Variation of flexural strength of cement mortar attacked by sulfate ions

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**ABSTRACT**

Under the environment of seawater, durability of concrete materials is one of the chief factors considered in the design of structures. The decrease of durability of structures is induced by the evolution of micro-damage due to the erosion of chlorine and sulfate ions, which is characterized by the reduction of modulus, strength, and toughness of the material. In this paper, the variation of the flexural strength of cement mortar under sulfate erosion is investigated. The results obtained in present work indicate that the erosion time, concentration of sulfate solution, and water-to-cement ratio will significantly affect the flexural strength.

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1. Introduction

Flexural strength is a very important parameter for concrete materials. In the design of concrete structures, such as concrete pavement, bridge, and building structures, flexural strength must be taken into account. Owing to the importance of flexural strength, some researchers paid close attention to the flexural behavior of concrete materials [1–4]. Under the environment of seawater, the durability of concrete structures will decrease, because the attenuation of modulus, compressive strength, and flexural strength of concrete material [5]. It is well known that there are two types of erosion for the concrete materials, namely, the attack of chlorine ions and sulfate ions [6]. If the sulfate ions get into the void in concrete materials, the nucleation and growth of calcium sulphoaluminate (ettringite) crystal may take place. When the crystal touched the boundary of void, it will apply a force to the concrete materials. Under the action of this inner force, the micro-damage will occur. The durability of concrete materials and structures decreases due to the evolution of micro-damage [7]. Park et al. [8] investigated the aging of strength of common concrete and high-strength concrete under the environment of sulfate. Boyd and Mindess [9] investigated the effect of water-to-cement ratio and cement type on the resistance of concrete to sulfate attack by means of tension testing method. Jin et al. [10] studied the properties of concrete materials under sulfate and chloride solution attack, and discussed the effect of interaction of that solution on the materials with and without fly ash. All mentioned researches paid close attention to the variation of compressive strength, but few works relate to the variation of flexural strength due to sulfate erosion. In fact, the effect of sulfate erosion on the compressive strength is different from that on the flexural strength. In the earlier stage of sulfate erosion, the compressive strength will increase, whereas the flexural strength decreases.

In this paper, close attention is paid to the variation of flexural strength due to sulfate erosion. First, the experiment on the variation of flexural strength under sulfate erosion is performed. Secondly, the theoretical model on the variation of flexural strength is proposed by means of micromechanics method. In this model, the void growth under the action of ettringite crystal is taken into account. Thirdly, the numerical calculation is carried out and compared with the experimental results. It is found that the concentration of sulfate solution, erosion time, and the water-to-cement ratio will significantly affect the flexural strength of cement mortar.
2. Experimental methods and results

Specimens of Portland cement mortars of 10 × 10 × 60 mm (Fig. 1) are prepared for detecting the variation of flexural strength. The water-to-cement ratios of the specimen are taken as 0.4, 0.6, and 0.8. The maximum aggregate size of specimen

Fig. 1. Specimen for detecting flexural strength: (a) the shape of the specimen (10 × 10 × 60 mm) and (b) specimen immersed in sulphate solution.
is 0.2 mm, and it is much less than the dimension of the tested specimen. The mix proportion of the cement mortars can be seen in Table 1.

The specimen is put into the solution of sodium sulfate with concentration of 3% and 8%. The maximum immersgence time for the specimen is 455 days. The size of the specimen is plotted in Fig. 2. The flexural strength is measured at different immersgence time by means of materials test machine (WE-30) shown in Fig. 3.

The variation of the flexural strength of the material under sulfate attack can be seen in Figs. 4–6, where $\sigma^*$ denotes the flexural strength of specimen under sulfate erosion, $\Delta \sigma = \sigma^* - \sigma(0)$. $\sigma(0)$ stands for the initial flexural strength of specimen (without sulfate erosion), which is obtained by the experiment method before being put in sulfate solution. The magnitudes of $\sigma(0)$ for specimen with different water-to-cement ratio are listed in Table 2.

One can see from the figures that in the initial stage of sulfate erosion, the flexural strength decreases quickly with the erosion time. However, in the latter erosion stage, the flexural strength can hardly decrease, even more, there is an increase

| Mix of mortars
<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>Cement</td>
<td>Sand</td>
<td>Water</td>
</tr>
<tr>
<td>1.0</td>
<td>3.0</td>
<td>0.4</td>
</tr>
<tr>
<td>1.0</td>
<td>3.0</td>
<td>0.6</td>
</tr>
<tr>
<td>1.0</td>
<td>3.0</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Fig. 2. Sketch for the test of flexural strength of specimen.

