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Numerical Simulation of Sulfate Ion Migration in Cement Concrete under Corrosion Fatigue

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Abstract: A mathematical model is presented to simulate sulfate ion migration in cement concrete that was subjected to the coupled action from sodium sulfate solution and alternating stresses. The crack factor was derived based on the model of the concrete's response to external sulfate solutions through revised methods, such as diffusion path division and crack homogenization. A formula for effective diffusion (coefficient D_t), which is used to characterize the effect of alternating stresses on the sulfate ion diffusion, was proposed. The research uses Fick's second law for the diffusion of sulfate ions. A solution to the diffusion equation was proposed to determine the sulfate concentration under corrosion fatigue as a function of time and space. The sulfate concentration responses were obtained and compared with a variety of available data. Model simulations indicate a reasonable agreement with experimental data available in the literature.

***Key words**: Alternating stresses; Corrosion; Cement concrete; Migration; Sulfate ion.*

Introduction

Sulfate attack is an important concern in concrete durability and performance and occurs all over the world. It happens in concrete exposed to marine environments, industrial sulfate bearing-solutions, seawater, and saline soils, such as in Western China and other arid areas in the world. However, as a widely used construction material, concrete is also subject to fatigue loading in many cases and requires high fatigue resistance when used in highway pavements, bridge slabs, railway sleepers, airport runways, etc. Meanwhile, corrosion is an external factor that causes material deterioration. Corrosion fatigue of concrete is defined in this study as the loss of concrete effectiveness due to cracks caused by the coupling action of corrosion solution and alternating loading. There have been many examples where concrete structures were damaged by corrosion fatigue [1].

There is ample research on external sulfate attack models. The finite-difference method is used to solve the diffusion equation with a first-order chemical reaction, as applied to the reaction between sulfates and portlandite. The random walker's method has also been applied to obtain the concentration profiles [2]. A solution to the diffusion equation with a term for first-order chemical reaction has been proposed to determine the sulfate concentration as a function of time and space [3, 4].

Tixier et al. have established a chemo-mechanical mathematical model to simulate the response of concrete exposed to external sulfate solutions [5, 6]. The effect of fatigue loading on sulfate solution diffusion is not considered in these studies. The deterioration of concrete performance is caused by the development and expansion of small cracks due to the coupled action of fatigue loading and corrosion.

On the other hand, the crack development process can be viewed as the gradual accumulation of damages in Portland cement concrete. The accumulation of damages causes gradual performance degradation. Therefore, the existence of a corrosion agent will accelerate fatigue cracking, and fatigue loading will promote further development of concrete corrosion damage. In this study, aspects of concrete physics and mechanics are applied to derive a one-dimensional model for predicting the sulfate ion migration in Portland cement concrete subjected to corrosion fatigue, and the model predictions are compared to test data.

Analytical Models

The Introduction of Alternating Stress Characterization Parameter (D_t)

1. Diffusion pathway

Sulfate solution gradually spreads in concrete in accordance with the non-steady-state free diffusion theory and reacts with active ingredients. New kinds of volume expansion substances were generated, and they caused inflation pressure that gradually destroyed the concrete. When the concrete is subjected to coupled action from sodium sulfate solution and alternating stresses, the alternating stresses exacerbate the generation of micro-cracks. The concrete is then divided into two parts: concrete matrix and cracks (Fig. 1). Therefore, the diffusion pathway of sulfate ion in the concrete can also be divided into two kinds: diffusion in the concrete matrix and diffusion in the micro-cracks (Fig. 2).

The total diffusion (D_t) is determined by the diffusion coefficient in the concrete matrix (D_m) and the diffusion coefficient in the cracks (D_c). The concrete with the micro-cracks is stressed by alternating stresses. When the concrete is in the load process, the micro-cracks are opened, and partial vacuum is generated in the cracks' tips so the solution penetrates into the cracks rapidly by the

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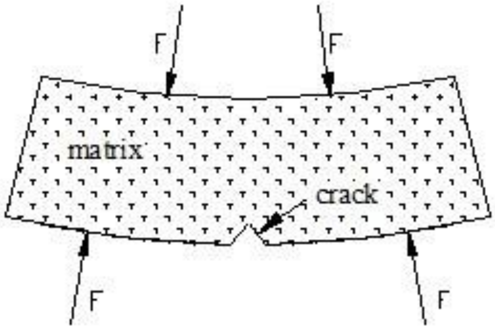

Fig. 1. Concrete Matrix and Crack.

