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Study on Chemical Failure Mechanism of Sulfate in Reinforced Concrete Structures

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According to Fick's second law, the unsteady diffusion equation of sulfate ion is established in concrete. The finite difference method is used to solve the equation to obtain the concentration distribution of sulfate ion in concrete. Based on the number of calcium vanadium, which is produced by the chemical reaction between sulfate ion and calcium aluminate in concrete, the formula is given for calculating the expansion of concrete in the process of calcium vanadium formation. In addition, the corresponding expansion of concrete is calculated from the constitutive relation of concrete stress to assess whether the concrete is cracked. In this paper, the diffusion process, swelling strain, stress change and cracking process in the concrete slab immersed in 2% Na_2SO_4 solution are simulated by numerical simulation. And the results show that the proposed method can quantitatively describe the damage law of concrete under the sulfate attack.

1. Introduction

Erosion of environmental factors is one of the direct causes of degradation of structural properties and shortened service life (Sui et al., 2015). Sulfate erosion is an important form of concrete damage, which is caused by environmental factors and damage caused by environmental factors. It involves the diffusion and transport of environmental sulfate ions in concrete (Xiong et al., 2016). The chemical reaction, swelling deformation and stress between ions and concrete components analysis, damage to concrete damage and many other issues, are the hot issues of concrete durability issues.

Sulfate erosion is not only an important part of the durability of concrete, but also the most complex and most harmful environmental corrosion (Wang et al., 2012). In 1892, Michalis first discovered the erosion of cement on the cement and called "cement bacteria", in essence, which is needle-like crystal hydrated calcium sulphoaluminate (Lei et al., 2013). Sulfate is widely distributed in various parts of the earth, and most of the soil contains some sulphate. In south-eastern of China, sulphate erosion damage buildings are basically red rock foundation and the depositional environment for the dry climate conditions inland. The water content and permeability of the debris structure are affected by the tectonic development degree and the filling material. In addition, the formation of flaky, needle-like and agglomerated gypsum in the rock formation are generally related to the weak water permeability of the rock (Zhu et al., 2017). Rocks, which are in the slow flow or retention and in the infiltration of the full dissolved salt minerals, become a higher degree of mineralization of chloride sulfate water. This groundwater sometimes exposes large amounts of white crystals due to evaporation of water, when the surface of the rock is cleaved or cracked. The karst rock is the important geological feature of the hydroelectric engineering foundation in the upper and middle reaches of the Yellow River (Qin et al., 2015). Therefore, the sulfate erosion in the water conservancy and hydropower projects is mainly concentrated in the upper reaches of the Yellow River in the northwest region. In 1985, Ministry of Water and Power Concrete Durability Investigation Group has built the power stations of the concrete disease and treatment of the investigation and analysis, of which the Bapanxia Hydropower station and Jinghui electric irrigation project are the most serious (Tzevelekou et al., 2013). An example of sulfate corrosion is shown in Figure 1.

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Figure 1: An example of sulfate corrosion

At present, people have carried out the theoretical research on the diffusion and transport properties of sulfate ions in concrete, and the experimental study on the mechanical properties such as the swelling and deformation of concrete and the decrease of strength and stiffness (Wu et al., 2013). These studies mainly focus on the ion diffusion in the process of sulfate attack and the mechanical properties of concrete materials. However, the quantitative description model, which can be used to the damage process and the change of the reaction time of the concrete after the erosion product, is still lacking. Therefore, the existing research results are also difficult to meet the requirements of the life prediction and durability design of concrete structures under sulfate attack (Páez et al., 2016). Thus, according to the diffusion of sulfate ions in concrete and the chemical reaction between concrete components, the change of strain stress, which is caused by the volume expansion of concrete, the cracking process of concrete cracking, is established quantitative analysis model of the whole process.

2. Sulfate attack mechanism

2.1 Sulfate erosion causes concrete appearance and performance degradation

The deterioration of the macroscopic properties of concrete under the action of sulfate is mainly related to the change of the microstructure and the disappearance of the old phase during the erosion process. Therefore, the erosion products are analysed by XRD and other microscopic methods to explore the mechanism of sulfate attack (Han et al., 2016). And it is important to explain the reason of the macroscopic degradation of performance for the study of evaluation methods. The effect of fly ash on sulfate resistance in concrete is given in the Table 1.

