

Damage Evolution of Concrete Exposed to Sulfate Attack Under Drying-Wetting Cycles

Lei Jiang¹ and Ditao Niu^{2,*}

¹College of Civil Engineering and Architecture, Anyang Normal University, Anyang, 455000, P.R. China; ²College of Civil engineering, Xi'an University of Architecture and Technology, Xi'an, 710055, P.R. China

Abstract: The damage evolution of concrete subjected to drying-wetting cycles in different concentration of sodium sulfate solution was investigated based on micro and macro-observations. Through the experiment, weight loss, compressive strength loss and the damage layer thickness of concrete were measured after different drying-wetting cycles. The mechanical properties degradation in the damage layer of concrete was also analyzed. Furthermore, the scanning electron microscopy and X-ray diffraction were used to investigate the corrosion products of concrete, and the damage mechanism was also investigated by the modern microanalysis techniques. The test results show that the deterioration degree of physical properties of concrete specimens increases with increasing concentration. Weight loss of specimens caused by sulfate attack is not obvious compared with the other evaluation index. When the damage layer thickness of concrete is thicker as well as the ultrasonic speed is lower, indicating that the deterioration degree of concrete increases, and the compressive strength loss in damage layer is serious. It was also found that the compressive loss of concrete is correspond with the observations for the damage layer thickness. Additionally, the main corrosion products of concrete in sulfate solutions subjected to drying-wetting cycles were confirmed to be ettringite and gypsum, and the quantity of corrosion products formed is proportional to the concentration of the solution.

Keywords: Concrete, damage layer thickness, drying-wetting cycles, sodium sulfate.

1. INTRODUCTION

Sulfate exists widely in seawater, groundwater, salt lake and sulfate soil, which is one of the most widespread and common forms of damage to concrete [1, 2]. The deterioration of concrete constructions resulting from sulfate attack is a severe problem affecting the durability and service life of concrete structures. Sulfate attack can manifest in the form of expansion and cracking of concrete. The deterioration of concrete caused by sulfate attack can take the form of expansion, cracking, loss of strength of concrete, and the damage layer of concrete is formed from the outside to the inside, eventually lead to damage of concrete. In sulfate environment, the elements of concrete construction situated in water table fluctuation, tidal zone and splash zone will suffer from more complex attack because of the drying-wetting cycles, which can accelerate the deterioration of concrete [3, 4].

The deterioration of concrete caused by sulfate attack is a process from outside to inside, the ultrasonic penetration testing can be used to locate the interface between solid and corroded concrete. Along with the development of ultrasonic testing technique, testing of the damage layer was widely used in the durability of concrete research. Naffa *et al.* [5] showed that it is possible to detect and characterize concrete cover degradation using high-frequency ultrasound. Chu *et al.* [6] suggested that the ultrasonic testing method can be

used to determine the damage caused by sulfate attack in concrete. Zhang *et al.* [7] investigated the damage thickness of concrete in sodium chloride solution exposed to freeze-thaw cycles based on ultrasonic detection methods. Zhang *et al.* [8] obtained that the interface between solid and corroded concrete can be determined by using ultrasonic penetration testing method.

Many researches about the damage process of concrete under sulfate attack have focused on expansion, mass change, the dynamic modulus of elasticity and the changes of mechanical properties of concrete [9-11]. However, little information is available about the depth of degradation of concrete under the coupled effect of sulfate attack and drying-wetting cycles. In this paper, weight loss and compressive strength loss of the concrete exposed to different concentration of sodium sulfate solution under drying-wetting cycles are investigated. Based on ultrasonic detection method, the damage thickness of the concrete specimen is detected according to the propagation speed difference of wave velocity in different materials [12]. The mechanical properties degradation of the damage layer of concrete is also analyzed, and the compressive strength in damage layer is obtained. Furthermore, the microstructure and corrosion products of concrete are determined using the scanning electron microscopy (SEM) and X-ray diffraction (XRD).

