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Modeling of diffusion-reaction behavior of sulfate ion in concrete under sulfate environments

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Abstract. This paper estimates theoretically the diffusion-reaction behaviour of sulfate ion in concrete caused by environmental sulfate attack. Based on Fick's second law and chemical reaction kinetics, a nonlinear and nonsteady diffusion-reaction equation of sulfate ion in concrete, in which the variable diffusion coefficient and the chemical reactions depleting sulfate ion concentration in concrete are considered, is proposed. The finite difference method is utilized to solve the diffusion-reaction equation of sulfate ion in concrete, and then it is used to simulate the diffusion-reaction process and the concentration distribution of sulfate ion in concrete. Afterwards, the experiments for measuring the sulfate ion concentration in concrete are carried out by using EDTA method to verify the proposal model, and results show that the proposed model is basically in agreement with the experimental results. Finally, Numerical example has been completed to investigate the diffusion-reaction behavior of sulfate ion in the concrete plate specimen immersed into sulfate solution.

Keywords: model; diffusion-reaction behavior; concrete; sulfate ion; model; EDTA.

1. Introduction

The long-term performance and durability of concrete structures are strongly influenced by the chemical corrosion due to ion aggression on concrete materials under permanently aqueous or chemically aggressive environments (Coussy *et al.* 2001, Marchand *et al.* 2002, Bertron *et al.* 2005, Yoon 2009). Recent advances in durability mechanics have exhibited the perspective for analyzing the influence of the chemical corrosion on the concrete durability deterioration, bridging the gap between the durability deterioration researches on the material and structural level and the service lifetime evaluation of concrete structures (Coussy *et al.* 2001, Kuhl *et al.* 2004). In the process of the concrete durability deterioration, the chemically induced deteriorations are generally associated with the diffusion-reaction behavior of the ions such as sulfate or chloride ions in concrete. In the present study, a model is developed to numerically investigate the diffusion-reaction behavior of sulfate attack, which is a major threat to the long-term durability of concrete exposed to the surroundings such as soils, groundwater, sea water, decaying organic matter and industrial effluent (Sun *et al.* 2001, Monteiro *et al.* 2003).

Sulfate attack is the result of chemical reactions between sulfate ions entering into concrete by the

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diffusion and some constituents of the hydrated cement pastes (Adam et al. 2004). Concrete deterioration under sulfate attack may occur in two different forms, cracking and spalling caused by concrete expansion or loss of strength and mass (Monteiro et al. 2003). In order to evaluate the concrete deterioration associated with the diffusion-reaction behavior under environmental sulfate attack, Marchand et al. developed the numerical model STADIUM to predict the diffusion of ions in unsaturated porous media, and the model considers chemical interaction of various ions with the cement hydrated products and the effects of chemically induced microstructural alterations on the diffusion properties of the material subjected to sulfate attack (Marchand et al. 2002, Samson et al. 2000, Samson et al. 1999); Gospodinov et al. proposed a mathematical model associated with sulfate ion diffusion into cement composites considering the influence of the microcapillary filling and subsequent liquid pressure due to chemical reaction products (Gospodinov et al. 1999, Gospodinov et al. 2005). Based on the experimental investigation on the expansion of PC mortar under sulfate attack, Goktepe et al. employed the statistical and neural network methodology to estimate numerically the nonlinear mapping between the sulfate expansion level of portland cement mortar and the related parameters such as C_3A content, C_3S/C_2S ratio of the cement, sulfate concentration and admixture substitution level (Goktepe et al. 2006); Sarkar et al. applied a numerical methodology to describe the diffusion of sulfate ions under a concentration gradient as well as under a chemical activity gradient, and further simulated the degradation of cementitious materials under external Sulfate attack (Sarkar et al. 2010). Clifton et al. utilized the finite difference method to solve the diffusion equation with the first order chemical reaction, as applied to the reactions between sulfates and portlandite, and the stresses of a concrete specimen subjected to sulfate attack are computed by modeling the specimen as an elastic matrix containing the expansion inclusions (Clifton et al. 1994, Ferraris et al. 1997); Tixier et al. proposed a mathematical model for simulating the responses of cement-based materials subjected to sulfate attack, and considered the effects of the products of the reactions between the aluminates and sulfates on the mechancial behaviors of the matrix (Tixier *et al.* 2003).

This paper investigates numerically the diffusion-reaction process of sulfate ions in concrete exposed to sulfate solutions. In Section 2, based on Fick's second law and chemical reaction kinetics, one dimensional diffusion reaction equation of sulfate ion in concrete is proposed. In Section 3, the diffusion-reaction equation is solved by the finite difference method with the C-N difference scheme. In Section 4, using EDTA method, the proposed model is verified by the experiments for measuring the sulfate ion concentration in concrete. In Section 5, numerical example is presented to explain the diffusion-reaction behavior of sulfate ion in concrete.

