DETERIORATION OF CEMENT MORTARS WITH DIFFERENT WATER CEMENT RATIO PARTIALLY IMMERSED IN SULFATE

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Abstract

Cement-based materials in sulfate rich areas will suffer from serious corrosion after semi-immersion. To study the degradation of cement mortars with different water cement ratio (w/c) partially exposed to sulfate solution, the mass change were employed to reveal damage progress. Moreover, porosity, erosion products and SO_4^{2-} content were monitored to study the damage mechanism. Results indicate that the porosity, SO_4^{2-} content and erosion products of mortars show an augment as the w/c increases. Correspondingly, high w/c leads to more severe mass change. XRD results reveal that the deterioration of drying portion is attributed to both chemical and physical sulfate corrosion. In addition, the water-soluble SO_4^{2-} content in drying portions is higher than that in immersed portion, implying more serious sulfate attack in drying portion.
Keywords: Sulfate attack; Partial immersion; Water cement ratio (w/c); Porosity; Erosion products

1. INTRODUCTION

Durability, the most important properties of cement-based materials, fails prematurely due to sulfate attack, which causes the dramatic life-span shortening of cement-based materials [1-3]. Over the few decades, many researches [4-6] have been done to describe the degradation behavior of cement-based materials under sulfate environment. Most studies focus on full immersion [7-9] and only a few researches concentrate on partial immersion [10, 11]. Under the condition of full sulfate immersion, sulfate can diffuse into the interior of cement-based materials and react

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with hydration products (hydrated calcium aluminate, $Ca(OH)_2$, C_3A, etc.) to form AFt and gypsum, resulting in expansion and cracking [4]. This is the most acceptable mechanism of chemical sulfate attack in full immersion. However, there are two main controversies about the mechanism of partial immersion. According to researches from Nehdi [12] and Harvey [13], concrete partially submerged in sulfate solution suffers from both chemical and physical attack (i.e., salt crystallization). This is in accord with the field experience that concrete partially immersed in sulfate suffers from surface scaling above ground level. On the contrary, Zanqun Liu [14] finds that Na_2SO_4 crystallization can't occur in the Portland cement concrete. Therefore, it's an important work deeply investigating the deterioration driving force of cement-based materials partially immerged in sulfate solution.

The performance of cement-based materials depends largely on w/c. According to the Jurlin's law [15], capillary absorption height is inversely proportional to the pore radius. Cement mortar with lower w/c has fine pore radius and stronger capillary absorption, which is conducive to the transport of sulfate solution and finally causes more serious erosion. Nehdi [16] has investigated the sulfate attack resistance of mortars with 0.3, 0.45 and 0.6 w/c. The results show that mortars with 0.45 w/c have the highest amount of crystal salt. On the contrary, other researchers [17, 18] get the opposite conclusion. Consequently, the degradation of cement-based materials with different w/c still needs investigation.

Contradictory data and theories still exist regarding the deterioration of cement-based materials partially immerged in sulfate solution. In present work, mass change, porosity, erosion products as well as SO_4^{2-} concentration have been studied to figure out the damage process and deterioration mechanism of cement mortars with different w/c partially immerged in sulfate solution.

2. MATERIALS AND METHODS

2.1. Materials and samples preparation

Portland cement (P·I 52.5) conforming to Chinese standard (GB 175-2007) was used for this investigation. The chemical composition and physical properties of cement are shown in Table 1. Tap water and river sand (<5 mm) with the fineness modulus of 2.6 were used.

Table 1: Chemical composition and physical properties of cement

Chemical composition (wt%)								Specific surface area (m^2/kg)	Specific gravity (g/cm^3)
CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O		
64.47	20.87	4.87	3.59	2.13	2.52	0.65	0.11	368.90	3.11

The water cement ratio (w/c) of cement mortars varies from 0.35 to 0.65 and the detailed mixing proportions of the samples are shown in Table 2. Cement and sand were added to a blender and stirred for 60 s, then the water was added to the blender and another 60 s was used for agitation, finally the mixture was blended with a high speed for 120 s. The fresh mortar was made into 40 mm × 40 mm × 160 mm samples.