Fig. 3. Test of evolution of flexural strength of cement mortar attacked by sulphate solution.
for the strength. This is because the effect of the nucleation and growth of delayed ettringite crystal (shown in Fig. 7). In the initial stage of erosion, the ettringite will contact the surface of microvoids in cement mortar, and the interaction between the ettringite and the surface of voids may lead to the evolution of micro-damage. Such evolution of the damage induces the decrease of flexural strength. In the latter erosion stage, the ettringite crystal may penetrate cross the surface and get into cement mortar matrix. In this case, the ettringite crystal can reinforce the cement mortar just like short fiber. Therefore, the flexural strength of the material will be slightly recovered.

From the experimental results, one can see that the variation of flexural strength of the material depends not only on the concentration of sulfate solution and the immergence time, but also on the water-to-cement ratio, w/c.
3. The theoretical model of variation of flexural strength

It is important to propose a theoretical model to describe the variation of the flexural strength under attack of sulfate. Cement mortar is a porous material. The variation of flexural strength is caused by the damage evolution due to sulfate ero-
sion. Under flexural loading, the crack expands initially at the bottom surface of the specimen. Hence, the calculation of overall stress and strain at the bottom surface should be performed. The overall stress and strain are defined by [11]

$$\langle \sigma \rangle = f_0 \langle \sigma_0 \rangle + f_v \langle \sigma_v \rangle, \quad \langle \epsilon \rangle = f_0 \langle \epsilon_0 \rangle + f_v \langle \epsilon_v \rangle$$

(1)

where $f_0$ is the volume fraction of matrix material, $f_v$ is the porosity of the material, and $f_0 + f_v = 1$. $\langle \sigma_0 \rangle$ and $\langle \epsilon_0 \rangle$ are the average stress and the average strain of matrix, respectively, and $\langle \sigma_v \rangle$ and $\langle \epsilon_v \rangle$ are the average stress and average strain of microvoids.

We assume that the flexural strength is governed by a threshold magnitude of overall strain. And the magnitude of overall strain can be ascertained by Eq. (1) if the average strain of matrix and void can be calculated.

Under small deformation, the relation between stress and strain in matrix can be approximately considered as linear elastic one. Therefore, we have

$$\sigma_0 = L : \epsilon_0, \quad \epsilon_0 = J : \sigma_0$$

(2a)

or

$$\langle \sigma_0 \rangle = L : \langle \epsilon_0 \rangle, \quad \langle \epsilon_0 \rangle = J : \langle \sigma_0 \rangle$$

(2b)

where $L$ and $J$ are the fourth order modulus and creep compliance, respectively, and

$$L = J^{-1}, L : J = I$$

(3)

where $I$ is the fourth order identity tensor.

In order to calculate the deformation of a void, the following two steps will be adopted. The first step is to calculate the void deformation under remote strain $\epsilon^v$, and the second step is to calculate the void deformation under the internal pressure, $P$, induced by delayed ettringite. The total deformation of a void is the summation of the results in the two steps.

In the first step, the void strain under remote strain has been obtained by means of Eshelby's equivalent method, and can be written as [12]

$$\epsilon^v(1) = (I - S)^{-1} : \epsilon^\infty$$

(4)

where $S$ is the Eshelby's tensor.

In the second step, we consider the deformation of the void under the action of internal pressure $P$. In this case, the void strain can be easily obtained follow the process illustrated by Chen et al. as the following [13]

$$\epsilon^v(2) = P(I - S)^{-1} : S : J : i_0$$

(5)

where $i_0$ is the second order identity tensor. The void strain is the superposition of $\epsilon^v(1)$ and $\epsilon^v(2)$, namely

$$\epsilon^v = (I - S)^{-1} : \epsilon^\infty + P(I - S)^{-1} : S : J : i_0$$

(6a)

If there are a lot of microvoids in the matrix material, the void strain in Eq. (6a) should be modified by means of Mori-Tanaka’s scheme [14], i.e., the remote strain $\epsilon^\infty$ should be replaced by the average strain of matrix, $\langle \epsilon_0 \rangle$. Therefore, the void strain of cement mortar is given by

$$\epsilon^v = (I - S)^{-1} : \langle \epsilon_0 \rangle + P(I - S)^{-1} : S : J : i_0$$

(6b)

From Eq. (6b), one can see that the voids strain does not depend on the its position in space, therefore

$$\langle \epsilon^v \rangle = \epsilon^v$$

(7)