2. MATERIALS AND METHODOLOGY

A Chinese standard Ordinary Portland Cement (OPC) of PO 42.5R produced by the Cement Factory of Tongchuan was adopted. Grade II fly ash from the Weihe Power Station,

river sand with a fineness modulus of 2.69 and coarse aggregate of crushed basalt stone with a diameter of 5 mm to 16 mm were used in the test. A naphthalene-type superplasticizer was used, and the dosage was adjusted to keep the slump of fresh mixed concrete in the range of 50 mm to 120 mm. The tap water was adopted as mix water. The chemical composition of cement and fly ash is shown in Table 1.

Table 1. Chemical composition of OPC and fly ash.

Constituent (wt.%)	SiO ₂	Al ₂ O ₃	CaO	MgO	SO ₃	Fe ₂ O ₃
OPC	21.66	5.13	64.37	1.06	2.03	5.25
Fly ash	49.02	31.56	4.88	0.83	1.2	6.97

In this experiment, the water binder ratio was 0.45. A series of sodium sulfate solution with the concentration (by mass) of 1%, 5% and 10% were used (denoted as N1, N5, N10 respectively). All specimens were demolded after 24 h of casting and cured in a condition of $20 \pm 3^\circ\text{C}$ and 95% relative humidity until the age of testing. The mixture proportion of the concrete is given in Table 2.

At the age of 90 days curing, the concrete specimens exposed to sulfate solution under drying-wetting cycles up to 360 days (see Fig. (1)). One wet-dry cycle lasted 15 days. First, the specimens were continuously immersed in the test solution for 7 days, and then were moved into the air to dry naturally for another 8 days. In this study, the drying state was natural drying in the air, which was more relevant to in-service conditions. Specimens of $100\text{ mm} \times 100\text{ mm} \times 400\text{ mm}$ prisms were used for the study of the weight loss and the damage thickness of concrete after every 30 days. Specimens of $100\text{ mm} \times 100\text{ mm} \times 100\text{ mm}$ cubes were used for the study of the compressive strength loss and the analysis of attack products of concrete by SEM and XRD at certain exposure times.



Fig. (1). Concrete specimens exposed to sulfate solution under drying-wetting cycles.

Table 2. Mix proportion of concrete.

Water-binder ratio	Cement /(kg·m ⁻³)	Fly ash /(kg·m ⁻³)	Water /(kg·m ⁻³)	Aggregate /(kg·m ⁻³)	Sand /(kg·m ⁻³)	Superplasticizer/%
0.45	285	70	160	1300	585	0.5

The damage thickness of the concrete specimen is detected according to the propagation speed difference of wave velocity in different materials [12]. A one-side non-destructive testing method was used to detect the surface damage of concrete by using a high-accuracy nonmetal ultrasonic analyzer according to CECS21-2000 [13]. Testing of weight loss of concrete was carried out in accordance with GB/T 50082 [14]. The compressive strength property measurement was carried out according to the GB/T 50081[15]. The microstructure of deteriorated surfaces were examined by SEM and equipped with an energy dispersive spectroscopy (EDS) detector. Furthermore, XRD method (Cu-K α) was performed on samples at regular intervals in order to identify any compounds formed during the exposure to sulfate solutions under drying-wetting cycles.

3. RESULTS

3.1. Weight Loss

As can be seen from the Fig. (2), the weight loss of concrete specimens exposed to sulfate solution under drying-wetting cycles exhibits three distinct stages. In Stage I, the weight loss decreases until to 30 days. In Stage II, from 30 days to 150 days, the weight loss keeps steady in the period. In Stage III, the weight loss increases at a steady rate after 150 days. The rate of the increase was seen to be higher for N10. In addition, there is no obvious distinction between N1 and N5. However, the weight loss of specimens caused by sulfate attack is unobvious compared with the compressive strength loss.

