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# EQUIVALENT MODEL OF EXPANSION OF CEMENT MORTAR UNDER SULPHATE EROSION ⋆⋆

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**ABSTRACT** The expansion property of cement mortar under the attack of sulfate ions is studied by experimental and theoretical methods. First, cement mortars are fabricated with the ratio of water to cement of 0.4, 0.6, and 0.8. Secondly, the expansion of specimen immerged in sulphate solution is measured at different times. Thirdly, a theoretical model of expansion of cement mortar under sulphate erosion is suggested by virtue of represent volume element method. In this model, the damage evolution due to the interaction between delayed ettringite and cement mortar is taken into account. Finally, the numerical calculation is performed. The numerical and experimental results indicate that the model perfectly describes the expansion of the cement mortar.

**KEY WORDS** size effect, microvoids, expansion, sodium sulfate attack

## I. INTRODUCTION

The expansion and damage evolution take place in concrete due to the sulphate erosion in the ocean environment. After diffusing in concrete, sulphate ions will be combined with the hydrate solution in microvoids to form ettringite crystals[1–6]. Such an ettringite is called as the delayed ettringite. At the contact of the delayed ettringite with the surface of the voids, the expansion of concrete will occur due to the growth of the voids and the nucleation of micro-cracks. It is well known that the damage evolution will affect the durability of concrete materials and structures, because of this, it is necessary to investigate the expansion and damage evolution for improving the durability of concrete structures.

Usually, the expansion and damage evolution take place in cement mortar or at the interface between the cement mortar and aggregates[3]. Hence, the expansion of cement mortar under sulphate erosion is investigated in this paper. Firstly, specimens of cement mortar are fabricated with different ratios of water to cement. Then the specimens are put into sulphate solution with different concentration. Secondly, the expansion of specimen immerged in sulphate solution is measured at different times. Thirdly, a theoretical model of expansion of cement mortar under sulphate erosion is suggested by virtue of volume element method. In this model, the cement mortar is considered as a porous material, the damage evolution due to the interaction between the delayed ettringite and cement mortar is taken

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into account. Finally, the numerical calculation is performed. The numerical and experimental results indicate that the model perfectly describes the expansion of the cement mortar.

## II. EXPERIMENTAL APPROACH

Specimens of Portland cement mortars of 40 × 40 × 160 mm are prepared as shown in Fig.1. The water-to-cement ratios of the specimen are taken as 0.4, 0.6, and 0.8. The maximum aggregate size of specimen is 0.2 mm, and it is much smaller than the dimension of the tested specimen. In order to measure more exactly the expansion behavior under the attack of sulphate radical ions, two small spherical metal balls are put into the ends of the specimen.

The erosion solution is chosen as the solution of sodium sulphate. In order to accelerate the expansion and damage evolution, the concentration of the solution is selected as 3.00 mass% and 8.00 mass% sodium (namely, $SO_4^{2-}$ concentration is 20,250 and 54,000 ppm, respectively). Pure water is also selected as a solution (controlled solution) for comparison.

After the common initial curing time, the original length of specimens is measured by micrometer, and then stored in three different solutions (shown in Fig.2.). The total immergence time is 472 days. During the immergence period, the length of the specimen is measured at different immergence times. Experiment results indicate that the length of the specimen under sulphate erosion may increase. The expansion strain of the specimen is obtained by the length change divided by the original length of the specimen. The experimental results are plotted in Figs.3∼5.

The expansion mechanism is the interaction between the delayed ettringite crystal and the cement mortar matrix. After the diffusing in cement mortar, sulphate radical ions will be combined with the hydrate solution in the voids of cement mortar, which leads to the nucleation and growth of ettringite. Figure 6 shows the SEM photo of the delayed ettringite. When the ettringite contacts the surface of voids, it will apply internal pressure to the surface of voids. Under the internal pressure, the specimen will expand.

It can be seen from the experimental results that the expansion strain of the cement mortar increases with the increasing concentration of sulphate solution. If the concentration of solution is 0 ppm, namely, pure water, there is almost no expansion for the specimen. We also note that there exists a characteristic

Fig. 1. Specimen of cement mortar with the $w/c = 0.6$.