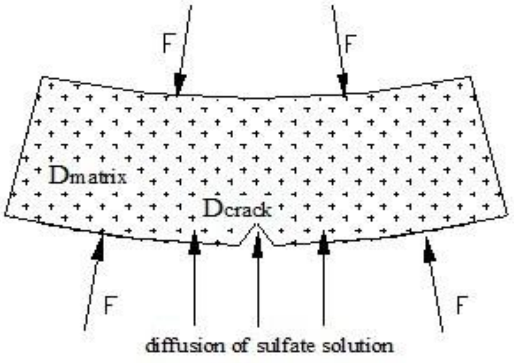

Fig. 2. The Diffusion Pathway.

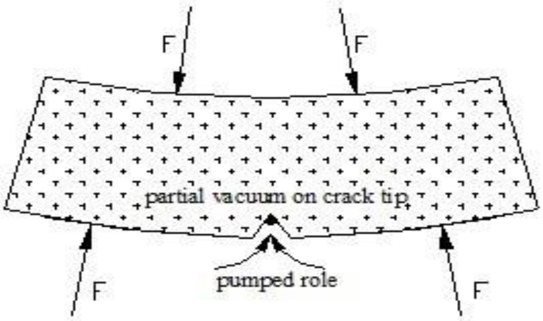

Fig. 3. Turbulent Diffusion of Crack with Load.

pump action (Fig. 3). When the concrete is in the off-load process, the micro-cracks automatically close by tensile stress, and the solution is ejected (Fig. 4). With the reciprocating action of the alternating stresses, the micro-crack opens and closes automatically. The diffusion rate of sulfate ions is increased by turbulent diffusion, which forms near the micro-cracks. In other words, D_c was increased greatly by the alternating stresses.

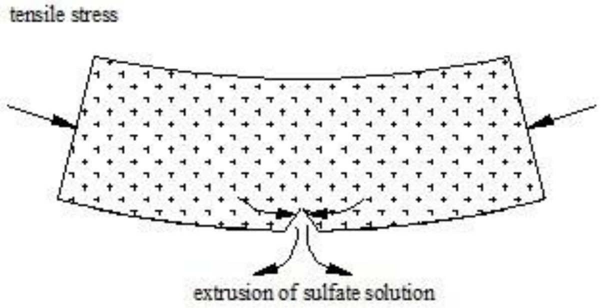

Fig. 4. Turbulent Diffusion of Crack with Unload.

2. The diffusion coefficient based on the crack factor

The concrete is assumed to be a homogeneous solid without any micro-cracks initially. So, in the initial stage, the sulfate solution corrosion is uniform. All the cracks are filled with water, so the diffusion of sulfate solution in the cracks is equivalent to the diffusion in water. Therefore, the diffusion in the concrete is the sum of the diffusion in the homogeneous materials and the diffusion in water.

The central part of the bottom of the concrete slab was subjected to the maximum flexural stress, so it was the weakest area. It was also the most vulnerable to damage by the coupled action from sodium sulfate solution and alternating stresses.

The distribution of the crack’s unit element in the middle part of the concrete’s bottom layer was taken, and the direction of the cracks was the same to the direction of the sulfate solution diffusion. Vertical directional diffusion on the bottom layer of the concrete is the only factor considered.

The volume of the concrete element ($\Delta V_{concrete}$) is represented in Eq. (1):

$$\Delta V_{concrete}=H_c\times H_m \tag{1}$$

The area of the crack (S_c) is represented in Eq.(2).

$$S_c=\frac{\pi H_c^{\ 2}}{4} \tag{2}$$

where:
H_c = the width (diameter) of the cylindrical crack;
H_m = the spacing between the concrete matrixes.

