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Expansion Behavior of Portland Cement Mortars under Sulfate Attack

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Abstract. The expansion behaviors are studied on mortars at water-cement ratio (w/c)=0.4, 0.6, and 0.8, stored in sodium sulfate solutions with sulfate concentration of 0 ppm, 20,250 ppm, and 54,000 ppm, respectively. The mortars stored in control solution show no expansion, whereas the expansion of the ones exposed to sodium sulfate solutions occurs in two stages (i.e., "dormant" and "speedup" Stages). The high concentration of sulfate accelerates the expansion, but control of water-cement ratio (0.60 in this case) can put up higher resistance to sulfate attack. The XRD analysis shown that the macro-expansion depends on the formation and growth of both ettringite and gypsum. The analysis obtained by means of Sigmoidal Fit Method indicates that the microdamage evolution depends strongly on the average size of microvoids in the material.

Introduction

Sulfate attack is the destructive process acting on concrete materials due to the formation and growth of expansion reaction products within concrete exposed to external sulfate sources. Under sulfate attacking, expansion of cement mortar, which can lead to cracking, spalling, and other damaging effects, is considered to be the main destructive form. However, what is the source of expansion during sulfate attack has attracted lots of discussions and controversies. Ettringite is believed by some researchers to be the only souce of expansion [1-6].

In the present paper, we will present the data at intervals of up to 472 days on the expansion of mortars stored in sodium sulfate solutions with sulfate concentration of 0, 20,250, 54,000, respectively. Further more, the XRD analysis is carried out, and the effect of growth of ettringite and gypsum on the expansion of Portland cement is investigated. The influences of sulfate concentration and water cement ratio on expansion behaviors are also studied. Combined with the speed of relative expansion of the specimen, the size effect of microvoids of Portland cement on the expansion of the material is discussed.

Specimens preparation and Experiment

Materials. The 425# cement consisting of 13.01 wt. % Al_2O_3, 2.63 wt. % SO_3, and 2.91 wt. % Fe_2O_3 is from Lvyang cement ltd. Co. Yangzhou. The ISO standard sand conformed to GB1717671 and is derived from Xiamen. AR-grade anhydrous sodium sulfate (Na_2SO_4) is produced from chemistry reagent Co. Shanghai, Chinese medicine group, molecular weight is 142.04. Pure deionised water is used to mix the paste.

The proportions of mortar prisms (40×40×160mm) by mass are 1.0 (cement): 2.5 (sand): 0.4 (water), 1.0 (cement): 2.5 (sand): 0.6 (water), 1.0 (cement): 2.5 (sand): 0.8 (water), respectively. During mixing, one brass nail with spherical ends is embedded in either centre of longitudinal ends (shown in Fig. 1). Another smaller specimens (10×10×70mm) are also prepared for XRD analysis. Mortar specimens used in this experiment are procured in their molds that are stored at 20℃ and 90%

relative humidity, and then removed from molds one day later. Subsequently, the specimens are exposed to standard curing for 28 days.

Experiments. After above common initial curing regime, specimens are stored in three different solutions, i.e., control solution (water); the sodium sulfate solution of 3.00 mass %, and the sodium sulfate solution of 8.00 mass % (i.e., the concentration of SO_4^{2-} is 0 ppm, 20,250 ppm, and 54,000 ppm, respectively). The mortar specimens are dried naturally after removal from the solutions. We assume that the expansion of the specimen is isotropic, therefore, only longitudinal expansion is measured by hand-strain gauge at intervals of up to 472 days. If the relative longitudinal expansion, i.e., the longitudinal strain, is denoted by ε, the volume strain of the specimen will be $\varepsilon_V=3\varepsilon$. The curves of ε versus eroding time t are plotted in Figs. 2~4. Smaller specimens are crushed and dried for XRD analysis, and the result is drawn in Fig.5.

