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Deterioration of mortars exposed to sulfate attack under electrical field

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HIGHLIGHTS

- The damage of mortars exposed to sulfate attack under electrical field was studied.
- The combined condition accelerated the damage process of mortars.
- The dissolution of portlandite and decomposition of C–S–H gel occurred.
- Electrical field accelerated the sulfate attack induced deterioration of mortars.

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ABSTRACT

The damage process of plain and blended cement mortars subjected to sulfate attack under electrical field was investigated in this paper. The deterioration of mortars was investigated by measuring the loss of compressive strength. To identify the changes of microstructure and mineral phases after the test, scanning electron microscopy, energy dispersive spectroscopy and X-ray diffraction analysis were performed on the selected samples. The results indicated that compared with sulfate attack alone, the combination of sulfate attack and electrical field accelerated the damage process of mortars, which can be explained through two different mechanisms. On the one hand, Ca^{2+} ions directionally moved and then leached out from mortars under the electrical field, leading to the dissolution of portlandite as well as the decomposition of C–S–H gel at the later stage. On the other hand, the electrical field accelerated the migration of sulfate ions and then they reacted with hydration products to form massive ettringite and gypsum, which resulted in the microcracks and strength loss of mortars. Moreover, the deterioration of the mortar blended with fly ash was still visible in spite of its better chemical resistance. The strength loss of limestone powder incorporated mortar increased in comparison with Portland cement mortar as a result of an increase in porosity.

1. Introduction

External sulfate attack is one of the key durability issues for cement-based materials and it has been investigated extensively for many decades. The entering sulfate ions can react with hydrated cement composites to produce gypsum and ettringite, which can cause expansion, cracking and spalling.

There are many reports on the damage process of concrete exposed to single sulfate attack through the sulfate immersion tests [1–5]. Nevertheless, there has often been the different performance of concrete in immersion test from that observed in a field exposure. As a result, researchers have also investigated the deterioration mechanism of concrete exposed to sulfate attack couple with other parameters existing in the field, such as drying-wetting cycles [6–8], flexural loading [6,7,9–11] and freeze-thaw cycles [8,12].

In the last decade, the urban rail transit systems have been developing rapidly in China and other developing countries. In these systems, stray current, which originates from the electrical railway line and then flows through the reinforced or prestressed concrete, could accelerate the deterioration of concrete structure. Bertolini et al. [13] investigated the corrosion behavior of steel in concrete in the presence of stray current, reporting that stray current initiated corrosion on rebars embedded in cement-based materials and remarkably increased the corrosion rate on corroded reinforcement bars in the chloride-contaminated concrete. Solgaard et al. [14] also found that stray current was able to promote corrosion initiation on steel fibers embedded in mortar, and the corrosion rate showed a significant increase in the specimens with 4% and 6% of chloride by mass of cement after the exposure to stray current. Saito et al. [15] studied the leaching tests on different

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mortars using an electrochemical method, indicating that electrical field accelerated the dissolution of Ca^{2+} ions from the mortar in contact with water, leading to the increase of water permeability and reduction in compressive strength of specimens. However, to the authors' knowledge, the effect of stray current or electrical field on sulfate attack induced deterioration of concrete has not been investigated so far, although sulfate attack is one of the main deterioration mechanisms of underground infrastructures.

In this study, a low-frequency pulsed electrical field was applied on mortar specimens exposed to sulfate solution, to simulate the effect of stray current. The coupling effect of sulfate attack and electrical field on the microstructure and compressive strength of mortars was investigated, and the corresponding mechanism was analyzed. In addition, the influence of fly ash and limestone powder on the damage of mortar was evaluated.

2. Experimental details

2.1. Materials and mix proportions

The Portland cement (PC) used in this investigation consisted of 95% of clinker and 5% of gypsum by weight. Fly ash (FA), limestone powder (LP, 95 wt% $CaCO_3$) and siliceous sand with the fineness modulus of 2.70 were used. The chemical composition of clinker, gypsum, FA and LP is shown in Table 1. The mix proportions of mortar are given in Table 2. 30% FA and 30% LP were used as a replacement of cement by weight in the FA-30 and LP-30 mortar mixtures, respectively. In all mixtures, the binder: sand: water ratio was kept constant as 1:3:0.5 by weight.

Each of PC, FA-30 and LP-30 mortars has 10 groups of specimens (3 specimens in each group): 3 groups for water immersion, 3 groups for sulfate immersion and 4 groups for combined test of sulfate attack and electrical field. Values of compressive strength and SO_3 concentration reported in this paper are all average over three specimens.

2.2. Experimental procedures

Generally, the dimension of mortar specimens is 40 mm × 40 mm × 40 mm for compressive strength measurement in Chinese standard. However, the specimens in this work need to be clamped for better cutting before SO_3 concentration measurement and the length of the clip is about 20 mm. Therefore, the dimension of specimens in this paper is determined to 40 mm × 40 mm × 60 mm.

Mortar mixtures were cast into the middle part of special molds (as shown in Fig. 1). 24 h later, the plates were moved out and then the specimens along with molds were cured in a condition of 20 ± 2 °C and above 95% of relative humidity.