2. One-dimensional diffusion-reaction model

2.1 Mathematical equation

When the concrete specimen such as underground plate or wall is subjected to the sulfate attack under the ambient ion concentration c_0 , the ion transportation processes are described as 1-D nonsteady diffusion in Fig. 1. We assume that the concrete is an isotropic porous material under the saturated states, and the diffusion coefficients of sulfate ion are same in the section along the x direction, as well as the molar concentration of the sulfate ion diffusing from the sulfate solution Σ to the interior Π in the specimen. Therefore, based on Fick's second law, the diffusion-reaction



Fig. 1 1-D diffusion model of sulfate ion in concrete

equation is expressed as

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left\{ D_c(x,t) \frac{\partial c}{\partial x} \right\} + \frac{\partial c_d}{\partial t}$$
Init. Cond.: $c(x,0) = 0, x \in \Pi$
Boun. Cond.: $c(0,t) = c_0, c(L,t) = c_0$
(1)

in which c = c(x, t) refers to the sulfate ion concentration; x and t represent for the section position and time respectively; $c_d = c_d(x, t)$ is the dissipation concentration of sulfate ion caused by chemical reaction, c_0 is the boundary concentration of sulfate ions, L is the thickness of the concrete plate, Π is the cross section area of concrete member and D_c is the diffusion coefficient of sulfate ion in concrete.

2.2 Ion diffusion coefficient in concrete

The concrete pore solution is regarded as a multi-component electrolyte solution containing Na⁺, K⁺, OH⁻, Ca²⁺, SO₄²⁻, Cl⁻. Using the electrolyte solution theory such as Davis model and mode coupling theory treatment of the electrolyte friction in Eq. (1) (Samson *et al.* 1999, Chandra *et al.* 1999), the model of the diffusion coefficient of sulfate ion considering the effects of the ion concentration on the diffusivity is expressed as (Zuo *et al.* 2010)

$$D_{c} = \frac{\varphi RT}{\tau_{c} z^{2} F^{2}} \left\{ 1 - \left[\frac{1}{4\sqrt{I}(1 + aB\sqrt{I})^{2}} - \frac{0.1 - 4.17 \times 10^{-5}I}{\sqrt{1000}} \right] A c z^{4} \right\} \cdot \left[\Lambda^{0} - (Cz^{2} + Dz^{3}w\Lambda^{0})\sqrt{c} \right]$$
(2)

where z is the sulfate ion valency, z = 1, T is the environmental temperature, A, B, C and D are the parameters related to the environmental temperature, w is a coefficient related to the ionic activity, $w \approx 0.586$, c is the concentration of sulfate ion, the other parameters are listed in Table 1. I is the

Value Unit Quantity Value Unit Quantity 2 8.31451 J/Kmol Universal gas constant Ionic valency R Z2.58×10⁻¹⁰ F 9.64853×10^4 C/mol Faraday constant m Ionic radius a 1.38066×10⁻²³ Λ_m^{\cdot} Sm²/mol Bolzmann constant 8.0×10^{-3} Sm²/mol Conductivity k 1.60218×10⁻¹⁹ CElementary charge 8.9×10⁻⁴ Kg/ms Viscosity е η_0 8.85419×10⁻¹² C^2/Jm Vacuum electric permittivity 78.54 Relative permittivity \mathcal{E}_r εn

Table 1 Natural constants related to sulfate ion and solvent at T=298K (Atkins 1998)

strength of ion in pore solution

$$I = \frac{1}{2} \sum_{i=1}^{N} z_i^2 c_i$$
(3)

N is the number of ion in the concrete pore solution, z_i is the valency of the ion *i*, c_i is the concentration of the ion *i*. The parameters τ_c and φ are respectively the tortuosity and porosity of concrete.

2.3 Parameters of concrete microstructures

2.3.1 Tortuosity

Based on the compositions and geometric features of concrete materials, a geometrical approach is used to obtain a two-dimensional geometrical model for the tortuosity of transport paths in concrete, and it has been expressed as (Zuo 2011)

$$\tau_{c} = \eta_{sa} \eta_{st} (1 + 0.35 \sqrt{f_{sa}}) (1 + 0.35 \sqrt{f_{st}}) \tau_{cp}$$
(4)

in which τ_c is the initial tortuosity of transport paths in concrete, η_{st} and η_{sa} are respectively the shape factors of the stone and sand as the equivalent spherical particles, f_{st} and f_{sa} are respectively the volume fractions of the stone and sand in concrete, which can be calculated by the mix proportions of concrete. τ_{cp} is the tortuosity of transport paths in hardened cement pastes, of which the water-cement ratio is the same as that of concrete. Generally, the cement hydration degree is over 0.8, thus the effects of unhydrated cement particles on the tortuosity of transport paths in hardened cement pastes may be ignored, so the tortuosity in hardened cement pastes may be expressed by (Zuo 2011)

$$\tau_{cp} = \omega_{wc} \eta_r h_{\alpha} \left[\frac{1}{1 - \sqrt{1 - \varphi}} \sqrt{\left(1 - \sqrt{1 - \varphi}\right)^2 + \frac{1}{4}} \right]$$
(5)