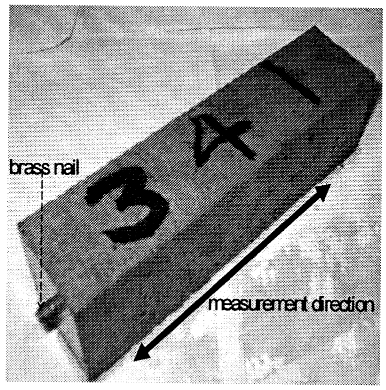

Fig. 1 The specimen for expansion measurement

Results and discussions

Fig.s 2~4 present the expansion data for three types of mortars at water-cement ratio (w/c)=0.4, 0.6, and 0.8, stored in sodium sulfate solutions with sulfate concentration of 0 ppm, 20,250 ppm, and 54,000 ppm, respectively. The change in length per unit length is displayed as a function of exposure time. It is noted that the mortars stored in control show no dilatation, whereas the ones exposed to sodium sulfate solutions occur in two stages, which is consistent with the results observed by Clifton et al. [7] and Tian et al.[4]. In Stage 1, the expansion is very low, and this stage can thus be called the "dormant period". After this period, the mortars show high degree of expansion until the specimen disintegrates. This stage is called as stage 2, and this stage may be named as "speedup period".

XRD experiments (shown in Fig. 5) indicate that the sudden increase in expansion in stage 2 occurs due to the increase in the amounts of gypsum and ettringite over that which can be accommodated by the mortar structure.

Moreover, we find that both sulfate concentration and water-cement ratio exert significant influences on expansion behavior of mortars. As far as the expansion of the mortars with same w/c is concerned, higher sulfate concentration leads to the earlier onset of stage 2 and higher expansion rate. Take w/c=0.8, the expansion for 20,250 ppm reached 1.32% when the final disintegrate occur, while for 54,000 ppm it is 5.04%. Similar expansion properties are also observed at w/c=0.4, and 0.6. On the other hand, higher w/c resulted in greater expansion. Take 54,000 ppm, the specimens with w/c=0.4 and 0.8 disintegrate with 1.77% and 5.04%, respectively, of expansion at 390 days. However, the expansion for w/c=0.6 reaches 2.18% at 472 days, but did not disintegrate. This is a very important result for the study on the failure mechanism of cement mortar materials.

In fact, cement mortar materials can be considered as porosity composites, and different value of w/c leads to different average size of microvoids. Under the sulfate attack, the expansion of the material is induced due to the pressure given by the delay ettringate and the expansion of matrix caused by the growth of gypsum. In the case of the action of the pressure of delay ettringate which grows in microvoids, expansion of the specimen includes the increase of the volume of microvoids and the volume of nucleated microcrack.

In order to further study the size effect of microvoids on the expansion and failure of the specimen, the relative speed of expansion, i.e., longitudinal strain rate, $\dot{\varepsilon}$, is simulated by means of Sigmoidal Fit Method (SFM) as shown in Fig. 6. From this figure we can see that there is always a crest for each curve. When the relative speed of expansion reaches to the peak value of the crest, the evolution of microcrack in the specimen begins to be acute. Therefore, the peak value of the strain rate, $\dot{\varepsilon}_{\max}$, and the position of the crest, i.e., the exposure time corresponding to the peak value of the crest, t_{cr}, are important parameters for describing the property of resisting sulfate attack. The higher the value of t_{cr}, the better the ability of resisting sulfate attack. Interesting phenomena is that for a certain value of w/c, the values of t_{cr} are almost the same. For instance, if w/c=0.6, both the values of t_{cr} for specimens eroded in the solutions with concentrate 20,250 ppm or 54,000 ppm are the same, namely, $t_{cr}\big|_{w/c=0.6} \approx 390$ days. Similar phenomena also appears in other curves as shown in Fig.6. From the results in Fig.6, we obtain $t_{cr}\big|_{w/c=0.4} \approx 340$ days and $t_{cr}\big|_{w/c=0.8} \approx 310$ days, respectively.

Therefore, $t_{cr}\big|_{w/c=0.6} > t_{cr}\big|_{w/c=0.4} > t_{cr}\big|_{w/c=0.8}$. This is why the specimen with w/c=0.6 eroded in the solution of 54,000 ppm dose not disintegrate till 472 days, whereas other specimens with w/c=0.4 or w/c=0.8 eroded in the same solution disintegrate when eroding time reaches to 390 days.