Fig. 2. Specimens immerged in sulphate solution.

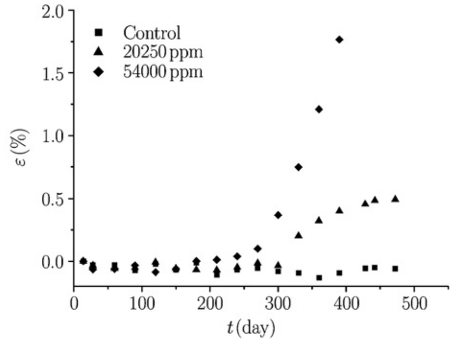

Fig. 3. Expansion strain of the specimen with $w/c = 0.4$.

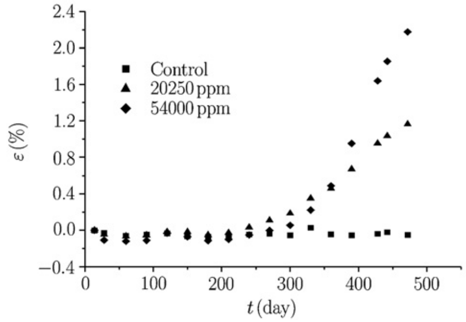

Fig. 4. Expansion strain of the specimen with $w/c = 0.6$.

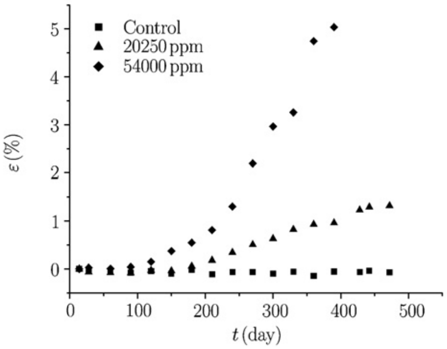

Fig. 5. Expansion strain of the specimen with $w/c = 0.8$.

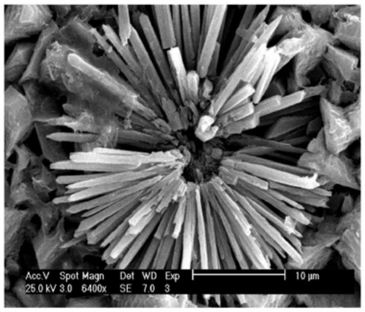

Fig. 6. SEM photo of delayed ettringite crystal.

time $t_0$, when the immergence time $t$ is less than $t_0$, the expansion can hardly occur. If, however, $t$ is equal to or greater than $t_0$, the expansion will take place. The characteristic time is affected by the concentration of sulphate solution and the value of $w/c$.

## III. EXPANSION MODEL OF CEMENT MORTAR UNDER SULPHATE EROSION

The cement mortar can be considered as a porous material (shown in Fig.7). The effect of the delayed ettringite is replaced by an internal pressure $P$. In order to propose a simple theoretical model of expansion, the method of represent volume element (RVE) with damage evolution is adopted (shown in Fig.8).

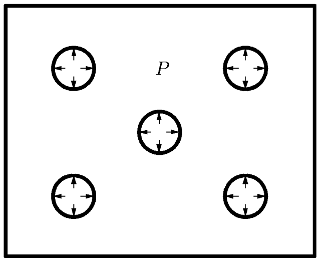

Fig. 7. Deformation of voids under internal pressure $P$.

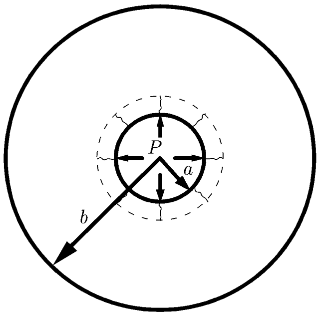

Fig. 8. Represent volume element considering microcrack.