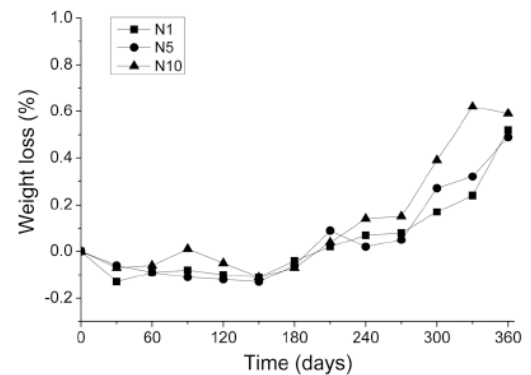


Fig. (2). Weight loss in concrete exposed to sulfate solution under drying-wetting cycles.

3.2. Compressive Strength Loss

Fig. (3) shows the results of compressive strength change of concrete exposed to different concentrations of sulfate solutions. The behavior of concrete specimens under the three solutions is similar. There is an initial increase in the compressive strength, the reason may be that the attack

products deposited in the pore spaces of concrete. However, the compressive strength shows a steady drop of concrete specimens in further test, and the damage rate of concrete has been greatly accelerated after 240 days of drying-wetting cycles. Obviously, the rate of the drop was seen to be higher for the high concentration solutions. As can be seen from the Fig. (3), the compressive strength of N1, N5 and N10 decrease by 7.1%, 10.2% and 14.6% after 360 days, respectively. The results of compressive strength loss are in good agreement with what were suggested by Najimi, *et al.* [16].

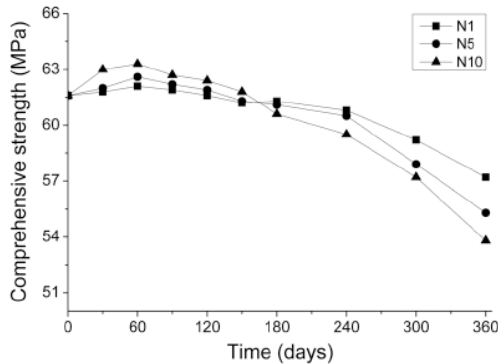


Fig. (3). Compressive strength loss in concrete exposed to sulfate solution under drying-wetting cycles.

3.3. The Damage Layer Thickness of the Concrete

It is known that the presence of horizontal layers that are formed when concrete is exposed to an aggressive environment. The damage of concrete caused by sulfate attack is a process from outside to inside. By measuring the damage layer thickness of concrete (defined as H_f) and the ultrasonic velocity in the damage layer (defined as V_f), the deterioration degree of concrete could be estimated effectively. Since the damage layer of concrete is not obvious at the beginning of the corrosion, the test is started from 210 days of drying-wetting cycles.

Table 3 shows the results of damage layer of concrete exposed to different concentrations of sulfate solutions. It is shown that the ultrasonic velocity V_f in the damage layer decreases with corrosion time increases. The V_f loss of N1, N5 and N10 under drying-wetting cycles of 360 days are 5.78%, 11.54% and 16.52%, respectively. Obviously, the V_f

of the specimens was seen to decrease with increasing concentration of sulfate solutions. The results for H_f change indicate a dependence on the concentration of the solution. As seen from Table 3, the rate of the increase in H_f of concrete was seen to be higher for the high concentration solution. Furthermore, the H_f increases with an increase of the corrosion time, which exhibits the opposites trend compared with V_f . It was found that the results of the temporal variation of H_f are in good agreement with those of compressive strength loss after 240 days shown in Fig. (3). When the damage layer thickness of concrete is thicker as well as the ultrasonic speed is lower, indicating that the deterioration degree of concrete increases.