After additional 27 days of curing, the upper surface of specimens was coated with Vaseline to prevent from carbonation. Then, a 5% Na_2SO_4 solution and a 2.8% NaOH solution were added into the cathodic and anodic cells, respectively. The combined action test of sulfate attack (SA) and electrical field (EF) is shown schematically in Fig. 2. The principle and idea of the experimental device design were derived from the measurement of chloride diffusion coefficients in a migration test using electrical filed. In consideration of stray current's non-stationary nature [13], a low-frequency pulsed electrical field was employed in this investigation. The voltage applied was 30 V, and the pulse cycle was 40 s during which both the circulation and interruption periods were 20 s [16]. For comparison, the specimens with the same mixture were immersed in the corresponding sulfate solution (namely sulfate attack alone) and water, respectively. It should be noted that, under the combined condition, only one of the end surfaces (40 mm × 40 mm) was exposed to sulfate solution. Therefore, one surface (close to sulfate solution) of the specimen was also exposed in immersion test, while the other five surfaces were sealed by Vaseline.

Table 1
Chemical composition of clinker, gypsum, FA and LP.

Constituent (wt%)	Clinker	Gypsum	FA	LP
SiO_2	19.99	4.47	45.08	2.50
Al_2O_3	4.80	0.99	29.11	0.60
Fe_2O_3	2.98	0.36	16.12	0.36
CaO	61.22	34.05	3.41	54.03
SO_3	0.23	40.61	0.76	0.01
MgO	3.27	1.84	0.49	0.54
Na_2O	0.18	0.08	0.88	0.08
K_2O	0.88	0.23	1.05	–
Loss on ignition	3.52	16.87	3.10	41.57

Table 2
Mix proportions of mortar.

Mixture	Binder	Water–binder ratio	Sand–binder ratio
PC	100%PC	0.5	3.0
FA-30	70%PC + 30%FA	0.5	3.0
LP-30	70%PC + 30%LP	0.5	3.0

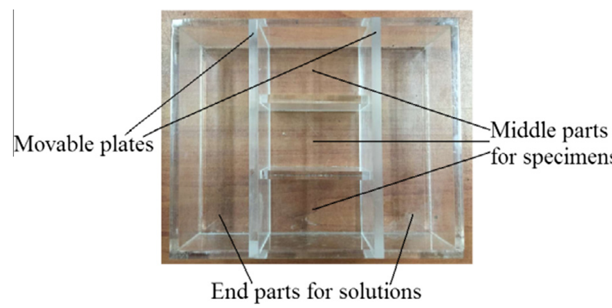

Fig. 1. Special mold.

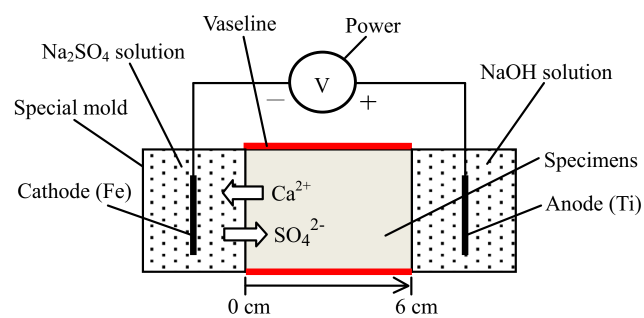

Fig. 2. Schematic drawing of combined action test of sulfate attack and electrical field.

2.3. Test methods

2.3.1. Sulfate and calcium concentrations

After slicing and grinding the samples, the sulfate-ion content, represented by SO_3 content (wt%, by weight of mortar), was determined by barium sulfate gravimetric method (chemical titration), according to GB/T 50476-2008 [17].

It should be noted that the measured sulfate content represents the total content, which refers to the sum total of external sulfate ions migrating into the specimen and the initial sulfate content. The initial sulfate content is the sulfate existing in a mortar from the raw materials before the test. They were measured at 1.18%, 0.99% and 0.84%, respectively for PC, FA-30 and LP-30 specimens. Thus, the migrated sulfate concentration can be calculated as the difference between the measured total and initial sulfate content.

The CaO content in mortars and the dissolved Ca^{2+} ions concentration into the cathodic compartment were measured by EDTA titration method, according to GB/T 176-2008 [18] and GB/T 15452-2009 [19], respectively.

2.3.2. Microstructure analysis

The surface part (0–20 mm depth from the exposed surface) of selected samples was vacuum dried at 50 °C for 48 h, and then coated with gold, finally examined by scanning electron microscopy (SEM, TESCAN VEGA 3 LMH with an acceleration voltage of 20 kV) equipped with an energy dispersive spectroscopy (EDS) detector. The average Ca/Si molar ratio of C–S–H gel was determined from 20 different measurement points through EDS analysis. More details about the measurement strategy can be found in the previous studies [20–22]. In addition, X-ray diffraction (XRD, PANalytical Empyrean system using CuKα radiation, operating at 60 kV and 55 mA) was performed on powder samples (particle size ⩽75 μm) to identify any compounds formed during the test.

2.3.3. Compressive strength

The damage of mortar specimens was investigated by measuring the relative compressive strength, which was calculated as follows:

$$R = f_{attack}/f_o \times 100\%$$