The diffusion coefficient of sulfate solution in the concrete matrix, the cracks filled with water, and the whole concrete material was defined as D_m, D_c and D_t, respectively. D_m ($D_m(x,t)$) is the function of the location and time, and its magnitude is $10^{-12}\mathrm{m}^2/\mathrm{s}$, which can be obtained by the sulfate attack model. D_c was the function of the sulfate ion concentration and was affected by the external fatigue loading that destroyed the original movement of sulfate ions and caused the chaotic motion that can greatly improve the diffusion coefficient of sulfate solution in water. The diffusion in the crack is changed into a disorder state diffusion by alternating stresses. So, D_c is the value of $1.73\times10^{-10}\mathrm{m}^2/\mathrm{s}$ under 25℃ and is much larger than the diffusion coefficient in concrete matrix.

In the diffusion process, the unit element diffusion flux should be equal to the sum of the flux in concrete matrix and the flux in the crack divided by the total area, as seen in Eq. (3):

$$J_t = \frac{J_c S_c}{S_c + S_m} \tag{3}$$

where:
J_t = the total diffusion flux (mol/（m^2.s）);
J_c = the diffusion flux in cracks (mol/（m^2.s）);
J_m = the diffusion flux in the matrix (mol/（m^2.s）);
S_c= the area of crack and matrix material that is vertical to J_c (m^2);
S_m = the area of crack and matrix material that is vertical to J_m (m^2).

The diffusion flux can be represented as the diffusion chemical potential multiplied by the diffusion coefficient, as seen in Eq. (4):

$$J_t=-D_t\times\mu \text{；} J_c=-D_c\times\mu \text{；} J_m=-D_m\times\mu \tag{4}$$

where:
μ = the diffusion chemical potential (mol/s), which is motivation for the diffusion of sulfate solution into the concrete.

With Eqs. (3) and (4), the coefficients D_t, D_c and D_m can be determined through Eqs. (5) and (6):

$$D_t = \frac{D_c S_c + D_m S_m}{S_c + S_m} \tag{5}$$

$$\frac{D_t}{D_m} = \frac{D_c S_c / D_m + S_m}{S_c + S_m} \tag{6}$$

At the assumption of

$$\beta = \frac{\text{the area of the crack}}{\text{the total area}} = \frac{S_c}{S_c+S_m}$$, β can be

determined by Eqs. (1) and (2).

$$\beta=\frac{\pi H_c}{4H_m} = 0.785\frac{H_c}{H_m} \tag{7}$$

where β= percentage of the crack area in the total area.

At the assumption of $\xi_1 = \frac{H_c}{H_m}$, Eq. (7) can be expressed by ξ_1.

$$\beta = 0.785\xi_1 \tag{8}$$

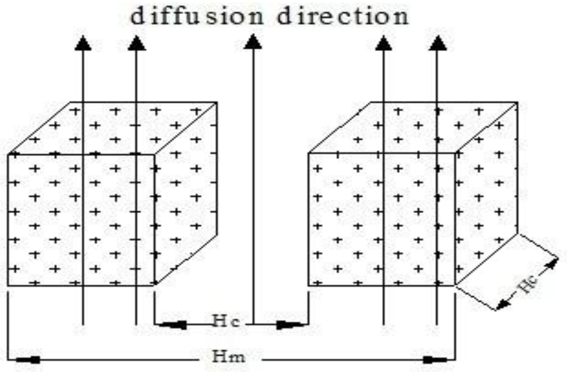

Fig. 5. The Distribution of the Micro-crack Unit Element.

where ξ_1= the crack factor.

From Eqs. (6), (7) and (8) , D_t can be deduced as follows:

$$\frac{D_t}{D_m} = 1 + \frac{S_c}{S_c + S_m}\left[\frac{D_c}{D_m} - 1\right] = 1 + 0.785\xi_1\frac{D_c}{D_m} - 0.785\xi_1 \tag{9}$$

$$D_t = \left[1 + 0.785\xi_1\frac{D_c}{D_m} - 0.785\xi_1\right]\times D_m \tag{10}$$

The Diffusion Coefficient under Alternating Stresses

According to the fatigue degradation mechanism of concrete, the deterioration process can be divided into three stages. After the second stage, the original micro-cracks expand stably. These cracks integrate to form a new crack. Therefore, the fatigue damage can be characterized by residual strain. The residual deformation, which is caused by the alternating stresses, was assumed to be δ_1 in the time period of T_1. The residual deformation caused by plastic deformation and the crack was equivalent to the maximum width of the transverse fatigue crack ($\delta_1=L_{cone}$). The crack was homogenized into cylindrical crack, ($L_{cone} = \delta_1/2$). The process of crack uniformization is shown in Figs. 5 and 6.