 ω_{wc} is the adjustment coefficient, η_r is the shape factor of cement particles, φ is the porosity of hardened cement pastes, which is the porosity of concrete and can be calculated by Eq. (7), h_{α} denotes the cement hydration degree, and may be approximately determined by (Masi *et al.* 1997)

$$h_{\alpha} = 1 - 0.5[(1 + 1.67\tau)^{-0.6} + (1 + 0.29\tau)^{-0.48}]$$
(6)

 τ is the cement hydrated time, which is sum of the curing time and the diffusion time.

2.3.2 Porosity

The porosity is an important parameter reflecting on concrete microstructures, and it may be determined by (Clifton *et al.* 1994)

$$\varphi = \begin{cases} f_{v_c} \frac{W}{C} - 0.39h_{\alpha} \\ \frac{W}{C} + 0.32 \end{cases}, \quad \frac{W}{C} > 0.39h_{\alpha} \\ 0 & , \quad \frac{W}{C} \le 0.39h_{\alpha} \end{cases}$$
(7)

where W/C is the water-cement ratio; f_{Vc} is the volumetric fraction of the cement in concrete, which may be determined by (Clifton *et al.* 1994)

$$f_{Vc} = \left[1 + \frac{\rho_c}{\rho_s} \left(\frac{S}{C}\right) + \frac{\rho_c}{\rho_w} \left(\frac{W}{C}\right) + \frac{\rho_c}{\rho_a} \left(\frac{A}{C}\right)\right]^{-1}$$
(8)

where ρ_c is the stacked density of the cement, ρ_s , ρ_w and ρ_a are the densities of the aggregate, water and air, respectively. S/C and A/C represent the mass ratios of aggregate to cement and entrained air to cement respectively.

2.4 Chemical reaction associated with concrete deterioration

2.4.1 Reaction equations

Based on the mechanism of sulfate attack on concrete (Ferraris *et al.* 1997, Tam *et al.* 2009), the concrete durability deterioration is caused by the potential volume expansions associated with the chemical reactions of sulfate ions with the hydrated calcium aluminates, and the volumetric expansion is evaluated by the formation of ettringite $(C_6A\overline{S}_3H_{32})$ from the combination of the hydration products (C_3AH_6) of the calcium aluminates such as C_3A with the second gypsum $(C\overline{S}H_2)$ produced by the reaction of sulfate ion (SO_4^{2-}) with calcium ion (Ca^{2+}) , and the chemical reaction process may be expressed by (Taylor *et al.* 2001, Tam *et al.* 2009)

$$C_3A + H_2O \rightarrow C_3AH_6 \tag{9}$$

$$C_3AH_6 = Ca_3[Al(OH)_6]_2 \rightarrow 3Ca^{2+} + 2Al(OH)_4^- + 4OH^-$$
 (10)

$$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow C\overline{S}H_2$$
(11)

$$3C\overline{S}H_{2} + C_{3}AH_{6} + 26H_{2}O \rightarrow 6Ca^{2+} + 2Al(OH)_{4}^{-} + 3SO_{4}^{2-} + 4OH^{-} + 26H_{2}O$$

$$\rightarrow Ca_{6}[Al(OH)_{6}]_{2}(SO_{4})_{3} \cdot 26H_{2}O = C_{6}A\overline{S}_{3}H_{32}$$
(12)

2.4.2 Chemical reaction kinetics in concrete

Depending on chemical reaction kinetic approach (Laidler 1987, Zang 1995), the second item in the right of Eq. (1), which represents for chemical reaction rate of dissipating sulfate ions in Eq. (11), may be obtained

$$\frac{\partial c_d}{\partial t} = -k_v \cdot c_{\operatorname{Ca}^{2+}} \cdot c \tag{13}$$

where k_v is the chemical reaction rate constant; c_d is the sulfate ion concentration dissipated by chemical reaction; c is the sulfate ion concentration; c_{ca}^{2+} is the calcium ion concentration in pore solution, which changes with the environmental temperature, when the temperatures are 0°C and 100°C, the concentrations of the calcium ions are respectively 25 mol/m³ and 10 mol/m³, and the calcium ion concentrations at the other temperatures can be obtained by the linear interpolation method (Perry 1997).