All samples were cured at 20 ± 1°C and 90% RH for 60 days before testing.

Table 2: Mixing proportions of samples

Sample	Cement (g)	Sand (g)	Water (g)	w/c
W35	1000	3000	350	0.35
W53	1000	3000	530	0.53
W65	1000	3000	650	0.65

2.2. Partial sulfate immersion

Following 60 days curing, the mortar specimens were placed in room temperature environment to remove the extra water on the surface of mortars. After drying, the mortar simples were put into a plastic box containing 5 wt% Na_2SO_4 solution, the height of the solution is 60 mm. Besides, each container has a lid with six 40 mm × 40 mm holes to reduce water evaporation and the pH value of the solution was controlled based on Chinese standard (GB/T 50082-2009, the Na_2SO_4 solution was replaced every month). The container details are depicted in Fig. 1. In addition, containers were placed in a temperature of 35°C and relative humidity of 50%, which can accelerate the sulfate attack and simulate the environment of South China Sea.

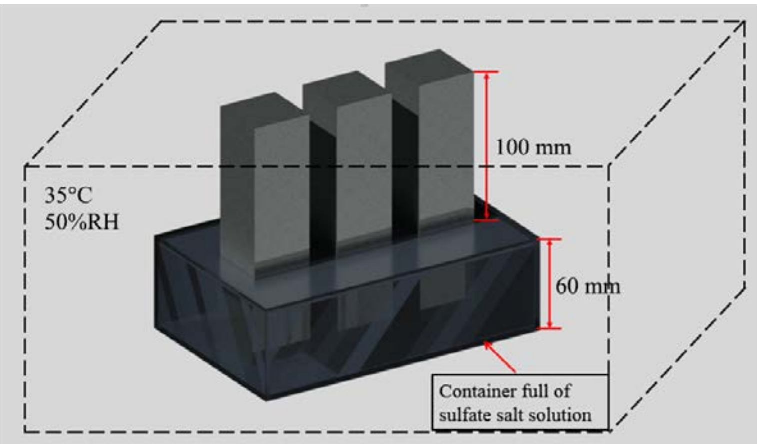

Figure 1: Diagrammatic drawing of partial sulfate immersion.

2.3. Test methodology

2.3.1. Mass

The mass of mortars were tested monthly during sulfate immersion. The crystalline substances and corrosion products on mortars surface were removed used a lint brush, then put mortars at room temperature for 6 h to release the excess water on the surface of mortars. Following that, an electronic balance (range: 5 kg, accuracy: 0.01 g) was employed to detect mass of mortars.

2.3.2. Mercury intrusion porosimetry

Mercury intrusion porosimetry (MIP, Micrometrics, AutoPore IV 9500, USA) technique was used to quantitatively evaluate the porosity of the samples after 6 months erosion. The pressure ranges from 0.5 to 60000 psia and the detectable pore diameter ranges from 3.6 nm to 400 μm. After being eroded for 6 months, the core portions were extracted from the drying part (under the efflorescence) with a deep of 5 mm - 10 mm. All samples were vacuum dried at 60 °C for 24 h before MIP tests to avoid structural damage.

2.3.3. X-ray diffraction analysis (XRD)

The X-ray diffraction data from 5° to 40° was collected by an X-ray diffractometer (Bruker, D8 Discover, Germany). The accelerating voltage, accelerating current, step size and dwelling time of tests were 40 kV, 30 mA, 0.02° and 0.15 s, respectively. Powders from drying part (under the efflorescence) was grounded to pass 200 mesh fineness to conduct the test.

2.3.4. SO_4^{-2} concentration

The water-soluble SO_4^{-2} concentration of mortars were measured by ICP (inductive coupled plasma emission spectrometer). Powders from drying portion (under the efflorescence) and immersed part (the bottom of the specimens) were collected and passed 200 mesh fineness and dried at 60°C to a constant weight. Subsequently, 3g dried powder was added to 100 mL distilled water and settled for 1 day, and the supernatant was diluted by distilled water to 0.1-100 ppm for ICP test.