The constitutive relation of the cement mortar matrix is approximately assumed to be linear viscoelastic, and it may be expressed as in[7]

$$\boldsymbol{\sigma}(t) = \int_0^t \boldsymbol{L}\,(t-\tau) : \dot{\boldsymbol{\varepsilon}}\,(\tau)\,\mathrm{d}\tau, \qquad \boldsymbol{\varepsilon}\,(t) = \int_0^t \boldsymbol{J}\,(t-\tau) : \dot{\boldsymbol{\sigma}}\,(\tau)\,\mathrm{d}\tau \tag{1}$$

where $\boldsymbol{L}(t)$ and $\boldsymbol{J}\,(t)$ are the fourth order relaxation modulus and creep compliance, respectively. By means of separation of variables[7], the stress and strain may be expressed as the product of time-dependent and spatial-dependent functions as follows:

$$\boldsymbol{\sigma}\,(\boldsymbol{x},t) = \hat{\boldsymbol{\sigma}}\,(\boldsymbol{x})\,f\,(t)\,, \qquad \boldsymbol{\varepsilon}\,(\boldsymbol{x},t) = \hat{\boldsymbol{\varepsilon}}\,(\boldsymbol{x})\,g\,(t) \tag{2}$$

Assume that $\boldsymbol{L}(t)$ and $\boldsymbol{J}\,(t)$ can also be expressed as in[8,9]

$$\boldsymbol{L}\,(t) = \hat{\boldsymbol{L}}l\,(t)\,, \qquad \boldsymbol{J}\,(t) = \hat{\boldsymbol{J}}j\,(t) \tag{3}$$

where

$$\hat{\boldsymbol{L}} = \boldsymbol{L}(0), \qquad \hat{\boldsymbol{J}} = \boldsymbol{J}(0) \tag{4}$$

and $l(t)$ and $j(t)$ are functions of time, and $l(0) = j(0) = 1$.

From Eqs.(1)-(3) we obtain

$$f(t) = \int_0^t l(t-\tau)\,\dot{g}(\tau)\,\mathrm{d}\tau, \qquad g(t) = \int_0^t j(t-\tau)\,\dot{l}(\tau)\,\mathrm{d}\tau \tag{5}$$

The relation between increments of stress and strain can be obtained as the followings:

$$\Delta\boldsymbol{\sigma} = \boldsymbol{\Lambda}(t) : \Delta\boldsymbol{\varepsilon}(t) \tag{6}$$

where

$$\boldsymbol{\Lambda}(t) = \psi(t)\,\boldsymbol{L}(0), \qquad \psi(t) = 1 + \frac{1}{\dot{g}(t)}\int_0^t \dot{l}(t-\tau)\,\dot{g}(\tau)\,\mathrm{d}\tau \tag{7}$$

Equation (6) indicates that the relation between the increments of stress and strain may be described by a 'linear elastic' relation with a variable fourth order tangential modulus, $\boldsymbol{\Lambda}(t)$.

Based on Eq.(6), the increment of displacement of the outside boundary of RVE is obtained as[10]

$$\Delta u = \frac{\Delta P}{E_0\psi(t)(b^3 - a^3)}\left[(1-2\nu)a^3 r + \frac{1+\nu}{2r^2}a^3 b^3\right] \tag{8}$$

Therefore, the increment volume strain of entire RVE can be obtained by

$$\Delta\varepsilon_{kk} = \frac{3\Delta u}{b} = \frac{9\Delta P f_v(1-\nu)}{2E_0\psi(t)(1-f_v)} \tag{9}$$

where $f_v = a^3/b^3$ is the volume fraction of voids as well as in cement mortar. Since the damage evolution takes place when the cement mortar is under the internal pressure, hence, $f_v$ includes two parts, one is the initial volume fraction of voids before the action of internal pressure, the other is the damage, namely,

$$f_v = f_{v0} + D(t) \tag{10}$$

where $D(t)$ is the equivalent volume fraction due to the damage evolution. Substituting Eq.(10) into Eq.(9) yields

$$\Delta\varepsilon_{kk} = \frac{9\Delta P\,[f_{v0} + D(t)](1-\nu)}{2E(t)[1 - f_{v0} - D(t)]} \tag{11}$$

Assume that the internal pressure is directly proportional to the immergence time, $t$,

$$\Delta P = P_0\Delta t \tag{12}$$

Also, we assume that the damage evolution is directly proportional to the internal pressure,

$$D(t) = Ct \tag{13}$$

where $C$ is the speed of the damage evolution.