According to the above derivation, the functional relations between crack factor and residual deformation can be established in the fatigue process as follows [7]:

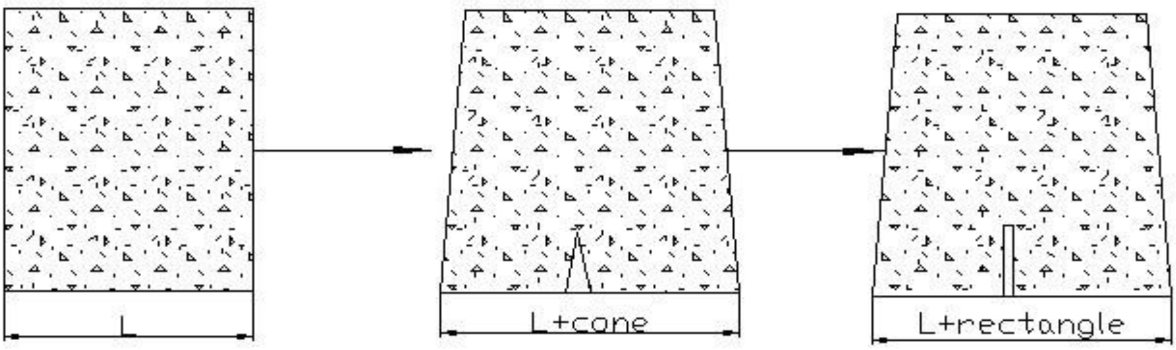

Fig. 6 The Process of Crack Uniformization.

$$\xi_1 = \frac{H_c}{H_m} = \frac{\delta_1/2}{L+\delta_1/2} \tag{11}$$

Make $\xi_2 = 1/\xi_1$,

$$\xi_2 = 1 + \frac{2L}{\delta_1} = 1 + \frac{2}{\delta_n{}^p}\ ,\ \xi_1 = 1\Big/\left(1+\frac{2}{\varepsilon_n{}^p}\right) \tag{12}$$

where:
L = the initial length of the concrete unit;
$\varepsilon_n{}^p$ = the residual deformation after n times of alternating stresses.

The longer the time for alternating stresses become, the greater the value of the residual deformation under the bottom surface is. The crack factor also increases gradually. The crack factor is the function between the load period and cyclic number and is expressed as follows:

$$\varepsilon_n^p = F(T,n) \tag{13}$$

where:
T = the load time
n = the number of loads

The related research indicates that the fatigue equation of concrete can be expressed by Eq. (14):

$$S = \alpha - \beta(1-R)\lg N \tag{14}$$

where:
S = the maximum stress level of alternating stresses;
R = the stress ratio;
N = the extreme fatigue life under the maximum stress level S;
α, β are experimental constants.

There are three stages in the fatigue deformation development. Jiang, J.-Y. et al established that the change of residual deformation is considered to be a linear change with the number of loads in the first and second stages [7]. These first two stages account for 90% of the whole fatigue deformation development. According to this assumption, Eq. (15) is derived.

$$\frac{24n_h}{0.9\times 10^{(s-\alpha)/\beta(1-R)}} = \frac{\varepsilon_n^p}{\varepsilon_B^P} \tag{15}$$

where:
$\varepsilon_B{}^p$ = the residual strain at the end of the second stage in the fatigue process;
N_f = the cycle life under alternating stresses.

From Eqs. (14) and (15), $\varepsilon_n{}^p$ can be obtained by Eq. (16)

$$\varepsilon_n{}^p = \frac{24n_h \times \varepsilon_B{}^p}{0.9\times 10^{(s-\varepsilon)/\beta(1-R)}} \tag{16}$$

where:
n_h = the load times per hour.

The residual deformation value, after n times of fatigue loading, is expressed in Eq. (17).

Table 1. Ingredients of Concrete.