3. RESULTS AND DISCUSSION

3.1. Mass change

The mass change of mortars after partial immersion in 5% Na_2SO_4 is presented in Fig. 2. Results show that the mass change of mortars includes two stages, i.e., slow decline and accelerated rise stages. The weight loss is attributed to the evaporation of water under lower RH. The weight starts to increase after a slow decline stage. The increment of weight is mainly due to the accumulation of erosion products. The weight of W65 and W53 starts to increase from the second and fifth corrosion months, respectively. However, the weight of M35 reduces all the time. In addition, W65 and W53 specimens rupture after corrosion for 7 and 9 months. Physical and chemical erosion leads to expansion and surface peeling of mortars, then causes the fracture of mortars. W35 mortar, however, has shown a constant reduction in weight during the 12 months and the mass of W35 decreases 1.33% after 12 months corrosion. The mass change results reveal that high w/c leads to more severe corrosion partially exposed to 5% Na_2SO_4.

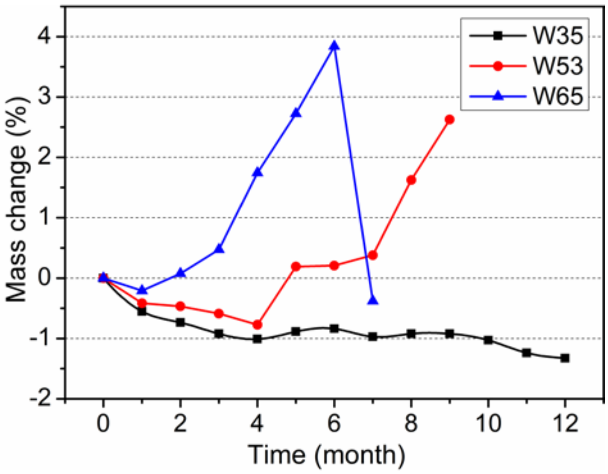

Figure 2: Mass change of mortars with different w/c partially immersed in 5% Na_2SO_4 solution.

3.2. Porosity of specimens

After 6 months corrosion, the drying portions were selected and the porosities were detected by MIP to estimate the effect of w/c on mortars partially immersed in sulfate solution.

The cumulative porosity of mortars after partially exposed to 5% Na_2SO_4 solution for 6 months in Fig. 3 shows that the porosity of cement mortars increases as the w/c augments. The porosities of W35, W53 and W65 are 9.09%, 11.90% and 20.45%, respectively. The high porosity caused by large w/c leads to a undesirable pore structure, increasing the connection of the pores, improving the capillary absorption and more sulfate ions penetrating into the drying portion (section 3.2) when cement mortar partially exposed to Na_2SO_4 solution. Besides, more sulfate ions will react with cement paste and crystallize to thenardite (section 3.2), finally causing more severe mass change (section 3.1).

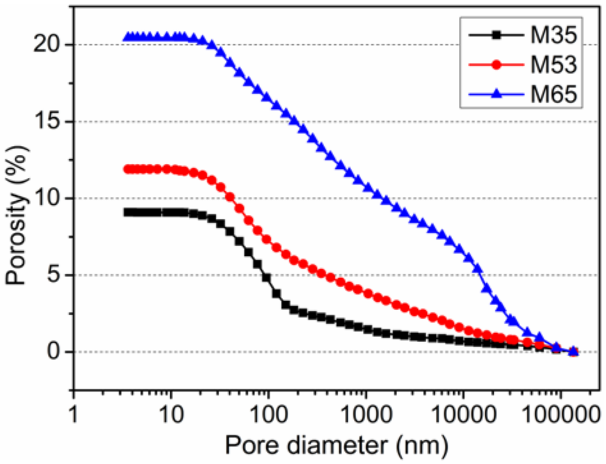

Figure 3: Porosity of mortars after partially exposed to 5% Na_2SO_4 solution for 6 months.

3.3. Erosion products

The XRD test has been employed to investigate the erosion products in drying portion (under the efflorescence zone) after 6 months erosion and the results have emerged in Fig. 4.