Substituting Eqs.(12) and (13) into Eq.(11) , then integrating Eq.(11), we obtain

$$\varepsilon_{kk} = \int_0^t \frac{9P_0(f_{v0} + Ct)(1-\nu)}{2E_0\psi(t)(1 - f_{v0} - Ct)}\mathrm{d}t \tag{14}$$

The expansion is isotropic, namely, the longitudinal strain, $\varepsilon$ is one third of $\varepsilon_{kk}$,

$$\varepsilon = \frac{1}{3}\varepsilon_{kk} = \int_0^t \frac{3P_0(f_{v0} + Ct)(1-\nu)}{2E_0\psi(t)(1 - f_{v0} - Ct)}\mathrm{d}t \tag{15}$$

where $P_0$ and $C$ are parameters to be determined. It is obvious that $P_0$ and $C$ are all greater than zero,

$$P_0 > 0, \qquad C > 0 \tag{16}$$

If Maxwell model is adopted to describe the constitutive relation of the cement mortar, we obtain

$$l(t) = \exp\left(\frac{-t}{\theta}\right), \qquad j(t) = 1 + \frac{t}{\theta} \tag{17}$$

It is easy to obtain

$$g(t) = \frac{t^2}{2\theta}, \qquad \dot{g}(t) = \frac{t}{\theta} \tag{18}$$

and

$$\psi(t) = \frac{\theta}{t}\left(1 - \mathrm{e}^{-t/\theta}\right) \tag{19}$$

The related parameters are taken as[11]

$$f_{v0} = 0.1, \quad \nu = 0.16, \quad E_0 = 0.4 \text{ GPa}, \quad \theta = 47.8 \text{ d} \tag{20}$$

Note the constraint condition.

From Eqs.(16)-(20) and Eq.(15), as well as the experimental results shown in Figs.3-5, the parameters $P_0$ and $C$ are obtained and listed in Table 1.

Table 1. **Magnitude of $P_0$ and $C$**

| Samples | $P_0$ (Pa) | $C$ (1/d) |
|---|---|---|
| $w/c = 0.4$, 20,250 ppm | $2.47 \times 10^4$ | $1.67 \times 10^{-4}$ |
| $w/c = 0.4$, 54,000 ppm | $2.18 \times 10^2$ | $3.84 \times 10^{-1}$ |
| $w/c = 0.6$, 20,250 ppm | $4.18 \times 10^4$ | $1.14 \times 10^{-4}$ |
| $w/c = 0.6$, 54,000 ppm | $5.07 \times 10^4$ | $1.77 \times 10^{-3}$ |
| $w/c = 0.8$, 20,250 ppm | $4.23 \times 10^4$ | $7.52 \times 10^{-6}$ |
| $w/c = 0.8$, 54,000 ppm | $2.66 \times 10^4$ | $1.30 \times 10^{-3}$ |

The curves of theoretical model and experimental results are plotted in Figs.9-14. From the results, we can see that the theoretical model coincides with the experimental results.

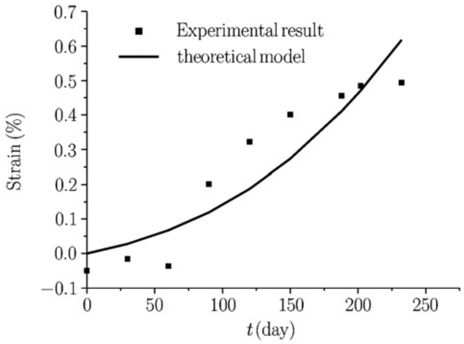

Fig. 9. Expansion strain of the specimen with $w/c = 0.4$, sulphate concentration of 20,250 ppm.