2.4.3 Dissipation of sulfate ion in concrete

As known in the above reaction Eq. (11), sulfate ions diffusing into concrete are dissipated by

chemical reaction with calcium hydroxide to form gypsum, so the dissipations of sulfate ions in concrete may be used to calculate the amounts of the ettringite formation. According to Eq. (13), during the total diffusion time T, the accumulative dissipation of sulfate ion in concrete, C_d , may be expressed as

$$C_d = \int_0^T (-k_v \cdot c_{ca^{2+}} \cdot c) dt \tag{14}$$

in which C_d is the accumulative dissipation of sulfate ions in concrete, T is the total diffusion time.

3. Methods of numerical solutions

3.1 Mesh

The concrete plate specimen with the thickness L is immerged into the sulfate solution with the concentration c_0 , and the diffusion processes of sulfate ion in the specimen are obtained by solving the nonlinear and nonsteady diffusion-reaction equation, formulated by Eq. (1). An implicit difference scheme is applied for solving numerically the Eq. (1) to obtain the concentration distribution of sulfate ion in the specimen.

Considering symmetrical diffusion of sulfate ion from the two surfaces to the interior of the specimen, the diffusion Eq. (1) is solved along a half of the specimen thickness L/2. The discretization scheme is that a half of the specimen thickness L/2 is divided into N parts with the proportional spacing and the increment h. The discretization step of the time Δt is selected to describe the sulfate ion aggressing history in the process of sulfate attack. Thus, the parallel lines are defined as: $x_i = ih$ (i = 0, 1, 2, ..., i, ..., M, M is the number of grid in the x direction), and $t_k = k\Delta t$ (k = 0, 1, ..., k, ..., K, K is the number of diffusion time). The section area $\Pi (L/2 \times 1)$ is divided into square grids ($M \times 1$), and the grid nodes are (x_i, t_k). Thus, the concentration of sulfate ion at the state (x_i, t_k) may be expressed by c_i^k .

3.2 C-N difference scheme

By using the finite difference method with Crank-Nicolson scheme (C-N scheme) (Li *et al.* 2009), the partial differentials $\partial c/\partial x$ and $\partial^2 c/\partial x^2$ in the intervals (t_k, t_{k+1}) may be expressed by the difference quotients at the time t_k , namely, the partial differentials in Eq. (1) may be replaced by the following difference quotients

$$\frac{\partial c_i^k}{\partial t} = \frac{c_i^{k+1} - c_i^k}{\Delta t} \tag{15}$$

$$\frac{\partial \left(D_{ci}^{k} \frac{\partial c_{i}^{k}}{\partial x}\right)}{\partial x} = \frac{1}{2h^{2}} \left[D_{ci+1/2}^{k} (c_{i+1}^{k} - c_{i}^{k}) - D_{ci-1/2}^{k} (c_{i}^{k} - c_{i-1}^{k}) + D_{ci+1/2}^{k+1} (c_{i+1}^{k+1} - c_{i}^{k+1}) - D_{ci-1/2}^{k+1} (c_{i}^{k+1} - c_{i-1}^{k+1})\right] (16)$$

$$\frac{\partial c_{d}}{\partial t} = k_{v} \cdot c_{Ca^{2+}} \cdot c = \frac{1}{2} k_{v} \cdot c_{Ca^{2+}} \cdot (c_{i}^{k} + c_{i}^{k+1})$$

$$(17)$$

In Eq. (16), the diffusion coefficient terms D_c may be replaced by

$$\begin{cases} D_{ci-1/2}^{k} = \frac{1}{2} (D_{ci-1}^{k} + D_{ci}^{k}) \\ D_{ci+1/2}^{k} = \frac{1}{2} (D_{ci}^{k} + D_{ci+1}^{k}) \\ D_{ci-1/2}^{k+1} = \frac{1}{2} (D_{ci-1}^{k+1} + D_{ci}^{k+1}) \\ D_{ci+1/2}^{k+1} = \frac{1}{2} (D_{ci}^{k+1} + D_{ci+1}^{k+1}) \end{cases}$$
(18)