Table 1: Effect of fly ash on sulfate resistance in concrete

Range of R	Sulfate attack resistance
<0.75	Considerable improvement
0.75~1.5	Medium improvement
1.5~3.0	Marked improvement
>3.0	Reduce

(1) Acid degradation - cement hydrate decomposition, the formation of non-gelatinous small particles, concrete aggregate exposed; lead to concrete component cross-section reduction and strength reduction; this deterioration is mainly due to CSH gel decomposition sulfate erosion;
(2) Denudation deterioration - concrete materials or components of the surface from the skin, peeling; this deterioration is mainly due to the formation of swelling products in the surface layer, which results in surface peeling and generally gypsum-type sulfate erosion mechanism;
(3) Expansion and deterioration - concrete expansion, cracking, strength reduction; this deterioration is mainly due to ettringite or gypsum-type sulfate erosion mechanism.

2.2 Main form of micro-erosion mechanism

(1) Gypsum-type sulfate attack

$$\begin{cases} Ca(\mathrm{OH})_2 + Na_2SO_4 + 2H_2O \rightarrow CaSO_4{\bullet}2H_2O + 2NaOH \\ Ca(\mathrm{OH})_2 + MgSO_4 + 2H_2O \rightarrow CaSO_4{\bullet}2H_2O + 2Mg\left(OH\right)_2 \end{cases} \tag{1}$$

Usually we think about the formation of harmful substances in the formation of concrete sulphate, and gypsum is one of them. The view that the formation of gypsum is caused by volume expansion, so that the role of the expansion of the pressure of concrete. And other studies have shown that: the beginning of 4 weeks is the incubation period (Hamada et al., 2007). Once the incubation period is over, the specimen will expand at a large expansion rate. But there are also views that the formation of gypsum does not cause expansion. (Sui et al., 2015) argues that the calcium hydroxide and sulfate ions can form a solid gypsum in the pores by solution reaction and they cannot occupy a larger volume of solid calcium hydroxide than the pore volume and solution in the reaction (Wang et al., 2016).

(2) Ettringite erosion

$$\begin{cases} 2CaO{\bullet}Al_2O_3+3CaSO_4{\bullet}2H_2O+26H_2O \rightarrow 3CaO{\bullet}Al_2O_3{\bullet}CaSO_4{\bullet}32H_2O \\ 6Ca+3SO_4+2\left[AlO_2\right]+4OH+32H_2O \rightarrow 3CaO{\bullet}Al_2O_3{\bullet}CaSO_4{\bullet}32H_2O \end{cases} \tag{2}$$

The formation of ettringite is considered to increase the volume by 2.77 times, which results in the expansion of stress generated and leaves the concrete cracking damage. In addition, the cracking of the concrete also makes it easier for the sulfate ions to penetrate into the concrete, which results in a vicious cycle. However, the mechanism of expansion of ettringite is still unclear. Some people think that it is the crystallization pressure of ettringite that leads to the expansion of pressure (Pa´ ez et al., 2000). It is also believed that the swelling of the water causes the expansion pressure due to the poor crystallinity of ettringite in the alkaline environment, and the rate of ettringite formation is strongly related to the source of aluminate. In many cases, the rate of formation of ettringite is determined by the dissolution rate of the aluminum-containing phase. The relationship between the amount of ettringite formed and the expansion has not yet received a good correlation. In many cases, the formation of ettringite is mainly determined by the dissolution rate of the aluminum phase.

(3) Physical erosion - sulfate crystalline erosion

$$\begin{cases} Na_2SO_4+10H_2O \rightarrow Na_2SO_4{\bullet}10H_2O \\ MgSO_4+7H_2O \rightarrow MgSO_4{\bullet}7H_2O \end{cases} \tag{3}$$

The resulting crystalline product can expand the volume by 4 to 5 times, which results the crystallization pressure, causes cracks to occur and leads to the deterioration of the concrete. In addition, it usually occurs in the dry and wet cycle. (Qin et al., 2015) thought that all other salts can be caused with the erosion of this sulphate, and therefore can be classified as the physical erosion.