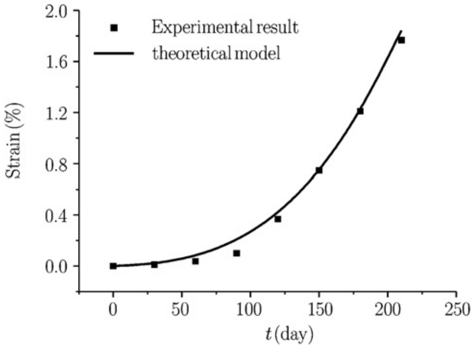

Fig. 10. Expansion strain of the specimen with $w/c = 0.4$, sulphate concentration of 54,000 ppm.

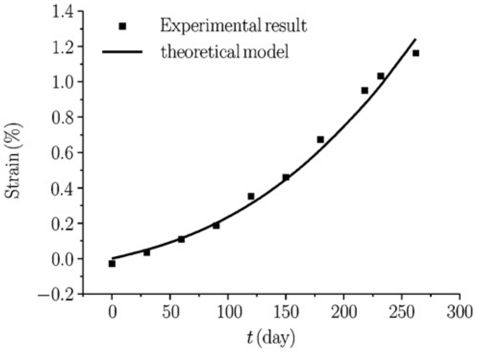

Fig. 11. Expansion strain of the specimen with $w/c = 0.6$, sulphate concentration of 20,250 ppm.

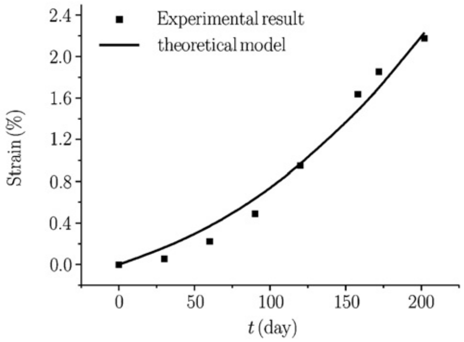

Fig. 12. Expansion strain of the specimen with $w/c = 0.6$, sulphate concentration of 54,000 ppm.

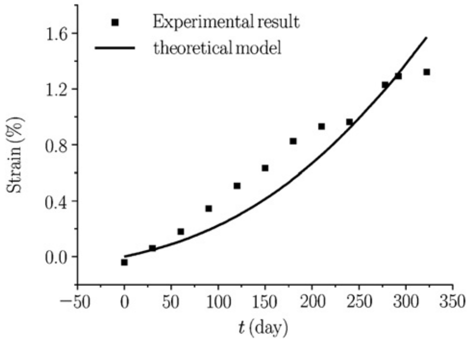

Fig. 13. Expansion strain of the specimen with $w/c = 0.8$, sulphate concentration of 20,250 ppm.

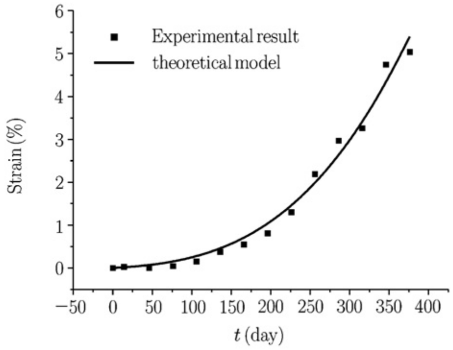

Fig. 14. Expansion strain of the specimen with $w/c = 0.8$, sulphate concentration of 54,000 ppm.

## IV. CONCLUSIONS

Some new results are obtained in the present work:

- Expansion of cement mortar is caused by the internal pressure due to the delayed ettringite. The viscosity and the damage evolution are the dominate mechanisms for the expansion.
- Expansion strain depends not only on the concentration of the sulphate solution, but also on the ratio of water to cement.
- Expansion of the cement mortar strongly depends on the relaxation time of the cement mortar.
- A new theoretical model for describing the expansion of the cement mortar is suggested.

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