3.4. The Compressive Strength in Damage Layer

The corroded concrete specimen under the coupling effect of drying-wetting cycles and sulfate solution is mainly composed by the damage layer and the internal solid concrete. When the damage layer thickness of concrete is thicker and the ultrasonic speed is lower, the compressive strength loss in damage layer is serious. So the compressive strength loss in damage layer has great influence on the bearing capacity of concrete structure. It is important to study the mechanical properties degradation in damage layer of concrete.

The following Eq. (1) was used to calculate the compressive strength loss in damage layer.

$$f'_c A = f'_c A_c + f'_f A_f \quad (1)$$

where, f'_c is the compressive strength of corroded concrete after certain exposure times (MPa), which can be obtained from the test as shown in Fig. (3); f'_c is the compressive strength of internal solid concrete (MPa), which can be defined as the compressive strength of concrete under curing condition at the same corrosion time; f'_f is the compressive strength in damage layer (MPa); A is the section area of concrete specimen (mm^2), $A=10^4 \text{mm}^2$; A_c is the section area of internal solid concrete (mm^2), $A_c=(100-2h_f)^2 \text{mm}^2$; A_f is the section area of damage layer concrete (mm^2), $A_f=(10^4 - A_c) \text{mm}^2$.

The calculated results of the compressive strength in damage layer exposed to drying-wetting cycles in different concentrations of sulfate solution are listed in Table 4. As

Table 3. The calculated H_f and V_f of concrete exposed to sulfate solution under drying-wetting cycles.

No.	N1		N5		N10	
	Corrosion time/d	$V_f/\text{km}\cdot\text{s}^{-1}$	H_f/mm	$V_f/\text{km}\cdot\text{s}^{-1}$	H_f/mm	$V_f/\text{km}\cdot\text{s}^{-1}$
	210	4.51	7.55	4.50	9.51	4.50
	240	4.47	8.23	4.50	10.56	4.46
	270	4.46	10.14	4.42	11.61	4.36
	300	4.39	11.67	4.34	12.97	4.21
	330	4.34	13.01	4.15	14.49	4.06
	360	4.25	14.17	3.92	16.70	3.75

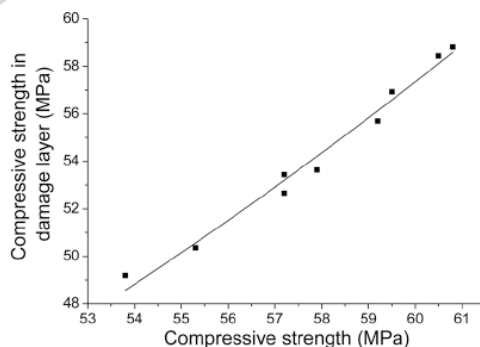
Table 4. Calculated results of the compressive strength in damage layer of concrete.

No.	Corrosion time	A_i/mm^2	A_e/mm^2	A_f/mm^2	f'_c/Mpa	f_c/Mpa	f_f/Mpa
N1	240d	10000	5875.99	4124.01	60.8	62.2	58.81
	300d	10000	5474.37	4525.63	59.2	62.1	55.69
	360d	10000	5135.13	4864.87	57.2	61.5	52.66
N5	240d	10000	5484.53	4515.47	60.5	62.2	58.44
	300d	10000	5043.47	4956.53	57.9	62.1	53.63
	360d	10000	4434.39	5565.61	55.3	61.5	50.36
N10	240d	10000	4878.99	5121.01	59.5	62.2	56.93
	300d	10000	4348.43	5651.57	57.2	62.1	53.43
	360d	10000	3742.43	6257.57	53.8	61.5	49.19

can be seen from the table, the compressive strength in damage layer of N1, N5 and N10 decrease by 14.4%, 18.1% and 20% after 360 days, respectively. Compared with the test results in Fig. (3), the compressive strength loss in damage layer is more serious. Obviously, the rate of the drop in compressive strength loss in damage layer was seen to be higher for the high concentration solution. Generally, the diffusion coefficient of sulfate ions in concrete specimens exposed to 10% sulfate solution is greater than that in the lower concentration. High rate of sulfate ingress in high concentration provides more free sulfate ions to chemically react with the cement hydration products. This is partially the reason why the damage layer thickness of concrete is thicker as well as the compressive strength loss in damage layer is more serious in the same time.