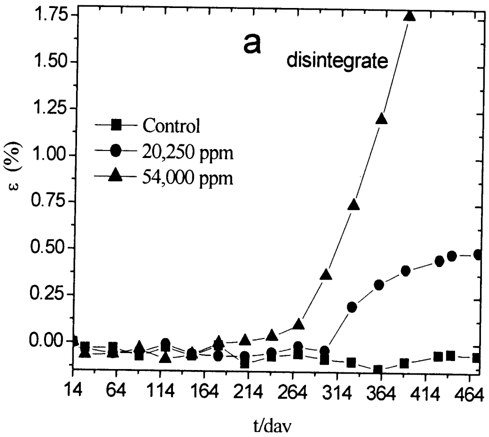

Fig. 2 Expansion strain of the specimen with W/C=0.4

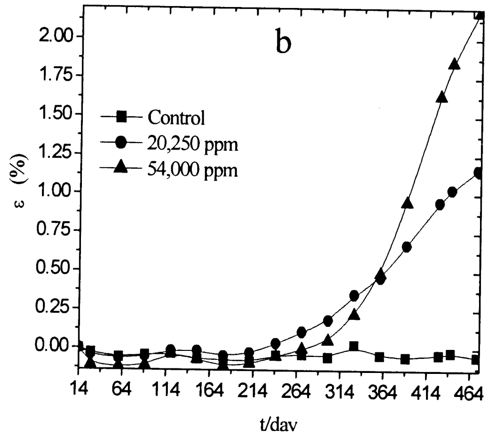

Fig. 3 Expansion strain of the specimen with W/C=0.6

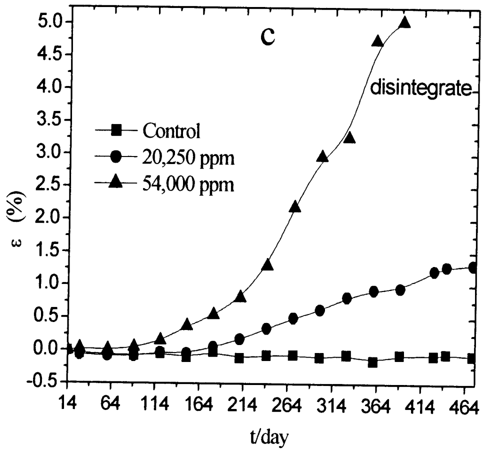

Fig. 4 Expansion strain of the specimen with W/C=0.8

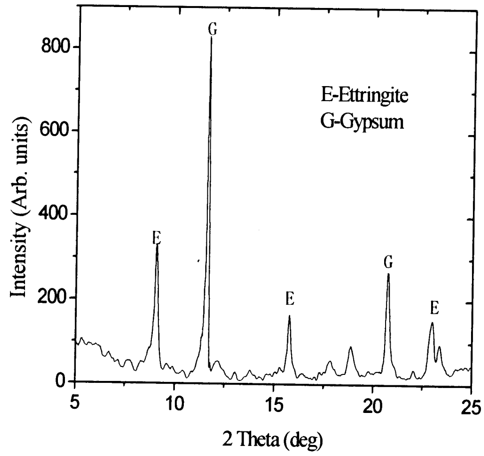

Fig. 5 XRD analysis of mortar attacked for 60 days

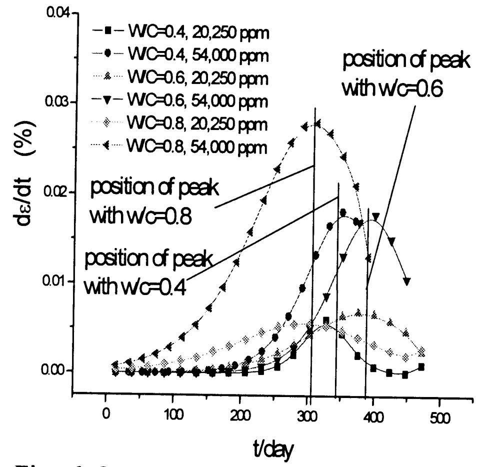

Fig. 6 Curves of expansion speed versus exposure time

Summary

From the presented experiments, the following conclusions can be drawn.

1) Expansion of Portland cement mortars in sodium sulfate solution follows a two-stage process, where an initial stage named as "dormant period" of very low expansion is followed by a sudden increase in the expansion ("speedup period"). High concentration of sulfate accelerates the expansion, but control of water-cement ratio (0.60 in this case) can put up higher resistance to sulfate attack.

2) The macro-expansion depends on the formation and growth of both ettringite and gypsum.

3) The maximum value of expansion strain rate and the corresponding eroding time are the most important parameters for describing the ability of resisting sulfate attack. Those parameters are related to the value of w/c. Therefore, the failure mechanism depends strongly on the average size of microvoids in the cement mortar.

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