compressive strength of the material.

In order to improve the property of sulfate resistance of concrete, some researchers adopted new mix design of concrete. For instance, Plowman and Cabrera [18] used fly ash as additive agent to polish up the microstructure of concrete; Chindaprasirt et al. [19] employed both fly ash and rice husk ash as new components of concrete for slowing down degradation of concrete; Lee et al. [20] replaced part of cement by silica fume to reduce the magnitude of delayed ettringite in concrete.

All those method can only slow down the rate of chemical reaction for DEF, however, it is difficult to completely prevent concrete from degradation. Therefore, it is still important to establish a reasonable prediction theory on the service life of concrete structure in marine environment. Kuhl et al. [21,22] suggested a new theoretical frame, which includes the coupling effect of chemistry and mechanics, to analyze the degradation of cementitious materials due to calcium leaching and mechanical damage. Nevertheless, few works on the degradation of concrete under sulfate attack have been reported.

In this paper, variation of dynamic modulus of concrete under sulfate attack was detected by virtue of ultrasonic technique. The average corrosion damage was defined as the relative decrease to the modulus, and it was determined from the experimental results. Then, the damage nucleation due to the action of internal expansion stress, which is produced by delayed ettringite, was analyzed by Eshelby's equivalent inclusion method. Based on the assumption that the expansion stress is directly proportional to the mass of delayed ettringite, the differential equation for the expansion stress is derived by considering the related chemical reaction as well as reaction rate. Finally, a new damage evolution model of concrete is proposed in terms of Weibull's weakest link model.

2. Experimental

Reference cement produced by China Building Materials Academy was adopted to form specimens of concrete. The components of the reference cement were listed in Table 1.

Cement-to-sand ratio of the specimens is 1:2, and water-to-cement ratio is 0.45. The shape of the specimens is cylindrical, which are 500 mm in length and 45 mm in diameter, respectively. The concrete specimens were cured 24 h at ambient condition, after then they were put into a concrete standard compartment for curing 28 days, which has the environment temperature of 20 °C and relative humidity of 90%.

After being cured 28 days, the specimens were moved into the solutions of sodium sulfate, with three different concentrations selected as, 3%, 5%, and 8%. During the period of immersion, the ultrasonic detection was carried out, and diagram of the detection was plotted in Fig. 1. When the frequency of ultrasonic is given, the wave propagates from one end of the specimen to the other end with a constant velocity.

In the situation shown in Fig. 1, the ultrasonic propagation is an axisymmetric problem. Just as pointed by Rayleigh, however, if the ratio of radius to wavelength is less 0.7, then it can be approximately referred to as one dimensional stress [23]. The relation between the elastic modulus, E, and the wave velocity, C, can be written as follows [24],

$$E = C^2 \rho \tag{1}$$

where the symbol "ρ" stands for density of the specimen. If the change of the density and the wave velocity are measured, then the variation of the modulus can be determined by Eq. (1).

By means of weight method, variation of density was measured at different immersion times and plotted in Fig. 2. It can be seen that the density monotonously increases due to a series chemical reactions, including reactions on continued hydration and DEF, etc.

Variation of modulus was measured by virtue of ultrasonic technique shown in Fig. 1, and the results were plotted in Fig. 3. The time interval of the first stage decreases with the increase of the concentration of sulfate solution. It was found that the variation of the modulus can be divided into two stages. In the first stage (initial stage) the modulus increases, but in the second stage it decreases. This implies that the damage evolution only takes place in the second stage, thus, we define that the damage in this stage is the relative decrease of the modulus, i.e.,

$$D = 1 - \frac{E}{E_{\max}} \tag{2}$$

where the symbol "$E_{\max}$" denotes the maximum modulus. From the experimental results in Fig. 3 and Eq. (2), the damage was obtained and plotted in Fig. 4. One can see that damage evolution is more fast in the sulfate solution of higher concentration.

After being immersed for 360 days, the macro-cracks can be observed in specimens as shown in Fig. 5.

For establishing a theoretical model of damage evolution, microscopic observation was performed using SEM technique. Fig. 6 shows the observation of DEF in pores of concrete and related energy spectrum analysis.

3. Theoretical model of damage evolution

Damage evolution in concrete can be studied by investigating the crack propagation [25], or predicting statistical evolution of damage by virtue of continuum damage [26]. In this study, a statistic method is adopted to investigate the damage evolution in concrete under sulfate attack. For this, the damage nucleation is studied first.

3.1. Damage nucleation

Experimental results indicate that DEF in pores of concrete is a dominant factor to induce the corrosion damage. The mechanism for damage nucleation is that sulfate ions diffused in pores of concrete react with pore solution in concrete, which leads to DEF (as shown in Fig. 7). This process can be divided into two steps: 1) reaction between sulfate ions, SO_4^{2-}, and calcium hydroxide, CH, to form gypsum, $C\bar{S}H_2$; 2) reaction of gypsum with tricalcium