Cement （kg/m^3）	Water （kg/m^3）	Sand （kg/m^3）	Coarse Aggregate （kg/m^3）	W/C
387	175	587	1,091	0.45

$$\varepsilon_n{}^p = \frac{24n_h \times \varepsilon_B{}^p}{0.9\times 10^{(a-s)/b}} \tag{17}$$

Eq. (17) plugs into Eq. (12), and is then expressed by Eq. (18), which defines the functional relationship between the reciprocal of the crack factor under the alternating stresses.

$$\xi_2 = 1 + \frac{2}{\varepsilon_n{}^p} = 1 + \frac{2}{\dfrac{24n_h \times \varepsilon_B{}^p}{0.9\times 10^{(a-s)/b}}} = 1 + \frac{2\times 0.9\times 1}{24n_h \times \varepsilon_B{}^p} \tag{18}$$

where:
$\xi_2(t)$ = the reciprocal of the crack factor at t time.

According to the equation $\xi_2=1/\xi_1$, the reciprocal of ξ_2 is plugged into Eq. (10), and D_t is expressed by Eq. (19).

$$\begin{aligned} D_t = D_m + 0.785D_c \times \frac{24n_h \times \varepsilon_B^P}{24\times n_h \times \varepsilon_B^P + 2\times 0.9\times 10^{(s-\alpha)/\beta(1-R)}} \\ - 0.785D_m \times \frac{24n_h \times \varepsilon_B^P}{24\times n_h \times \varepsilon_B^P + 2\times 0.9\times 10^{(s-\alpha)/\beta(1-R)}} \end{aligned} \tag{19}$$

Solving the Sulfate Concentration

According to the external sulfate attack models in references 5, 6, 8, and 9, SO_4^{2-} concentration can be calculated by Eq. (20). Diffusion coefficient (D) in Eq. (20) is replaced by the effective diffusion coefficient (D_t), which is derived from Eq. (19). The formulation of SO_4^{2-} concentration in cement concrete under the corrosion fatigue is obtained and shown in Eq. (21).

$$\frac{\partial U}{\partial T} = D\frac{\partial^2 U}{\partial X^2} - kU \tag{20}$$

$$\frac{\partial U}{\partial T} = D_t\frac{\partial^2 U}{\partial X^2} - kU \tag{21}$$

where:
U = the sulfate ion concentration;
D_t = the effective diffusion coefficient;
k = the rate of sulfate's take-up, which may be considered the solubility rate.

Experimental and Calculation

Raw Material and Test Method

Raw Materials

Grade 42.5 Portland cement (ASTM C150, Type II), manufactured by Jidong Cement Company, was used in this research. Middle sand with a fineness modulus of 2.83 and limestone with a size ranging

Fig. 7. Mechanical Corrosion Fatigue System.

from 5–20 mm were used as aggregates. In addition, the corrosion test adopted 5.0% of Na_2SO_4 solution. The corrosion fatigue test was carried out at room temperature. To accelerate chemical corrosion, a mixer was used to make the corrosion solution reach the state of continual locomotion to avoid the reactant, which did not dissolve the depositing on the surface or beside the concrete specimens.

The mixture ratio used in the corrosion fatigue tests was optimized, as shown in Table 1.

Corrosion Fatigue Test Method

The corrosion fatigue test is closely correlated with time, stress levels, and load spectrum. The authors designed a set of mechanical corrosion fatigue systems to conduct fatigue loading and unloading in corrosion solution, as shown in Figs. 7 and 8.

According to the mixture ratio listed in Table 1, standard test specimens in dimensions of 100 mm×100 mm×400 mm were made. To corrode the concrete specimen one-dimensionally, all surfaces of the specimen were treated with anti-corrosion coating, except for the top and bottom (Fig. 9). According to the design, three specimens in every group were put on the corrosion fatigue test equipment bracket. Preliminary third point loading was applied to the specimens, and then 5.0% Na_2SO_4 solution was poured in. After soaking for 24 hours, the specimens were subjected to alternating loads. For those specimens subjected to fatigue loading, the loads were applied and released successively for 24 hour. Each loading and unloading cycle included constant loading and unloading for 2.5 minutes.

The test was stress controlled. The maximum stress level was expressed as S_{max}= 0.60, and the minimum stress level was S_{min}= 0.10. The loading specimens were unloaded together when they reached the specified age. The surface of the soaking and corrosion fatigue concrete specimens was cleaned. After the specimens' surfaces dried at room temperature, a sulfate ion concentration test was carried out.

