In situ observing the erosion process of cement pastes exposed to different sulfate solutions with X-ray computed tomography

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HIGHLIGHTS

- The damage process of cement pastes in sulfate solutions was visually monitored by X-ray CT.
- The X-ray CT technique allows in situ monitoring the evolution of pore structure.
- The relationship between the crack volume fraction and erosion time is established.

ARTICLE INFO

ABSTRACT

The damage process of cement pastes exposed to different sulfate solutions (sodium sulfate solution, magnesium sulfate solution, a mixed solution of sodium sulfate and sodium chloride) was in situ quantitatively investigated by X-ray computed tomography (X-ray CT). The X-ray diffraction (XRD) was also employed to determine the content of corrosion products. The results show that the three-dimensional crack distribution of cement pastes for different immersion times can be extracted by using X-ray CT. When the solution contains the sulfate and magnesium ions, the specimen deteriorates faster. The presence of chloride ions alongside sulfate ions significantly reduces the degree and speed of sulfate attack. The porosity and pore number of specimens markedly decrease with the increase of immersion time when the pore volume exists between 0.01 and 0.1 mm^3. Gypsum and ettringite are formed to the least extent in the mixed solution of sodium sulfate and sodium chloride, and most evident for the magnesium sulfate solution. In addition, the relationship between the crack volume fraction and the erosion time of specimens in different sulfate solutions is established, respectively, which all conforms to a quadratic function relationship.

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1. Introduction

The deterioration of cement-based materials exposed to sulfate attack has become a serious problem throughout the world [1–5]. When the sulfate ions penetrate into the cement-based materials, chemical reactions between the solid phase and the sulfate ions occur, these chemical reactions can form ettringite as well as gypsum crystals. In turn, the ettringite and gypsum can lead to the strength of cement-based materials to gradually lost accompanied by surface spalling [6–9]. Furthermore, the marine environments contains not only sulfate ions, but also chloride ions and magne-

sium ions, which are also very harmful to the durability of cement-based materials constructions. In recent years, there are many works focused on the effect of chloride and magnesium ions on sulfate attack [10–13]. Such as Maes et al. [10] investigate the influence of chloride ions on sulfate ions by measuring length and mass change of specimens and resulted showed that the presence of chloride has the effect of reducing sulfate attack; Baghabra et al. and Rasheeduzzafar et al. [11,12] investigated the effect of magnesium ions and sulfate ions on the cement pastes and found that magnesium-sodium sulfate environment is more damaging to all cements in general and the mechanism of attack is predominantly controlled by the magnesium-oriented type of sulfate attack. Zhang et al. [13] determined that the expansion of concrete under attack of sulfate and sulfate–chloride ions. The research results indicated that the higher the concentration of chloride ions in the mixed solution, the lower the expansion of concrete speci-

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mens. However, the traditional methods for studying the sulfate attack of cement-based materials are to measure the mass change, strength change, observe the erosion products using scanning electron microscopy (SEM) and X-ray diffraction (XRD). These methods can't study the damage evolution of three-dimensional. X-ray computed tomography (X-ray CT) provide an opportunity to track the damage evolution of three-dimensional internal structures of cement-based materials in situ.

X-ray CT is an analytical tool developed in recent years, which uses X-rays to scan samples and reconstruct the internal spatial distribution characteristics [14,15]. X-ray CT has a wide range of applications. For example, the porous and multiphase structure of concrete can be characterized by X-ray CT with different grayscale images [16–18]. X-ray CT has the advantage of high resolution in the observation of fine cracks and micropores, and it can be used to observe cracks and pores in the size range of dozens of microns [19].

This paper presents some researches into the damage process of cement paste exposed to different sulfate solutions. In this study, the changes of crack volume, crack width, pore distribution and gray value distribution with time were monitored for cement paste exposed to different sulfate solutions by using X-ray CT. X-ray diffraction (XRD) analysis is performed in order to study the reaction products.

2. Experimental

2.1. Materials

To perform the experiments, a Chinese standard P. I type Portland cement was used. The composition is given in Table 1. The water-to-cement ratio (w/c) was maintained at 0.55 by weight.

2.2. Sample preparation

Cylinders with a diameter of 35 mm and height of 50 mm were prepared and then these specimens were cured at 20 ± 3 °C and under 95% of relative humidity for 60 days. After that, the specimens were placed in 5 wt% (mass fraction) sodium sulfate solution, 5 wt% magnesium sulfate solution, a mixed solution of 5 wt% sodium sulfate and 20 wt% sodium chloride, respectively.