By comparing the test results of Fig. (3) and Table 4, it is shown that the compressive strength of corroded concrete in sulfate solution under drying-wetting cycles is correspond with the observations for the compressive strength in damage layer. The relation curve is shown in Fig. (4), and the quantitative fitting equation (Eq. (2)) based on the regression of experimental data is obtained. On the basis of this empirical formula, the compressive strength in damage layer can be calculated more simply. It also has significant meaning on the analysis of concrete damage degradation and the bearing capacity of corroded concrete calculation.

$$f_f = 11.489 \exp(0.268 f'_c) \quad (2)$$

**Fig. (4).** Relationship between the compressive strength in damage layer and the compressive strength of the corroded concrete.

3.5. Microstructural Investigations by SEM

Figs. (5) present the microstructure observation of concrete subjected to drying- wetting cycles in the sodium sulfate solution. It is clearly seen from the Fig. (5a) that the cement hydration products form with each other in a continuous phase with no microcracks before drying-wetting cycles. During the initial corrosion time, the calcium hydroxide crystal began to erode with a slightly serrated border. Little needle-like crystals can be observed around some part of the calcium hydroxide crystals (see Fig. (5b)). As shown in Fig. (5c), needle-like crystals and some microcracks can be clearly observed from the micrograph. The EDS technique was used to characterise the chemical compositions of the needle crystals. Careful observation of the EDS results showed that needle crystals consist of the elements Al, Si, S and Ca, which indicated that the needle crystals are ettringite crystals (see Fig. (5d)). As shown in Fig. (5e), short columnar crystals can be observed the interface transition zone between paste and aggregate of concrete. The EDS spectra of these crystals indicated that they are gypsum, which detected the elements S and Ca (Fig. (5f)).

3.6. XRD Analysis

Fig. (6a) shows the XRD patterns of concrete after drying-wetting cycles for a period of 180 days. The results show that the ettringite and gypsum peaks are strong, which demonstrates that they are main corrosion products. Compared with XRD pattern of N5 and N10, the diffraction peaks of ettringite and gypsum of N1 were not obvious. The concentrations of gypsum and ettringite of concrete with highest concentration are higher than those for the lower concentration of solution. This may be explained as the low concentration of solution delayed the diffusion coefficients of sulfate ions in concrete, thus reducing the amount of corrosion products caused by the chemical reactions between sulfate and hydration products. Moreover, the quantity of gypsum in concrete is less than that of ettringite in the experiment, and no gypsum is checked at 180d when the concentration of sulfate solution is 1%.

Fig. (6b) shows the XRD patterns of N1, N5 and N10 exposed to sodium sulfate attack after drying-wetting cycles for a period of 270 days. Obviously, gypsum and ettringite