Substituting Eqs. (15)~(18) into Eq. (1), and it is assumed that $J = k_v \cdot c_{Ca^+}$ and $r = \Delta t/4h^2$, the finite difference with the C-N scheme of Eq. (1) at the intervals (t_k, t_{k+1}) may be obtained that

$$-\frac{r}{4}(D_{ci-1}^{k+1}+D_{ci}^{k+1})c_{i-1}^{k+1} + \left[1 - \frac{1}{2}J \cdot \Delta t + \frac{r}{4}(D_{ci-1}^{k+1}+2D_{ci}^{k+1}+D_{ci+1}^{k+1})\right]c_{i}^{k+1} - \frac{r}{4}(D_{ci}^{k+1}+D_{ci+1}^{k+1})c_{i+1}^{k+1} = \frac{r}{4}(D_{ci}^{k}+D_{ci+1}^{k})c_{i+1}^{k} + \left[1 + \frac{1}{2}J \cdot \Delta t - \frac{r}{4}(D_{ci-1}^{k}+2D_{ci}^{k}+D_{ci+1}^{k})\right]c_{i}^{k} + \frac{r}{4}(D_{ci-1}^{k}+D_{ci}^{k})c_{i-1}^{k} \quad (i=1,2,...,k,...,K)$$
(19)

3.3 Iterative solution of equation

The iterative scheme of Eq. (1) at the time interval (t_k, t_{k+1}) may be obtained from Eq. (19)

$$[A]\{c_i^{k+1}\} = [B]\{c_i^k\} + \{e\}$$
(20)

where $\{c_i^{k+1}\}$ refers to $M \times 1$ order vector, which represents for the concentrations of sulfate ion at every point x_i (*i*=1, 2, ..., *M*) at the time t_{k+1} . The other matrixes and vectors in Eq. (20) are expressed by

$$[A] = \begin{bmatrix} a_{1} & b_{1} & & & \\ b_{1} & a_{2} & & [0] \\ & & a_{n} & b_{n} & \\ & & b_{n} & a_{n+1} \\ & & & b_{n} & a_{n+1} \\ & & & 2b_{M-1} & a_{M} \end{bmatrix}$$
(21)
$$[B] = \begin{bmatrix} h_{1} & f_{1} & & & \\ f_{1} & h_{2} & & [0] \\ & & h_{n} & f_{n} \\ & & f_{n} & h_{n+1} \\ & & & 2f_{M-1} & h_{M} \end{bmatrix}$$
(22)

$$a(n) = 1 - \frac{\Delta t}{2} \cdot J + \frac{r}{4} [D_c(n+2,k+1) + 2D_c(n+1,k+1) + D_c(n,k+1)] \qquad (n = 1, 2, \dots, M)$$
(23)

$$b(n) = -\frac{r}{4} [D_c(n+1,k+1) + D_c(n+2,k+1)] \quad (n=1,2,\dots,M-1)$$
(24)

$$h(n) = 1 + \frac{\Delta t}{2} \cdot J - \frac{r}{4} [D_c(n+2,k) + 2D_c(n+1,k) + D_c(n,k)] \quad (n = 1, 2, ..., M)$$
(25)

$$f(n) = \frac{r}{4} [D_c(n+1,k) + D_c(n+2,k)] \quad (n = 1, 2, \dots, M-1)$$
(26)

$$\{e\} = \left\{\frac{r}{4}c_0[D(1,k+1) + D(2,k+1) + D(1,k) + D(2,k)], 0, 0, 0, 0, 0, \dots, 0\right\}^T$$
(27)

Using the combination of the chase method and the iterative method to solve Eq. (20), the sulfate ion concentrations c_i^k at the points x_i and the time t_k can be obtained, and then they are substituted into Eq. (14) to calculate the accumulative dissipations of sulfate ions in concrete. Therefore, the above models can be utilized to describe the diffusion-reaction behaviors of sulfate ion in concrete under the environmental sulfate attack. Based on the above proposed models, and using MATLAB language, the computing programme SDRC.M have been completed to investigate numerically the diffusion-reaction behaviors of sulfate attack.

4. Experiments on sulfate ion diffusivity in concrete

4.1 Materials and specimens

In this experiment, the cement is commercial Portland II 42.5 type produced by China Jiangnan Corporation, the chemical compositions of which are given in Table 2. The fine aggregate is a kind of river sand with the maximum particle size being 2 mm, the apparent density 2.64 g/cm³ and the modulus of fineness 2.5. The coarse aggregate is the crushed wacke stone with the diameter 5-10 mm, the apparent density 2.54 g/cm³ and the cumulate density 1.6 g/cm³. The mix weight proportions of concrete with the strength of C40 are presented in Table 3. The initial concentrations of the main ions in the concrete pore solution are respectively 107.10, 116.50, 2.33, 1.88 and 224.47 mol/m³ corresponding to Na⁺, K⁺, Ca²⁺, SO₄²⁻ and OH⁻. The four concrete specimens with 100 × 100 × 300 mm³ prism are cast according to the mixture proportions of the concrete in Table 3, and they are