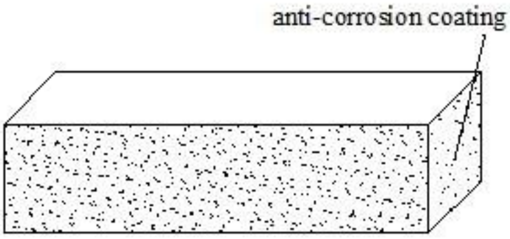

Fig. 9. The Treatment of Specimen.

The Sulfate Ion Concentration Test Method

1. Preparation of Concrete powder

After 50 days of soaking the specimens, concrete powder within the range of 10 - 20 mm deep from the erosion surface was taken to measure the concentration of sulfate ion every 30 days. During this preparation, the concrete powder (10-20 mm deep) was chiseled out with an electric drill at the mark location, and the number of the position was over five. The powder was mixed thoroughly, and 5 grams of powder was screened with micromesh to prepare for the test.

2. Testing Steps

The powder (5g) and 50 ml of water were put into a beaker. After dissolving fully, the solution was obtained. The concentration of sulfate ion was measured with EDTA complexometry. The steps are as follows:

The first step: V_{L0} solution was measured accurately in a 250 ml conical flask and soured with 1 ml hydrochloric acid solution. Then, 10-30 ml of barium chloride solution from the burette was added, and the volume (V_1 (in ml)) was recorded.

The second step: After washing the inner wall of the conical flask with 1-2 ml of distilled water, the solution was heated to a boiling point. After the solution cooled to room temperature, 10 ml of Mg-EDTA, 100 ml of anhydrous ethyl alcohol, 2 ml of hydroxylamine hydrochloride, 3 ml of triethanolamine, 10 ml of buffer solution, and 3-5 drops of eriochrome black T stable solution were added into the conical flask. The solution was titrated with EDTA. When the color of the solution turned from red-purple to pure blue, the volume of EDTA (V_2(ml)) was recorded.

The third step: V_{L0} =5ml sample was measured accurately in a 250ml conical flask with 20ml distilled water, and the solution was soured with 1ml chlorhydric acid solution. 2ml hydroxylamine hydrochloride, 3ml triethanolamine, 10ml buffer solution and 3-5 drops of eriochrome black T stable solution were added into the solution. The solution was titrate with EDTA. When the color of solution turned from red purple to pure blue, the volume of EDTA (V_0(ml)) was recorded.

The fourth step: According to the above test result, the quantity concentration of sulfate ion ($\rho_{SO_4{}^{2-}}$) can be calculated by Eq. (21).

$$\rho_{SO_4{}^{2-}} = \frac{c_1V_1 - c_2\left(V_2 - V_0\right)}{V_{L0}} \tag{21}$$

where:

$\rho_{SO_4{}^{2-}}$ = the quantity concentration of sulfate ion (g/L);

c_1 = the concentration of $BaCl_2$ standard solution (0.05 mol/L);
V_1 = the volume of consumed $BaCl_2$ standard solution (mL);
c_2 = the concentration of EDTA standard solution (0.02 mol/L);
V_2 = the volume of consumed EDTA standard solution (mL);
V_0 = the volume of consumed EDTA standard solution with a 5.00 mL sample when the total quality of Ca and Mg is tested.

