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Expansion and degradation of cement paste in sodium sulfate solutions

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HIGHLIGHTS

- The expansion behavior was investigated based on strain gauge measurement system.
- The change of sulfur distribution was studied by EDS elemental mapping.
- The crack development was discussed based on BSE micrograph and CT scanning.
- The experimental results offered the needed information for further numerical study.

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ABSTRACT

External sulfate attack is a progressive degradation process that may cause expansion, cracking, loss of binder cohesion and increased permeability in cementitious materials. Crystallization pressure theory has often been referred to as the most likely mechanism. However, thus far the stress causing the expansion has not been quantified. In this study, small cement paste pipes with a wall thickness of 2.5 mm were prepared and immersed in sodium sulfate solutions with SO_4^{2-} ion concentrations of 1.5 g/L and 30 g/L. Three types of longitudinal restraints were applied on the specimens before exposure, which were created by a spring, a thin or a thicker stainless steel bar that was centered in the hollow specimens in order to facilitate the non-, low- or high-restraint condition. The free expansion, restrained expansion and generated stress were quantified. The pore size distribution, sulfur distribution and crack pattern were periodically analyzed during the sulfate immersion tests up to 420 days. The generated stresses were found to be as high as 13.1 MPa in high sulfate solution and 8.3 MPa in low sulfate solution under high-restraint condition after 420-day immersion. For the unrestrained specimens immersed in low sulfate solution, an almost uniform sulfur distribution along the diffusion direction was found at 189-day immersion. However, for the unrestrained specimens immersed in high sulfate solution, a layer or several layers of mainly gypsum were formed subparallel to the exposed surface from 133-day immersion.

1. Introduction

External sulfate attack is a progressive degradation of cementitious materials upon being exposed to external sulfate ions. It is a complex issue in which ionic transport, expansive reactions and mechanical damage are responsible in varying degrees for gradually increased macroscopic expansion and severe mechanical damage [1–3]. Sulfate ions present in seawater, rivers, groundwater and industrial effluent can penetrate into the hardened concrete, and react with cement hydration products to form ettringite as well as gypsum crystals, if higher sulfate concentrations are available [4–7]. Such formations result in a solid volume increase and cause local expansive stress within the pore network. Although the solid volume increase may initially reduce the porosity of cement paste, it will cause cracking at a later stage as the generated expansive stress exceeds the tensile strength of cement paste. This, in turn, leads eventually to a total strength loss and an increased permeability of concrete.

Even though the theories concerning the exact origin of the expansive stresses are under debate, ettringite formation from monosulfate is generally considered as the major cause [8–11]. Lothenbach et al. [10] showed that the increase in solid volume caused by external sulfate attack did not exceed the total capillary porosity and concluded that the formation of ettringite within the matrix leads to the observed expansion. Yu et al. [9] provided evidence that sulfate related expansion is linked to the formation of ettringite from monosulfate crystals embedded within the C-S-H. Müllauer et al. [8] concluded that the damage is due to the

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formation of ettringite in small pores (10–50 nm) which generates stresses up to 8 MPa exceeding the tensile strength of the binder matrix. Ettringite formation also takes place in larger pores, but the generated stress is negligible. In this case, the most likely expansion mechanism can be the crystallization pressure developing inside the nanopores within the cement paste.

According to the crystallization pressure theory [12–15], the driving force for crystallization pressure is the supersaturation of the pore solution. Then, the crystal growth in the confined space leads to the expansive stress on the pore walls. An inverse relationship between the expansive stress and the pore size is critical. Müllauer et al. [8] calculated a spherical crystal with a radius of around 25 nm and found that this is in equilibrium at a maximum stress of around 8 MPa. Yu et al. [9] also calculated the crystallization pressure as high as 21 MPa from a supersaturated solution to form ettringite. The magnitude of the expansive stress on the walls of nanopores can be predicted based on the crystallization pressure theory. However, an experimental verification is still missing since direct measurement of the expansive stress on nanopore walls is highly challenging. Therefore, the authors propose determining the expansive stress indirectly through modeling the expansion behavior of larger scale specimens under various degrees of restraint, which can be verified by the experiments.