(4) Calcium Sulfite Calcium Sulfate Erosion

$$3Ca+SO_4+CO_3+\left[\mathrm{Si}\left(OH\right)_6\right]+12H_2O \rightarrow Ca_3\left[\mathrm{Si}\left(OH\right)_6\right]\left(CO_3\right)\left(SO_4\right){\bullet}12H_2O \tag{4}$$

The carbon sulfosilicate is formed at a lower temperature (0 to 15°C), which is the product of CSH and SO42- and CO32- or CO2 reactions. Since the formation of carbon and sulfosilicate has a direct participation of CSH, which can make the cement slurry into no cohesive force of the object and reducing the strength of concrete. But also the expansion of destruction is not a typical destruction caused by carbon and sulfurite, which is accompanied by expansion of damage (Rodriguez M, 2012). Phenomenon indicates that it is also possible to produce carbon-sulfur-siliconite at higher temperatures, so the low temperature may not be a necessary condition for its formation.

2.3 Tropical ductile expansion

Thermal hysteresis expansion, which is also known as the delayed ettringite formation, is a relatively rare internal sulphate attack that allows the hardened concrete to expand and create cracks. Only special chemical composition of the concrete in the higher temperature conditions will be affected by such effects (Abbeche et al., 2010). It usually occurs in the first few hours after the concrete pouring molding, the high temperature of the primary ettringite decomposition, so that sulfate and alumina are firmly adsorbed in the cement paste CSH gel to prevent the normal formation of ettringite. After cooling in a humid environment, the sulphate in the hardened concrete reacts with the monosulfide type hydrated sulphoaluminate from the bondage of the C-S-H gel to produce ettringite. And the ettringite is formed in the confined space of the cement, which is crystallized due to space constraints and supersaturation after several months to several years of absorption process.

3. Constitutive relation and strength criterion of concrete

Considering the consumption of calcium vanadium in concrete filled with pores, the average volume expansion of concrete, which is caused by the growth of calcium vanadium, can be expressed in the following equation:

$$\varepsilon_V = 0.48\frac{V_{CA1}}{V} + 0.55\frac{V_{CA2}}{V} + 1.31\frac{V_{CA3}}{V} - f\Phi \tag{5}$$

ε_V: The average concrete swelling volumetric strain;
V: The total volume of concrete;
V_{CA1}, V_{CA2}, V_{CA3}: Chemical reaction and consumption of CAH413, CASH412, C3A;
f: The coefficient from 0.3 to 0.4;
Φ: The total number of aggregates at a time.
According to the average volume expansion strain of concrete (Han et al., 2016), which is produced by calcium carbonate growth, the corresponding average line expansion strain can be calculated according to the formula:

$$\varepsilon = \frac{\varepsilon_V}{3} \tag{6}$$

In order to calculate the expansion stress of concrete produced by the growth of calcium carbide, the expansion strain of concrete is equivalent to the tensile strain of concrete, and the corresponding expansion stress is calculated according to the constitutive relation of concrete under uniaxial condition:

$$\sigma = \begin{cases} 1.2\dfrac{\varepsilon f_t}{\varepsilon_{tp}} - 0.2 f_t \left(\dfrac{\varepsilon}{\varepsilon_{tp}}\right)^6, \varepsilon \le \varepsilon_{tp} \\ \dfrac{\varepsilon f_t}{0.312 f_t^2 \varepsilon_{tp}\left(\dfrac{\varepsilon}{\varepsilon_{tp}} - 1\right)^{1.7} + \varepsilon}, \varepsilon \ge \varepsilon_{tp} \end{cases} \tag{7}$$

σ: The expansion stress of concrete;

ε: The expansion strain of concrete
f_t: The ultimate tensile stress
ε_{tp}: The ultimate tensile strain of concrete