Table 2 Main chemical compositions of raw materials

420

180

C40

		1						
Main chemical compositions (w/%)								
SiO ₂	Al_2O_3	CaO	MgO	SO_3	Fe ₂ O ₃	Na ₂ O	K ₂ O	LOI
20.60	5.03	65.10	0.55	2.20	4.40	0.20	0.40	1.30
Table 3 Prop	ortions of con	crete mixes	design					
Concrete strength	Cement kg/m ³	Wa kg/i	ter m ³	Sand kg/m ³	Aggregate kg/m ³	Agent %	Water-c	ement ratio w/c

Notes: Water-water supply; Sand-River sand, Apparent density 2.64 g/cm³; Aggregate-wacke, Diameter 5~10 mm, Apparent density 2.5 g/cm³, Cumulate density 1.6 g/cm³.

1116

0.9

0.43

684

86

cured in 20°C water. After being cured for 28 days, two symmetrical planes of the specimens along the long direction are chosen as the erosion surfaces, the other four planes are sealed with the epoxide resin to prevent the external media entering into the specimen from these planes. After filled with water to be saturated concrete, two of the four sealed specimens are immersed into 2% water solution of sodium sulfate, and the others are kept in 5% sodium sulfate solution. Therefore, four sealed specimens are subjected to sulfate attack in two symmetrical planes, and the diffusionreaction behaviors may be described by the above proposed model.

4.2 Experimental methods and results

4.2.1 Sample selection

The four specimens are immersed into the sodium sulfate solutions for first 80 days, afterwards, in every interval 30 days, the concrete power is obtained with the electric drill in the scope of 10-13 mm depth from the erosion surfaces for measuring the change of sulfate ion concentrations in the specimens. The power is selected from at least five dilled points in the specimen every time. After five-point concrete power is evenly mixed, 5 g concrete powder is screened out for measurement from the drilled powder using the micro-mesh with 100 μ m aperture.

4.2.2 Measurements of sulphate ion concentration

The screened 5 g concrete power is placed into the beaker with a capacity of 100 ml, and then the beaker is filled with 50 ml de-ionized water. After the concrete power is fully "dissolved", the clear solution in the upper supernatant layer of the beaker is picked up for measuring indirectly the sulfate ion concentration in the mixed solution using EDTA complexometric titration, which depends on ASTM D511 standards (ASTM 2003). The detailed procedure is as follows.

The first step, pick up the clear solution with $V_{L0} = 5$ ml in the upper supernatant layer of the beaker accurately, and drop into 250 ml cone cup, then drop 1 ml chlorhydric acid into the cone cup to acidize the clear solution. Afterwards, 10-30 ml barium chloride solution is gradually dropped into the acidized solution by using the burette. In the process of titration, shake the cone cup ceaselessly to reduce the precipitation and adsorption of the solution in the inwall of the cup, and then record the volume V_1 (ml) of the dissipated barium chloride solution.

The second step, the inwall of the cone cup is flushed with 1-2 ml de-ionized water, after that, the mixed solution in the cone cup is heated and boiled for 2 minutes, and then cooled to the room temperature. Next, 10 ml Mg-EDTA solutions, 10 ml absolute ethyl alcohol, 2 ml hydroxylamine hydrochloride, 3 ml triethanolamine, 10 ml buffer solution, 3-5 drop *T*-chrome black indicators are dropped into the cooled mixed solutions. When dropping each above reagent, the cup should be shaked evenly. In the process of using the standard EDTA solution to drop gradually into the above mixed solution, once the color of the mixed solution changes from the violet red to the ethereal blue, the volume V_2 (ml) of the standard EDTA solution dissipated is recorded.

The third step, the clear solution with $V_{L0} = 5$ ml is accurately picked up to drop into 250 ml cone cup once again, and then fill 20 ml de-ionized water into the cup, afterwards, 1 ml chlorhydric acid is dropped into the cone cup to acidize the solution. Next, 2 ml hydroxylamine hydrochloride, 3 ml triethanolamine, 10 ml buffer solution, and 3-5 drops *T*-chrome black indicators are slowly dropped into the mixed solution. Similarly, in the process of using the standard EDTA solution to drop gradually into the mixed solution, once the color of the mixed solution changes from the violet red to the ethereal blue, record the volume V_0 (ml) of the standard EDTA solution dissipated by calcium and magnesium.

