Deterioration Mechanism of Cement Matrix Long-term Exposed to Sulfate Solution

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Abstract

The objective of this work is to understand the deterioration mode of ordinary portland cement pastes and mortars immersed in 5% sodium sulfate solution for 510 days. In order to achieve the goal, x-ray diffraction (XRD) and scanning electron microscopy (SEM) are presented in this experimental work. Strength deterioration (SDF) and length change of the mortars were also measured to evaluate resistances to the attacking solution. The mortars were prepared by using water-cement ratio of 35%, 45% and 55%, respectively, and the water-cement ratio of pastes was fixed at 45%. Conclusively, the deterioration by sodium sulfate attack was primarily due to the formation of ettringite and thaumasite. This process of deterioration may submit the reasonable understanding on the sulfate attack mechanism of hardened cement pastes, mortars, and concretes.

1. Introduction

It has been recognized for a long time that sulfate ions in soils, particularly below ground, can cause severe damage to concrete structures. Until now, however, it has been difficult to define the precise nature of the mechanism of sulfate attack because of its complex behavior. There have been numerous field studies on the distress caused to concrete structures generated by sulfate attack. Many research studies have also been carried out to unravel this complex phenomenon through immersion tests in the laboratory as well as in the field.

In this study, the results of tests on sulfate attack by 5% Na_2SO_4 solution on ordinary portland cement paste and mortar are introduced. In order to evaluate the performance of the cement matrix subjected to sulfate attack, compressive strength and length change of mortar were periodically measured up to 510 days of sulfate immersion. Additionally microstructal observations such as x-ray diffraction and scanning electron microscopy are performed on paste exposed to similar conditions. These well supported the deterioration mechanism of ordinary portland cement matrix by sulfate attack.

2. Experimental

2.1 Materials and sample preparation

2.1.1 Cement

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The cement used in this study was Type-I cement (OPC) satisfying ASTM C 150 standard specification. The chemical composition and physical properties data, as provided by the cement manufacturer, are presented in Table 1. The C_3A content in the cement was 10.3% and the mass ratio of C_3S to C_2S was 3.3.

Table 1. Chemical composition and physical properties of cement

Chemical composition (%)							Physical properties	
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Ig. loss	Specific gravity	Fineness (cm^2/g)
20.2	5.8	3.0	63.3	3.4	2.1	1.2	3.13	3,120

2.1.2 Aggregate

River sand, which is a fine aggregate immune to most agent and has little organic compounds, is employed for manufacturing mortar specimens. The fine aggregate were entirely passed from the sieve of 5mm. The specific gravity, absorption and fineness modulus of fine aggregate are 2.60, 0.80% and 2.80, respectively. During testing, it is assumed that no chemical influences by fine aggregate are excluded.

2.1.3 Test solution

The exposure solution used to provide sulfate attack to the specimens was made by dissolving reagent grade chemical in tap water. The chemical used was Na_2SO_4. The calculated concentrations of Na^+ and SO_4^{2-} ions were 16,200 and 33,800 ppm, respectively. For comparison, tap water with similar temperature was used as control.

2.1.4 Sample preparation

50 mm cubes were used for measurement of compressive strength. The prism bars with a size of 25 x 25 x 285 mm were used for length change due to expansion. The mixture proportion of the mortars is cement : sand = 1 : 2. Mortar specimens were made at water-cement ratio of 35, 45 and 55%. The mixing procedure of mortar followed a method based on KS L 5105. Microstructural observations were performed on deteriorated parts of paste samples by sulfate attack.

2.2 Test techniques

2.2.1 Strength deterioration factor (SDF)

The deterioration of cube mortar specimens is investigated by measuring the strength deterioration factor (SDF), which is given by following equation.

$$SDF = \{(A - B) / A\} \times 100\ (\%)$$

where, A is the average compressive strength of mortar specimens cured in tap water and B is the average compressive strength of mortar specimens immersed in sulfate solution. Compressive strength tests were performed on each mixture at 0, 28, 91, 180, 270, 360 and 510 days of immersion.

2.2.2 Length change

Based on ASTM C 1012, length change was measured at each immersion period. All length change values were compared with the initial length of prism mortar (after 7 days of curing in tap water).

2.2.3 X-ray diffraction

In order to determine the solid phases in the paste specimens qualitatively, x-ray diffraction analysis technique is used. The XRD is conducted using the RINT D/max 2500 (Rigaku) X-ray diffractrometer. The source of radiation is CuKα with a wavelength of 1.54 Å at a voltage of 30 kV. The 2 theta angle range covered for paste specimen is from 5° to 40°. The scanning speed is 2°/min.

2.3.4 Scanning electron microscopy

SEM investigation is used to analyze the microstructure of the paste specimen attacked by sulfate attack. An XL30ESEM (Philips) equipped with EDXA Falcon Energy System 60SEM was used for microscopic examination. Deteriorated small piece of paste specimen was dried in a vacuum desiccator for 1 day. This was sputter coated with a gold coating. The accelerating voltage is 20 kV.

3. Results and discussion

3.1 Strength deterioration and length change of cement matrix

The SDFs of OPC mortars immersed in 5% sodium sulfate solution are shown in Fig. 1. This confirms that water-cement ratio is a key factor in the compressive strength loss of OPC mortar samples exposed to sulfate attack. Namely, the SDF increased as the water-cement ratio increased. For example, after 510 days of immersion in sulfate solution, the SDFs of the mortars with water-cement ratio of 35%, 45% and 55% were about 38%, 64% and 92%, respectively.