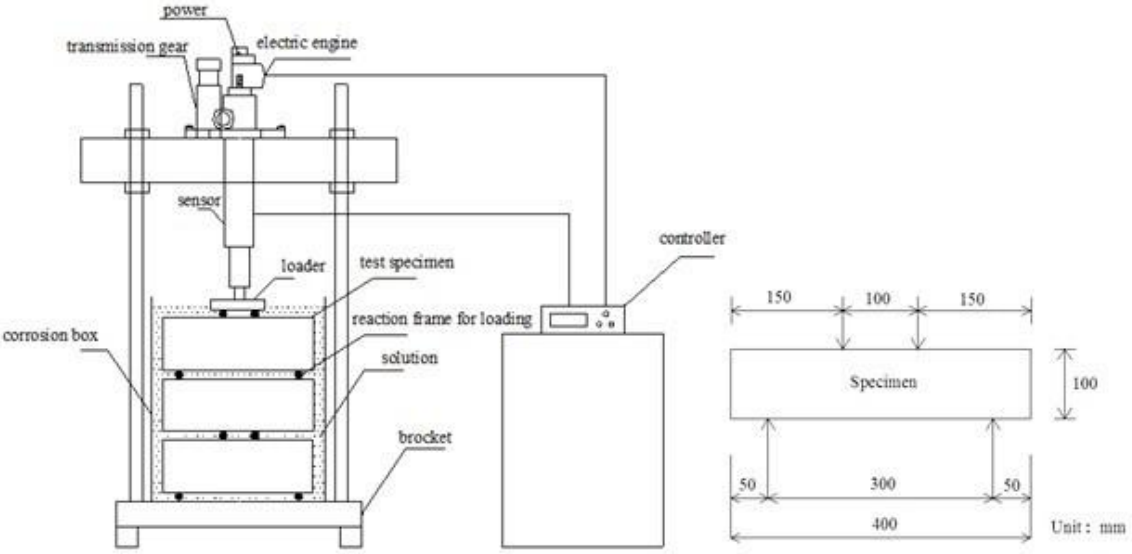

Fig. 8. Sketch of the Mechanical Fatigue Loading System.

Table 2. Main Parameters in Calculation Model.

Item	Value	Item	Value
Thickness L	100 mm	A	1.07
D_c	$1.73e^{-10}\ m^2/s$	B	0.098
R	0.08	The Initial Content of C_3A	$164.9\ mol/m^3$
The Initial Content of Gypsum	$66.1\ mol/m^3$	C_3A without Hydration	$44.9\ mol/m^3$
Reaction Rate K	$3.05e^{-8} m^3/mol \cdot s$	$\varepsilon_B{}^p$	$120e^{-6}$
w/c	0.45	S	60%

Table 3. Resulting Comparison between the Theory Model and the Experiments.

Corrosion Fatigue Time（Days）	The Sulfate Ion Concentration（g/L）		Relative Error（%）
	The Calculation Value	The Experimental Value	
80	1.21	1.07	-13.08
110	5.23	4.86	-7.61
140	6.92	6.38	-8.46
170	12.81	11.86	-8.01
200	18.19	16.82	-8.15
230	24.16	22.05	-9.57
260	29.67	27.01	-9.85
290	29.67	28.98	-2.38
320	29.67	29.14	-1.82
350	29.67	29.27	-1.37

Resulting Comparison between the Theory Model and the Experiments

The values of the main parameters in the calculation model are shown in Table 2. The calculation values of the sulfate ion concentration are shown in Table 3. According to the test method, the experimental values of the sulfate ion concentration is shown in Table 3.

To evaluate the calculation of the concentration of sulfate ion, the relative error of the concentration between the calculation values and test results in a solution of 5% sulfate was calculated (shown in Table 3). This computation formula can be expressed as Eq. (22):

$$err = \frac{\left(Cso_{4\ -\mathrm{exp}}^{2-} - Cso_{4\ -\mathrm{mod}}^{2-}\right)}{Cso_{4\ -\mathrm{exp}}^{2-}} \times 100\% \qquad (22)$$

where:

err = the relative error between the calculated values and the test values;

$Cso_{4}^{2-}{}_{-\exp}$ = the test value;

$Cso_{4}^{2-}{}_{-\mathrm{mod}}$ = the calculated value.

According to the theory model, the concentration of sulfate ion within 20 mm deep of the concrete sample surface is the calculated value of the concentration and is compared to the test results listed in Table 3.

From Table 3, the relative errors are all restrained within 10%, except for the initial values at 80 days. Considering the experimental measurement error, the calculated values based on this model are consistent with the experimental values. The convergence and the accuracy of the model are also verified by the test results.

Conclusions

Corrosion fatigue of concrete arises from the interaction of corrosion and alternating stresses. The impact of the sulfate solution diffusion in cement concrete is much more than a single action by corrosion agents. A theoretical, one-dimensional model for the prediction of sulfate ion migration in cement concrete specimens under alternating stresses has been proposed based on the derivation of effective diffusion coefficient D_p, which is used to characterize the effect of alternating stresses on the sulfate ion diffusion and Fick's second law. According to the relative error between the calculated values and the experimental values, the calculated values based on this model are consistent with the experimental values. Thus, the theory and assumptions used in the derivation of the model are rational and scientific.

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