It can be observed from Fig. 4 that the erosion products (i.e., ettringite (AFt), gypsum and thenardite) are observed in all mortar specimens. AFt and gypsum are generated due to the chemical reaction between cement paste and Na_2SO_4. With respect to thenardite, it's mainly owing to the crystallization of Na_2SO_4 transported from the immersed portion. The results illustrate that the degradation of cement mortars partially exposed to sulfate solution is ascribed to both chemical and physical attack, which is in agreement with the Ref. [12]. Besides, the content of corrosion products shows an augmentation with the increased w/c. It's attributed to the large porosity caused by high w/c (section 3.2).

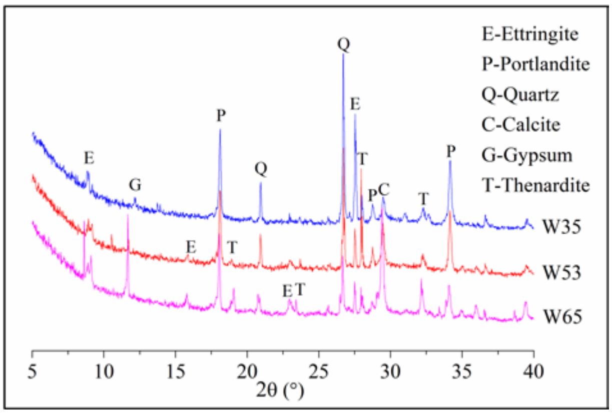

Figure 4: XRD patterns of mortar specimens with different w/c.

3.4. SO_4^{2-} diffusion

In order to evaluate the SO_4^{2-} diffusion of mortar under partially immersed in sulfate solution, the SO_4^{2-} concentration of mortar in drying portion (under the efflorescence) and immersed portion (the bottom of the specimens) after 6 months immersion has been tested and the results are presented in Fig. 5.

As can be obviously seen in Fig. 5 that the water-soluble SO24- concentration in drying portion is higher than that in immersed portion for all mortars. The reason is that SO 24- ions can transport from immersed part to drying part with water transportation by the capillary absorption, while the water can evaporate and SO24- ions will accumulate in drying part. It can be concluded that the drying portion with higher SO24- concentration suffers from more severe sulfate attack (both chemical and physical attack according to section 3.3). Besides, Fig. 5 also shows thatthe water-soluble SO24- concentration in both drying and immersed parts presents a gradually increment with the w/c increasing. Mortars with high w/c have larger

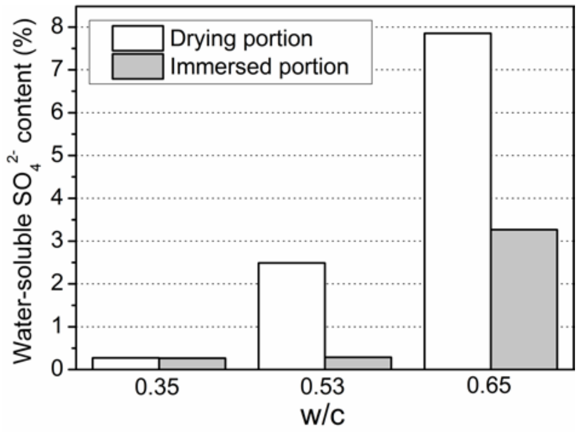

Figure 5: Water-soluble SO_4^{2-} content in drying/immersed portions of mortars with different w/c.

porosity (section 3.2) and better pore connection, leading to the enhanced capillary effect and finally resulting in higher sulfate concentration. This result is accord with the mass change observation.

4. CONCLUSIONS

This paper focuses on the deterioration behavior of cement mortars with different water cement ratio partially immersed in sulfate. From the experimental results obtained, the following conclusions are advanced:

(1) High w/c can increase the porosity of mortar, leading to more severe mass change;

(2) Both chemical and physical sulfate attacks are contributed to the degradation of drying part and the content of corrosion products (i.e., AFt, gypsum and thenardite) show an increase with the augmentation of w/c;

(3) The water-soluble SO_4^{2-} content in drying portions is higher than that in immersed portion, which can lead to more serious sulfate attack in drying portion.

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