Length change of OPC mortar specimens tested in present study was measured on the basis of ASTM C 1012. Length change of OPC mortar specimens with different water-cement ratio levels stored in a 5% sodium sulfate solution is presented in Fig. 2. It was clearly evident that mortar specimen with a higher water-cement ratio of 55% showed a significant expansion (0.817% after 180 days) in the solution. For mortar specimen with water-cement ratio of 35%, length change was as little as about 0.132% even at 510 days of sulfate exposure. The lower permeability of mortar specimen due to a low water-cement ratio restricted the diffusion of SO_4^{2-} ions forming the expansive products. The mortar specimens with water-cement ratio of 45% and 55% had disintegrated at 210 and 180 days of exposure to the sulfate solution, respectively, whereas mortar specimens with water-cement ratio of 35% showed a relatively low expansion at the same age. These data indicate that the sodium sulfate solution produces significant expansion in OPC mortar except a water-cement ratio of 35%.

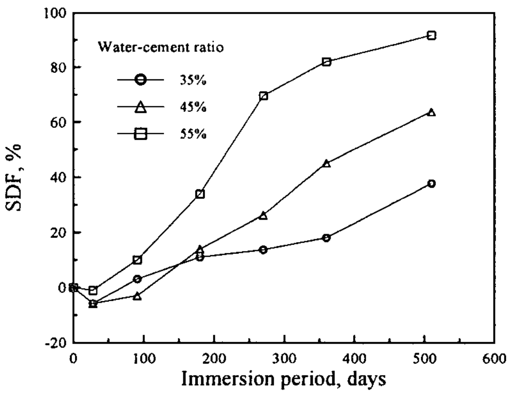

Fig. 1 Strength deterioration factor of OPC mortars

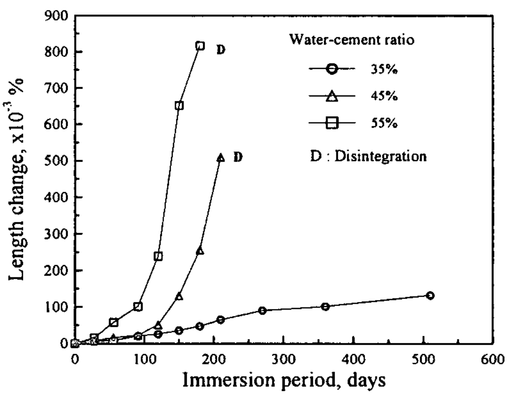

Fig. 2 Length change of OPC mortars

3.2 Microstructual observations

The x-ray diffraction pattern of the OPC paste specimen exposed to sodium sulfate solution is presented in Fig. 3. The surface of the paste sample had spalled and was mushy. The ettringite and thaumasite formed in the paste specimen led to much deterioration and was confirmed by XRD analysis. However, the main thaumasite peak was very intense compared with the ettringite peak at 9.1° 2θ. Because thaumasite and ettringite have similar crystal structure, actually, their XRD patterns show similarities. In particular, the two major peaks, at around 9.1° and 16.0° 2θ, are present in both minerals. Therefore, it is difficult to distinguish them when only small amounts are present, especially if both may be present in a paste sample. Unlike ettringite peak patterns, the thaumasite peaks are present at around 19.5, 23.4, 26.0 and 28.0° 2θ. The prominent evidence of thaumasite can be confirmed at 22.9° 2θ in XRD patterns. The XRD pattern also indicates the strong peaks for gypsum at around 32.2° and 11.7° 2θ. Additionally, the presence of portlandite was confirmed at 18.1° and 34.1° 2θ. This suggests that the possibility of further deterioration by sulfate attack remains on the paste.

The SEM image of a deteriorated OPC paste specimen immersed in sodium sulfate solution for 270 days is shown in Fig. 4. EDXA profile of the area marked with circle of the image showed the distribution of elements of O, Al, Si, S, and Ca. The profile is from an area close to the edge of the specimen and indicates the presence of ettringite, although a small Si peak was observed. This product seems to cause the extensive expansion by SO_4^{2-} attack in OPC mortar specimen, as previously presented in Fig. 2.

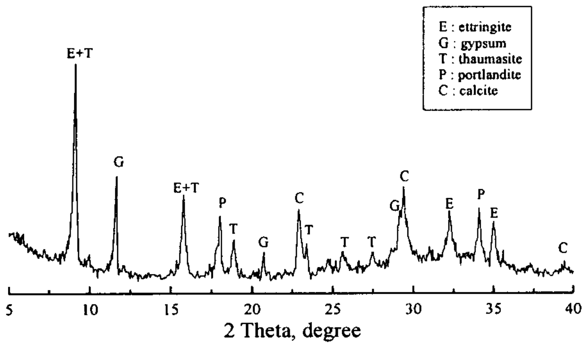

Fig. 3 X-ray diffraction analysis (510 days)

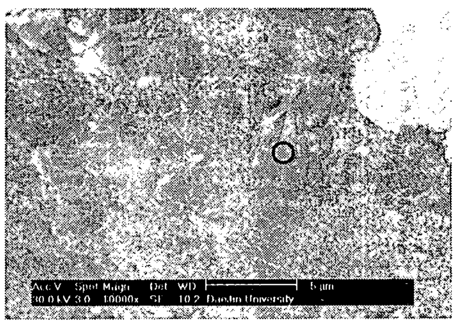

Fig. 4 SEM image (270 days)

4. Conclusions

(1) Based on the test results of SDF and length change, low permeability of mortar specimen with a lower water-cement ratio of 35% played a key role to resist sulfate attack.

(2) The capability for high absorption of sulfate ions into OPC mortars may explain the severe deterioration in terms of compressive strength loss and expansion.

(3) From the microstructural observations, the main deterioration mode of OPC matrix in sodium sulfate solution was the formation of ettringite and thaumasite.