External sulfate attack under continuous immersion condition is a slow diffusion process. Even though high water/cement ratios and high sulfate ion concentrations have been adopted as acceleration methods, research shows that the attack depth remains shallow even after several months [9,16]. Therefore, specimens with a small thickness along the diffusion direction could be preferred for experimental research in order to ensure a faster exposure of the entire cross-section. Müllauer et al. [8] considered the problem mentioned above in their research. The thin-walled hollow mortar cylinders with a wall thickness of 2.5 mm and the specially constructed stress cell with different diameters of central steel bars were used as their experimental setup. The expansion behavior and generated stress of mortar pipe were studied. In our research, in order to eliminate the influence of aggregates and reach a relatively uniform distribution of local expansion stress at each attack depth, cement paste specimens were chosen over mortar and concrete. Strain gauges were used for the measurements of restrained expansions and generated stresses, with the purposes of increasing the measurement accuracy and obtaining continuous experimental results. Sulfur distributions at different immersion time and crack developments caused by external sulfate attack were also studied.

The ingress of the external sulfate ions is a process, which involves a dynamic local expansive stress gradient along the diffusion direction. Therefore, the sulfur profile and the pore size distribution within the same depth were determined in this research. Theoretically, the dynamic local expansive stress gradient is related with the dynamic sulfur gradient, which can offer the needed information for the input of the modeling. The reader is referred to Ma et al. [17] for the framework of modeling of this mechanism. The outputs of the model are expansion, generated stress and crack pattern, which can be validated by the experimental results. Therefore, all the experimental results presented in this paper were expected to contribute significantly to the simulations including a gradient distribution of local expansive stress along the diffusion direction, which reflects the process of external sulfate attack. This research aims at understanding the relationship between the local expansive stresses generated within nanopores and the global expansion characteristics through computational simulations and experimental methods. This paper focuses on the experimental results.

2. Experimental approach

2.1. Specimen preparation and test setup

An ordinary Portland cement (CEM I 42,5 N) with a water/cement ratio of 0.40 was used in this study. PVC moulds with stainless steel rods in the center (Fig. 1) were fabricated in order to produce the cement paste pipes with a wall thickness of 2.5 mm (outer diameter 30 mm, inner diameter 25 mm), based on the earlier study of Müllauer et al. [8,18]. During casting of the cement paste pipes, the moulds were put on a vibration table to make the casting easier and also remove the air from the fresh paste. Then the unmoulded specimens were wrapped with plastic foil and kept in curing room (20 ± 1 °C, 96 ± 2 % RH) for 24 h. After that, the specimens were demoulded and cured in saturated limewater at 20 ± 1 °C for another 90 days [17]. Upon completion of the curing period, the cement paste pipes were cut and polished at both ends to ensure that they were parallel and that the length was 70 mm.

Three types of longitudinal restraints were applied on the cement paste pipes in this study [8,17]. The restraints were created by a spring, a thin stainless steel bar or a thicker stainless steel bar that were centered in the pipes in order to facilitate the non-, low- or high-restraint condition (Fig. 2). The middle part diameters of thin steel bars and thick steel bars are 3 mm and 7 mm, respectively. Strain gauges were used for the thin and thick steel bars to measure the deformation of the bars and determine the restraint and resulting stresses. In order to reduce the influence of bending during tests, two strain gauges were glued on the opposite side of the middle part of each steel bar, and the average reading of the two strain gauges was used as the final strain. Then a special coating was applied on the surfaces of strain gauges to protect the strain gauges when exposed to sulfate solutions. The strain values of the strain gauges were measured continuously with a CompactDAQ system connected to a computer.

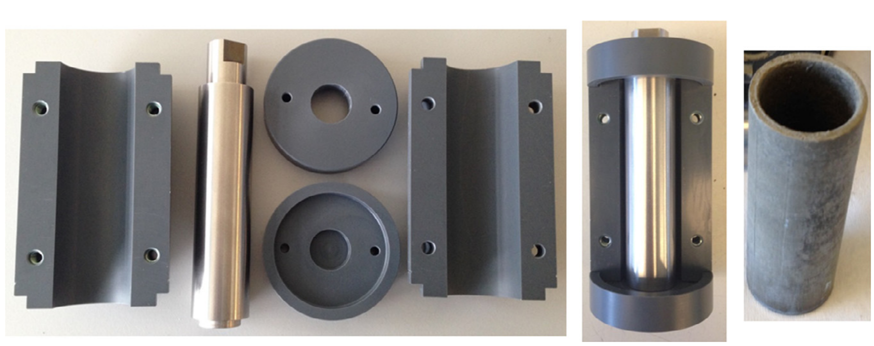

Fig. 1. PVC moulds and specimens.