The fourth step, based on the above measuring results, the concentration of sulfate ions c may be calculated by the following formula

$$c = \frac{c_1 V_1 - c_2 (V_2 - V_0)}{V_{I0}} \tag{29}$$

in which, c is the concentration of sulfate ions in concrete, mol/l; c_1 is the concentration of the standard barium chloride solution, $c_1 = 0.05 \text{ mol/l}$; c_2 is the concentration of the standard EDTA solution, $c_2 = 0.02 \text{ mol/l}$; V_{L0} is the volume of the clear solution after dissolving the concrete power, $V_{L0} = 5 \text{ ml}$; V_0 is the volume of the standard EDTA solution dissipated by calcium and magnesium in 5 ml clear solution; V_1 is the volume of the dissipated barium chloride solution, ml; V_2 is the volume of EDTA standard solution dissipated, ml.

4.2.3 Experimental results

Based on the above experimental methods, the concentrations of sulfate ions, which are located in the scope of 10-13 mm depth from the erosion surfaces in the specimens (100 mm \times 100 mm \times 300 mm) immersed in the 2% and 5% sodium sulfate solution respectively, are measured during the date 2008-8 to 2009-9, as shown in Table 4.

4.3 Comparison between the model and experimental results

Use Eq. (1) and its iterative Eq. (20) to calculate the sulfate ion concentrations located in the depths 10 mm and 13 mm from the erosion surfaces in the specimens, and the related parameters

	Concentration of sulfate ion (mol/m ³)								
Diffusion time (days)	2%	Na ₂ SO ₄ soluti	on	5% Na ₂ SO ₄ solution					
(uujb)	Experiment	Model	Error	Experiment	Model	Error			
80	4.27	4.82	12.88	8.29	10.74	29.54			
110	8.17	6.96	14.81	18.45	15.80	14.39			
140	9.36	7.97	14.85	22.70	19.31	14.93			
170	10.57	9.17	13.29	21.61	21.61	0.02			
200	11.45	9.81	14.37	26.37	23.61	10.49			
230	10.53	10.34	1.85	23.22	25.19	8.46			
260	12.08	10.82	10.43	24.99	26.42	5.70			
290	11.80	11.18	5.30	27.3	27.47	0.60			
320	10.40	11.53	10.87	28.10	28.29	0.66			
350	10.92	11.81	8.15	26.23	29.23	11.44			
380	12.01	12.04	0.25	29.22	29.67	1.54			
410	12.52	12.25	2.16	28.89	30.16	4.40			
440	11.80	12.40	5.04	27.72	30.65	10.55			
470	12.86	12.49	2.92	28.92	30.93	6.95			

Table 4 Experimental and model results of sulfate ion concentration in concrete



Fig. 2 Comparison between model and test results of sulfate ion concentrations

are shown in Tables 2 and 3. Fig. 2 presents the comparison of sulfate ion concentrations between the model calculation and experimental results when the specimens are respectively immersed into 2% and 5% sodium sulfate solutions. In order to evaluate the model Eq. (20) for the calculation of sulfate ion concentration, the error, $[(c_{exp}-c_{mod})/c_{exp}] \times 100\%$, expressing the difference degree between the model and experimental results for the sulfate ion concentrations, are calculated as listed in Table 4, in which the model value c_{mod} is the sulfate ion concentration at the depth 12.5 mm of the specimen, c_{exp} and c_{mod} denote the experimental and model value of the sulfate ion concentration respectively. It may be seen from Table 4 that, expect for the error 29.54% at 80 days in 5% Na₂SO₄ solution, the other errors between the experimental and model values of sulfate ion concentrations are less than 15% at the different diffusion time, and the errors at the first 170 days are greater than one at the later diffusion time. This is because, at the first diffusion time, the diffusion and reaction don't attain the equilibrium, the concentrations of sulfate ion in concrete are relatively low; after 170 days, the diffusion and reaction are in dynamical equilibrium state, and the sulfate ion concentrations maintain basically stable, so the errors at the later diffusion time are relatively small. As a result, it may be known from Fig. 2 and Table 4 that the model results are basically in agreement with the experimental results.

5. Numerical examples

Numerical results are given for the specimen that is kept in 5% water solution of sodium sulfate. The cement in the specimen is commercial Portland II 42.5 type, the mineral compositions of which are presented in Table 2. The mix weight proportions of the concrete materials are shown in Table 3. One-dimension diffusion-reaction behaviors of sulfate ions in the specimen with thickness 100 mm are considered based on the above proposed model and numerical methods, and the calculation parameters are listed in Table 5.