We assume that the internal pressure in every void is the same, namely

$$\langle \sigma^v \rangle = \sigma^v = -Pl_0$$

(8)

Substituting Eq. (8) into the first formula of Eq. (1) yields

$$\langle \sigma_0 \rangle = \frac{1}{f_0} (\langle \sigma \rangle - f_v Pl_0)$$

(9)

By substituting Eq. (9) into Eq. (2b), we obtain

$$\langle \epsilon_0 \rangle = J : \langle \sigma_0 \rangle = \frac{1}{f_0} J : (\langle \sigma \rangle - f_v Pl_0)$$

(10)

The average strain of cement mortar can be obtained by substituting Eqs. (6) and (9) into the second formula of Eq. (1) as the following:

$$\langle \epsilon \rangle = A : J : \langle \sigma \rangle + Pf_v B : J : i_0$$

$$A = I + (f_v/f_0)(I - S)^{-1}, \quad B = A + (I - S)^{-1} : S$$

(11)
where
\[ J = \frac{1}{3k} I^{(m)} + \frac{1}{2\mu} I^{(s)} \] (12)
\[ I^{(m)} = \frac{1}{3} k_0 \otimes I_0, \quad I^{(s)} = I - I^{(m)} \]
and \( k \) and \( \mu \) are the bulk modulus and shear modulus of the material, and can be expressed by
\[ k = \frac{E}{3(1 - 2\nu)}, \quad \mu = \frac{E}{2(1 + \nu)} \] (13)
where \( E \) and \( \nu \) are the modulus and Poisson’s ratio of the material.

Because of the influence of ettringite, the modulus of cement mortar does not remain a constant but a function of immersion time, and may be written as
\[ E = E_0[1 - D(t)] \] (14)
where \( D(t) \) is used to describe the influence of damage on the modulus, \( E_0 \) is a initial modulus of the material.

The compliance of the material can be expressed by
\[ J = \frac{1}{1 - D(t)} J^0 \]
\[ J^0 = \frac{1}{3k_0} I^{(m)} + \frac{1}{2\mu_0} I^{(s)} \] (15)
\[ k_0 = \frac{E_0}{3(1 - 2\nu)}, \quad \mu_0 = \frac{E_0}{2(1 + \nu)} \]

Under the concentration force, \( F \), the damage evolution firstly occurs at the bottom surface. Assume the bottom surface is in macro uniaxial tensile stress state, namely, \( \langle \sigma_{11} \rangle \neq 0 \), and all other components are equal to zero. In this case, the component of average strain of the bottom surface of the specimen will be given by
\[ \langle \varepsilon_{11} \rangle = A_{11j} g_{j11} (\sigma_{11}) + P f \ B_{11j} [j_{g11} + j_{g22} + j_{g33}] \] (16)
where \( A_{11j}, j_{gik} \) and \( B_{11j} \) can be calculated from Eqs. (11) and (12). It is easy to obtain the relation between \( \langle \sigma_{11} \rangle \neq 0 \) and the flexural force \( F \)
\[ \langle \sigma_{11} \rangle = \frac{M}{W} = \frac{F l}{4W} \] (17)
where \( M \) is the bending moment at the middle cross section of specimen, \( W \) is the section moduli of the cross-sectional area, \( l \) is the length of specimen. Substituting Eq. (11) to Eq. (12) yields
\[ \langle \varepsilon_{11} \rangle = A_{11j} g_{j11} \frac{F l}{4W} (\sigma_{11}) + P f \ B_{11j} [j_{g11} + j_{g22} + j_{g33}] \] (18)