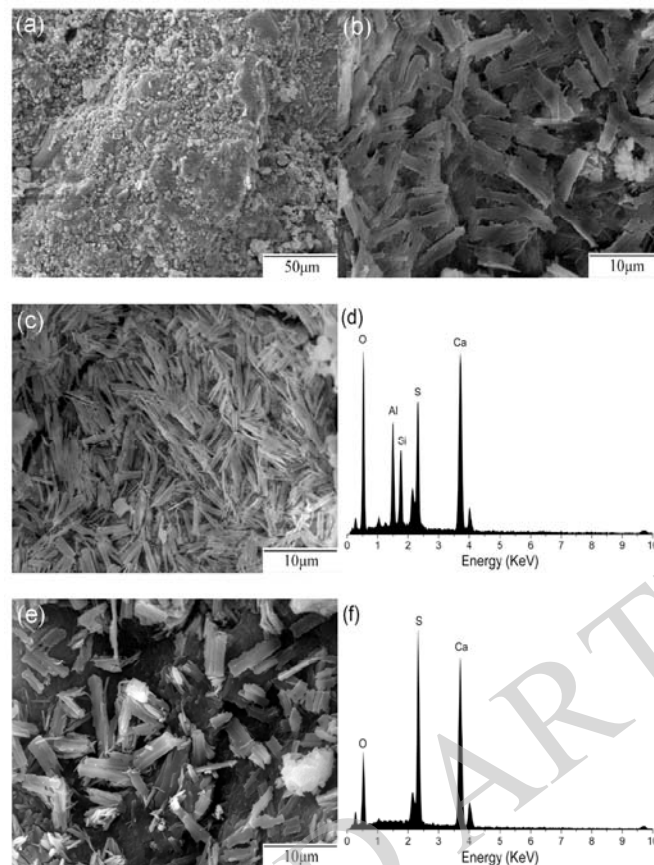


Fig. (5). Microstructure of concrete specimens exposed to sodium sulfate solution under drying-wetting cycles.

are also main corrosion products, and the concentrations of gypsum and ettringite increase with the corrosion time. Moreover, the concentration of calcium hydroxide gradually decreases along with the corrosion time growth.

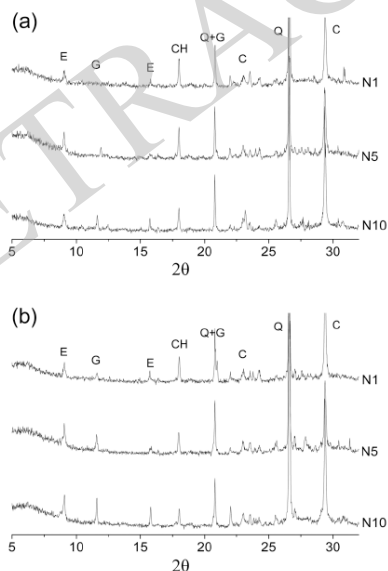


Fig. (6). XRD patterns of concrete exposed to different concentration of sodium sulfate solution under drying-wetting cycles. (a) 180d and (b) 270d. (E:ettringite; G:gypsum; CH: calcium hydroxide; Q:quartz; C:calcite).

CONCLUSION

The changing process of weight loss of concrete in the three sulfate solutions can be classified to three stages: (I) decreased stage, (II) steady stage and (III) increased stage. Weight loss of specimens caused by sulfate attack is not obvious compared with the other evaluation index. The compressive strength loss of concrete exhibit the following three periods: (I) increased period, (II) decreased period and (III) accelerating decreased period. The rate of the drop in compressive strength loss of concrete was seen to be higher for the high concentration solutions.

By measuring the damage layer thickness of concrete by pulse velocity, the deterioration degree of concrete could be estimated effectively. When the damage layer thickness of concrete is thicker as well as the ultrasonic speed is lower, indicating that the deterioration degree of concrete increases. The compressive strength loss of concrete is well correspond with the observations for properties of the damage layer. The deterioration degree of concrete specimens increases with an increase of sulfate ions concentration. Furthermore, the compressive strength in damage layer can be calculated according to the test results of the compressive strength after different drying-wetting cycles.

Additionally, the main corrosion products of concrete in sulfate solutions subjected to drying-wetting cycles were confirmed to be ettringite and gypsum by using the modern microanalysis techniques. The quantity of corrosion products in concrete were seen to increase and the corresponding

amount of calcium hydroxide decreases steadily with an increase of the concentration of sulfate solution. The quantity of gypsum in concrete is less than that of ettringite in the experiment, and some gypsum is checked only after a certain corrosion time when the concentration of sulfate solution is 1%.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

This project was supported by Program for Changjiang Scholars and Innovative Research Team in University (IRT13089).

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Received: September 16, 2014

Revised: December 23, 2014

Accepted: December 31, 2014

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