Fig. 3 shows the concentration distribution of sulfate ion in the section of the specimen with the diffusion time, considering the sulfate ion dissipation caused by chemical reaction in Eq. (13). It is seen from the figure that, under the solution concentration 5% immersed, the concentration of the sulfate ions in the specimen has an increase with the diffusion time, but the increasing rate of the

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Specimen thickness	L	100 mm	Aggregate density	$ ho_{s}$	2.5 g/cm^{3}
$CA(C_3A, C_4AH_{13}, C_4A\overline{S}H_{12})$ content		465.7 mol/m ³	Cement stack density	$ ho_c$	1.4 g/cm^{3}
Na2SO4 solution concentration	c_0	5% or 352 mol/ m^3	Water density	$ ho_{\scriptscriptstyle W}$	1.0 g/cm^{3}
Adjustment coefficient	ω_{wc}	1.28	Air density	$ ho_a$	0.0013 g/cm^3
Reaction rate constant	k_v	$1.22 \times 10^{-9} s^{-1}$	Aggrecement ratio	<i>S/C</i>	2.66
Environmental temperature	Т	25°C	Water-cement ratio	W/C	0.43
Cement shape factor	η_r	1.77	Air-cement A/C	A/C	≈0.0
Sand shape factor	$\eta_{\scriptscriptstyle sa}$	1.08	Thickness interval	Δx	0.5 mm
Stone shape factor	η_{st}	1.38	Time interval	ΔT	1 days

Table 5 Related calculation parameters in model



Fig. 3 Concentration distribution of sulfate ion in the specimen

ion concentration descends gradually from the surface to the interior of the specimen. It can be also seen from Fig. 3 that the sulfate ion concentrations increase quickly with the diffusion time at the first 1800 days. After 1800 days, the concentrations of sulfate ion basically tend stable. This is because, after the diffusion time attains 1800 days, the chemical reaction rate is equal to the diffusion rate of sulfate ion in concrete, and the diffusion reaction is basically in dynamic equilibrium states, as shown in Fig. 3(a). At the section midpoint of the specimen x = 0.05 m, the concentration of sulfate ions is close to zero before 500 days, while after 500 days, the ion concentration gradually increases, at $t_M = 1800-4591$ days, the ion concentration $c(0.05 \text{ m}, t_M)$ is 2.70 mol/m³.

According to chemical reaction Eqs. (11) and (12), the parts of sulfate ion diffusing into concrete react with calcium ion to produce gypsum, which then reacts with the hydrated product of the calcium aluminates C_3AH_6 to result in the ettringite formation, so the quantities of sulfate ion dissipated by chemical reaction may determine the amounts of the gypsum and ettringite formation and the calcium aluminated dissipation. Fig. 4 illustrates the quantities of dissipated sulfate ions changing with the section position and the diffusion time. It can be seen from the figure that the dissipated sulfate ion quantities in the specimen increase and decrease gradually with the diffusion time from the surface to the interior of the specimen. In the same interval $\Delta t = 300$ days, the dissipated ion quantities are approximately equal to 50 mol/m³ on the surface of the specimen, but the dissipated ion quantities decrease gradually on the interior. This is because, the concentrations of



Fig. 4 Quantity changes of dissipated sulfate ion caused by chemical reaction

the sulfate ions on the specimen surface keep a constant 75.5 mol/m³. In addition, it is obtained from Fig. 4 that the dissipated sulfate ion quantity at the midpoint of specimen section x = 0.05 m is about 21.0 mol/m³ when the concrete on the point yields at 1660 days (Zuo 2011). Therefore, after 1660 days' diffusion, although the concrete in specimen has yielded, the diffusions and reactions of the sulfate ion in the concrete are always on progress, and in fact, the dissipated sulfate ion quantities due to chemical reaction continue to increase until the calcium aluminates are fully dissipated.

6. Conclusions

(1) Based on Fick's second law and chemical reaction kinetics, a model of the diffusion-reaction behaviour of sulfate ions in concrete is proposed, and the finite difference method is applied for solving the diffusion-reaction equation, and the numerical solution is used to simulate the process of diffusion and reaction and the concentration distribution of sulfate ion in concrete.

(2) The experiments on the sulfate ion diffusivity in concrete are carried out by using EDTA method to verify the proposal models, and the modelling results are basically agreement with the experimental results. On the basis, Numerical simulation has been completed to investigate the diffusion-reaction behavior of sulfate ion in the concrete plate specimen immersed into sulfate solution, and the results show that the proposed model can predict the responses of concrete with the diffusion time, such as sulfate concentration distribution, sulfate ion dissipation.

(3) The proposed model may be utilized to estimate numerically the diffusion-reaction behaviors of sulfate ion in concrete, and can avoid the difficulties in the measurement of sulfate ion concentration in concrete. Meanwhile, the proposed model is the basis for obtaining the expansive strain and stress of concrete due to the formation and growth of ettringite. Calculating quantitatively the expansion strain and stress of concrete and analyzing the durability deterioration of concrete materials and structures caused by sulfate attack will be the further research work.

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