We assume that the fracture strain is denoted by \( \varepsilon_{11cr} \), and it remains a constant, therefore we have
\[ \varepsilon_{11cr} = A_{11j} g_{j11} \frac{F l}{4W} (\sigma_{11}) + P f \ B_{11j} [j_{g11} + j_{g22} + j_{g33}] \] (19)
where \( F^* \) is the flexural force, and it is a function of immersion time. \( F^*(0) \) is the initial flexural force. From Eq. (19) we obtain
\[ F^* = \frac{4W}{l} \left( \frac{1}{A_{11j} g_{j11}} \right) \varepsilon_{11cr} - \frac{4W}{l} \left( \frac{1}{A_{11j} g_{j11}} \right) P f \ B_{11j} [j_{g11} + j_{g22} + j_{g33}] \] (20)
\[ F^*(0) = \frac{4W}{l} \left( \frac{1}{A_{11j} g_{j11}} \right) \varepsilon_{11cr} \] (21)
\[ \Delta F^* = F^*(t) - F^*(0) = - \frac{4W}{lA_{11j} g_{j11}} \left[ D(t) \varepsilon_{11cr} + P f \ B_{11j} [j_{g11}^0 + j_{g22}^0 + j_{g33}^0] \right] \] (22)
Therefore, the relative variation of flexural strength of specimen can be expressed by
\[ \frac{\Delta \sigma^*}{\sigma^*(0)} = \frac{\Delta F^*}{F^*(0)} = \frac{F^*(t) - F^*(0)}{F^*(0)} = - \left[ D(t) + \frac{P f}{\varepsilon_{11cr}} B_{11j} [j_{g11}^0 + j_{g22}^0 + j_{g33}^0] \right] \] (23)
We assume that the influence of ettringite on the modulus, \( D(t) \), may be written by a logarithmic function as the following:
\[ D(t) = a \ln t \] (24)
where \( a \) is a parameter to be determined. Obviously it is related to the concentration of sulfate solution, and the ratio of cement to water of specimen. Because the ettringite crystal may lead to the damage evolution, and sometimes it may also reinforce the cement mortar, the parameter \( a \) may be positive or negative.

The internal pressure, \( P \), is assumed to be directly proportional to the increment of ettringite crystal. The experimental results indicate that the relationship of increment of ettringite crystal and erosion time may be described by a power function.\(^1\) Hence, the internal pressure, \( P \), can also be expressed by

\[
P = P_0 \sqrt{t}
\]

Substituting Eqs. (29) and (30) into Eq. (30), we obtain the variation model of flexural strength of specimen as the following:

\[
\frac{\Delta \sigma}{\sigma^*(0)} = -(a \ln t + b \sqrt{t})
\]

where

\[
b = \frac{P_0}{\beta_{11r}} B_{111} \left( j_{111}^0 + j_{222}^0 + j_{333}^0 \right)
\]

Symbol \( b \) is a parameter to be determined. It can be see from Eq. (27) that the parameter \( b \) is related the concentration of sulfate solution, the water-to-cement ratio, and the magnitude of critical fracture strain, the bulk modulus and shear modulus of cement mortar, and the size and shape of microvoids in the material.

4. Numerical results of the variation model of flexural strength of cement mortar

From the experimental results we can see that variation of flexural strength of cement mortar is not a monotonic function of immersion time. The flexural strength decrease with the erosion time, however, in the latter erosion time, the flexural strength may present an increase due to the reinforced effect of delayed ettringite. In fact, such an increase of the flexural strength has no meaning of application in engineering. The close attention has to be paid to the initial decrease of the strength.

We assume that the shape of microvoids in cement mortar is spherical, and in this situation, the Eshelby’s tensor can be further expressed by

\[
S = q_m I^{(m)} + q_s I^{(s)}
\]

\[
q_m = \frac{1 + \nu}{3(1 - \nu)}, \quad q_s = \frac{2(4 - 5\nu)}{15(1 - \nu)}
\]

Substituting Eqs. (12) and (28) into Eq. (11) yields,
\[ A = \alpha I^{(m)} + \beta I^{(s)} \]
\[ \alpha = 1 + \frac{1}{1 - q_m} \frac{f_v}{f_0}, \quad \beta = 1 + \frac{1}{1 - q_s} \frac{f_v}{f_0} \]

and

\[ B = \frac{1}{f_0} \frac{1}{1 - q_m} I^{(m)} + \frac{1}{f_0} \frac{1}{1 - q_s} I^{(s)} \]  

The variation model can be calculated by substituting Eq. (30) into Eq. (23), and the results are plotted in Figs. 8–10.
The constants $a$ and $b$ with different concentration of sulfate solution and water-to-cement ratio of the specimen are listed in Table 3.

5. Conclusions

Some new results are obtained in the present work as the following:

- The decrease of flexural strength of cement mortar depends on the concentration of sulfate solution and the water-to-cement ratio of the specimen. When the concentration of the solution or the water-to-cement ratio increase, the decrease of the flexural strength quickly.

- The experimental results indicate that the mechanism of the variation of the flexural strength is the influence of delayed ettringite, which is produced by the sulfate ions. The flexural strength decreases due to the damage evolution caused by the delayed ettringite.

- A theoretical model for describing the variation of the flexural strength is suggested by means of micromechanics method. It is found that the model is properly consistent with the experimental results.

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References