2.3. Experimental methods

In this study, the model of X-ray CT scanner was Y.CT Precision S X-ray CT scanner (YXLON, Germany). The sample platform can rotate for 360°. The working voltage and current of X-ray tube are 195 kV and 0.34 mA. The X-ray CT raw data are collected by 1530 projection images that recorded by a CCD camera with an array of 1024 × 1024 pixels. The 3D voxel size was 0.052 mm × 0.052 mm × 0.054 mm. First, the specimens were scanned by X-ray CT before immersed in different sulfate solutions, and then put them into different sulfate solutions. After the specimens were immersed for 3 months, 6 months, 9 months and 12 months, the progress of sulfate attack was monitored in situ by X-ray CT, respectively.

The X-ray diffraction of D8-ADVANCED was used to quantitatively analyze the erosion products of the cement paste immersed in sulfate solutions for 0 months, 3 months and 9 months. The working voltage was 40 kV and the current was 40 mA, and the angle scan range was chosen from 5° to 80°.
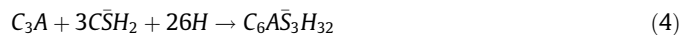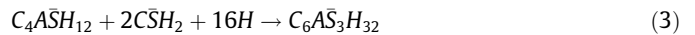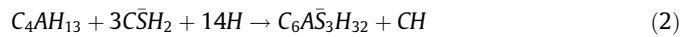
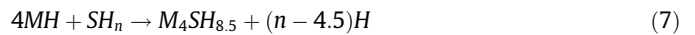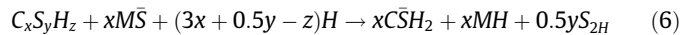## 3. Results and discussion

3.1. Visual inspection

Fig. 1 shows the outer surface of the cement paste exposed to 5 wt% sodium sulfate solution for different times. As shown in Fig. 1, small cracks appeared on the surface of the specimen after immersion for 3 months. With the increase in immersion time, the width of the cracks increases; furthermore, the cracks become more numerous on the surface of the specimen. Fig. 2 shows the outer surface of cement paste exposed to 5 wt% magnesium sulfate solution for different times. After 9 months of immersion, many cracks at the top edges of specimen was observed. In addition, from the outer surface of specimen, it also can be seen that the cement paste immersed in magnesium sulfate solution is more seriously damage. The outer surface of cement paste immersed in a mixed solution of 5 wt% sodium sulfate and 20 wt% sodium chloride is shown in Fig. 3. A small crack appeared on the surface of specimen when the immersion time was up to 6 months. Comparing Figs. 1 and 2, it reveals that there is greater erosion of specimens when sulfate and magnesium ions coexist in the erosion solution. The reason accounting for this phenomenon is that when the sulfate ions penetrated from sulfate environments react with calcium hydroxide (CH) in pore solution to produce the gypsum ($C\bar{S}H_2$), according to the following equation:

$$CH + SO_4^{2-} \rightarrow C\bar{S}H_2 + 2OH^- \tag{1}$$

Gypsum could precipitate as an intermediate phase in cement paste, and continue to react with calcium aluminates to produce the ettringite ($C_6A\bar{S}_3H_{32}$), according to the following equation:

$$C_4AH_{13} + 3C\bar{S}H_2 + 14H \rightarrow C_6A\bar{S}_3H_{32} + CH \tag{2}$$

$$C_4A\bar{S}H_{12} + 2C\bar{S}H_2 + 16H \rightarrow C_6A\bar{S}_3H_{32} \tag{3}$$

$$C_3A + 3C\bar{S}H_2 + 26H \rightarrow C_6A\bar{S}_3H_{32} \tag{4}$$

When magnesium and sulfate ions coexist, the sequential reactions of magnesium sulfate ($M\bar{S}$) with the cement hydration products are shown below:

$$CH + M\bar{S} + 2H \rightarrow C\bar{S}H_2 + MH \tag{5}$$

$$C_xS_yH_z + xM\bar{S} + (3x + 0.5y - z)H \rightarrow xC\bar{S}H_2 + xMH + 0.5yS_{2H} \tag{6}$$

$$4MH + SH_n \rightarrow M_4SH_{8.5} + (n - 4.5)H \tag{7}$$

This attack is, therefore, characterized by softening and deteriorating of the surficial layers of the hardened cement paste as well as the profuse formation of gypsum, brucite and M-S-H. Thereby accelerating the diffusion of magnesium ions and sulfate ions to the interior of the specimen [20–22]. Comparing Figs. 1 and 3, it reveals that the presence of chloride ions can significantly alleviate the degree and speed of sulfate attack on a specimen when sulfate ions coexist with chloride ions. The reason for this is that when sulfate ions and chloride ions coexist, the transmission rates of chloride ion is greater than that of sulfate ions. Chloride ions can penetrate the specimen more rapidly and react with tricalcium

Table 1
Chemical compositions of cement.

Material	Chemical composition/wt%								Specific surface area/(m²·kg⁻¹)	Density/(kg·m⁻³)
	SiO₂	MgO	Al₂O₃	Fe₂O₃	CaO	Na₂O	K₂O	LOI		
Cement	20.87	2.13	4.87	3.59	64.47	0.11	0.65	0.77	309	3115