4. Experiments and analysis

In the whole process of sulfate erosion damage simulation of concrete slabs, the thickness of a concrete slab is 40mm concentration of 2% sodium sulfate solution, and the mineral composition of cement concrete (mass fraction) contains: *SiO* 220.6%, Al_2O 35.03%, *CAO* 65.06%, *MgO* 0.55%, *SO* 32.24%, Fe_2O 34.38%, and 1m3 used concrete cement, water. In addition, sand coarse aggregate is respectively 587282587kg and 1091kg. With the numerical calculation of the model, the following parameters are related to specimen thickness: L=40mm, Na_2SO_4 concentration c_0=2%, concrete water cement ratio of M(W)/m(c)=0.48, the initial porosity of 8% diameter, ettringite pore filling reduction coefficient f=0.4, cement volume fraction of f_c=0.332, the tensile strength of f_t=1.42MPa concrete, concrete ultimate tensile strain ε_{tp}=0.00015, c^0_{C3A} =673mol/m3 initial concentration of C_3A in concrete, the initial content of β=3% gypsum, the content of C_3A =134.6mol/m3 unhydrated concrete, C_4AH_{13}=8.1mol/m content in concrete $C_{C4A}\bar{S}_{H13}$=16.2mol/m3 content in concrete, chemical reaction rate constant $k=3.05\times10^{-8}/s$, $\Delta x=0.5mm$ thickness increment, the increment of time T=1d, the diffusion coefficient $D_s=3.5\times10^{-10}m^2/s$ of sulfate ions in the pore solution.
Figure 2 is the variation of sulfate ion concentration distribution with diffusion time in concrete specimens. It can be seen from Figure 2 that the concentration of sulfate ion in each point of the sample increases with the increase of diffusion time. The closer the surface of the sample is, the greater the concentration of sulfate ion is. At the same time with the increment Δt=200*d*, cumulative concentration of sulfate ions in concrete increases with the increase of diffusion time, and the farther away from the surface of specimen, the concentration of the rising speed is greater. At the midpoint of the specimen x=0.02m, the ion concentration of the former 200d is close to zero, but after 220d, the concentration of sulfate ion begins to increase gradually at 3401d, at which point the ion concentration is equal to 5.07mol/m3.

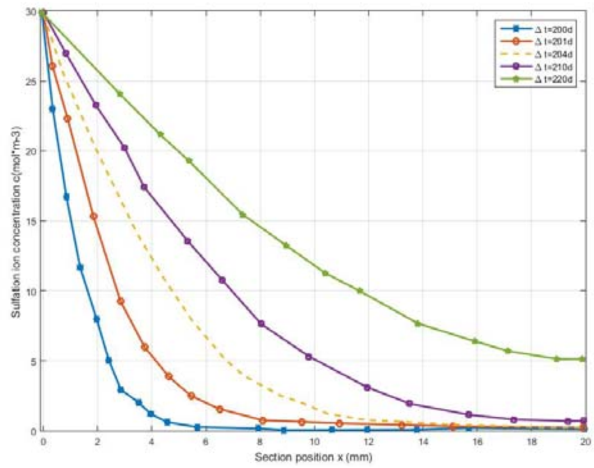

Figure 2: Concentration distribution of sodium sulfate and root ion in test specimens

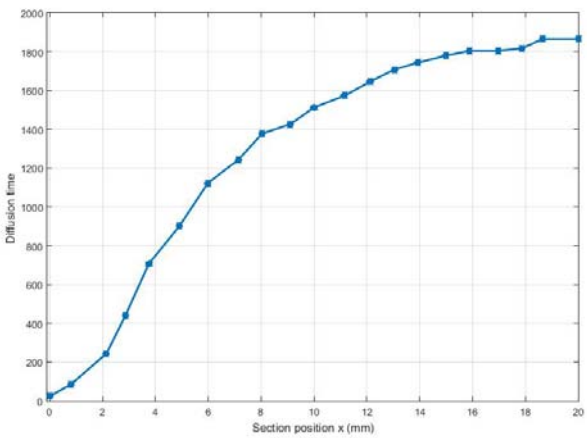

Figure 3: The movement of the crack point with the diffusion time in the specimen

The movement of the crack point with the diffusion time in the specimen is given in Figure 3. We can see that cracking speed point gradually speed up the device with the increase of diffusion time, when the crack point is from the surface of specimen inward moving from 0.007m to 0.014m and then move inward by the 520d time, finally from the 0.014m center inside position 0.02m mobile specimens with only 140d of the time, while the entire specimen tensile failure experiences about 1880d. Obviously, when the concrete in one-dimensional member is under sulfate attack, the failure rule is gradually from the surface to the internal crack in the initial stage of erosion. And then the destruction speed of concrete increases with the erosion time, and specimen damage speed is gradually accelerated.

5. Conclusion

According to the failure damage of concrete durability of concrete slab, one-dimensional walls, which result in sulfate erosion of chemical mechanical damage analysis model, is established for analysis of the whole damage process of the concrete durability of ion diffusion, chemical reaction, which are based on the mechanical analysis method. In the model, a non-steady state diffusion equation considers the sulfate ion consumption of chemical reaction in concrete and it’s solving method. In addition, the paper also present the chemical reaction of ettringite, which is caused by the concrete expansion method, to calculate the strain and stress of concrete cracking process. The method presented in this paper can provide some reference value for the life prediction and the durability design of concrete structures under sulfate attack.

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