

Damage of concrete attacked by sulfate and sustained loading

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Abstract: The damage processes of ordinary concrete and high strength concrete, attacked by solutions of 2.5%, 5.0% and 10% Na_2SO_4 (mass fraction) are studied. And the effects of flexural loads with stress ratios of 25% and 50% of the initial flexural strength on the damage process of concrete are also investigated. The results show that the damage process of concrete attacked by sulfate salt exhibits an initial damaged stage, a performance improving stage and a performance worsening stage. When the concentration of Na_2SO_4 in a solution increases from 2.5% to 5.0%, the service time of the concrete decreases approximately 25%. Furthermore, it decreases to even 40% with an increase in a Na_2SO_4 concentration up to 10%. And the flexural load accelerates the deterioration rate of the concrete in the latter period. The stress ratio increases from 0 to 25%, the failure time of the concrete decreases 15%; and the failure time decreases between 25% and 35% when the stress ratio increases from 25% to 50%. In addition, sulfate corrosion products of concrete are studied by SEM (scanning electron microscopy), EDS (energy disperse spectroscopy) and XRD (X-ray diffraction).

Key words: concrete; sulfate; flexural load; microstructure

Abundant inorganic sulfates exist in salt lake solutions and the surrounding soil in the northwest of China; for example, the concentration of SO_4^{2-} is 36 445 mg/L in the inner Mongolia salt lake solution, and the SO_4^{2-} concentration is 12 728 mg/L in Bositeng Lake's groundwater, where concrete structures attacked by sulfates have been reported^[1-2]. Additionally, deterioration of concrete structure due to sulfate corrosion has been reported in California, South Dakota, Magdeburg and west of Canada^[3]. With regard to the concrete damaged by sulfate, many researchers have reported their research results^[4-7]. Jiaozhou Bay sub-sea tunnel is the second one in China, where SO_4^{2-} concentrations of 2 560 mg/L exist in the groundwater and inorganic sulfate salts occur in surrounding rocks which may release SO_4^{2-} into the groundwater under high water pressure. Both lead to high concentrations of SO_4^{2-} and, therefore, may damage the shotcrete and tunnel lining concrete structure. Besides, sub-sea tunnel lining concrete resists not only the compressive loading, but also the flexural load according to its structure type, for instance, a flexural load with 0.65 MPa impacted in the dome of tunnel lining^[8]. Obviously, sub-sea tunnel

concrete service time suffers from the multiple damage factors of sulfate corrosion and sustained loading. However, some reports of concrete damage by sulfates and loading are qualitative conclusions rather than quantitative ones^[9].

Therefore, this study is conducted to assess the damage processes of concrete caused by SO_4^{2-} with different concentrations and to assess the deterioration of concrete caused by multi-influences of sulfate ions and sustained loading.

1 Experimental Procedure

1.1 Materials

A Chinese standard P·II·42.5 Portland cement similar to the ASTM type I ordinary Portland cement, with a compressive strength of 42.5 MPa at an age of 28 d, is provided for this experiment by Jiangnan Cement Corporation in China. Its chemical composition is shown in Tab. 1. River sand with a fineness modulus of 2.6, and a coarse aggregate of crushed limestone with a maximum size of 10 mm are used in the experiment. A naphthalene-type super-plasticizer is used and the dosage is adjusted to keep the slump of fresh concrete in the range of 100 to 160 mm. Two sets of concrete are used in this investigation. One set is high strength concrete (HSC) with a strength grade of C60, and the other is ordinary concrete with a strength grade of C30. The mixture proportions and the corresponding compressive strengths of the concretes are given in Tab. 2.

1.2 Testing programs

The concrete specimens (40 mm × 40 mm × 160 mm) are cast and cured at room temperature with modules. The mould is removed after 24 h. Then, all specimens are cured under conditions of (20 ± 3) °C and 95% relative humidity for a period of 60 d. Two erosion regimes are applied to investigate the damage process of the concrete. One is natural immersion regime and the other is an accelerated regime. For the natural immersion regime, concrete specimens from each mixture are submerged in a Na_2SO_4 solution (2.5%, 5.0% and 10% by the mass fraction of Na_2SO_4) at room temperature for about 1 000 d. For the accelerated regime, concrete specimens are subjected to drying-immersion cycles: First, concrete specimens are dried at 60 °C for 24 h, then cooled in air at room temperature for 3 h, and finally submerged in the above-mentioned solution at room temperature for 45 h.

The relative dynamic modulus of elasticity E_{rd} of the concrete is measured by using a high-accuracy nonmetal ultrasonic analyzer^[10]. According to the test procedure, the specimen is considered to be a failure if the E_{rd} drops to 60% or less. Mass change, which is determined by Eq. (1), is measured by an electron balance with a precision of 0.1 g.

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Tab. 1 Chemical compositions of cement used in experiment

Compositions	w(SiO ₂)	w(Al ₂ O ₃)	w(Fe ₂ O ₃)	w(CaO)	w(MgO)	w(SO ₃)	Loss	%
P·Ⅱ 42.5	21.66	5.13	5.25	64.37	1.06	2.03	0.5	100

Tab. 2 Mix proportion and compressive strength of concrete

Sample	Mix proportion of concrete/(kg·m ⁻³)			m(W)/m(C)	Compressive strength/MPa	
	Cement	Sand	Aggregate		28 d	180 d
OPC	350	760	1 140	0.45	43.0	54.5
HSC	540	670	1 134	0.29	77.5	83.9

Note: m(W)/m(C) is the mass ratio of water to cement.

$$\Delta W = \frac{G_0 - G_t}{G_0} \times 100\% \quad (1)$$

where ΔW is mass change and G_0 and G_t are the weights of the concrete specimens at an age of 60 d curing and at an exposure period of t (g). The sustained flexural load setting was designed by Southeast University. And the concrete specimens are loaded for 4-point-flexural with stress ratios of 25% and 50% of the initial flexural strength.

2 Results and Discussion

2.1 Deterioration of concrete in sulfate solution

The deterioration of the concrete in solutions of 2.5%, 5.0% and 10% Na₂SO₄ is illustrated in Fig. 1. The damage

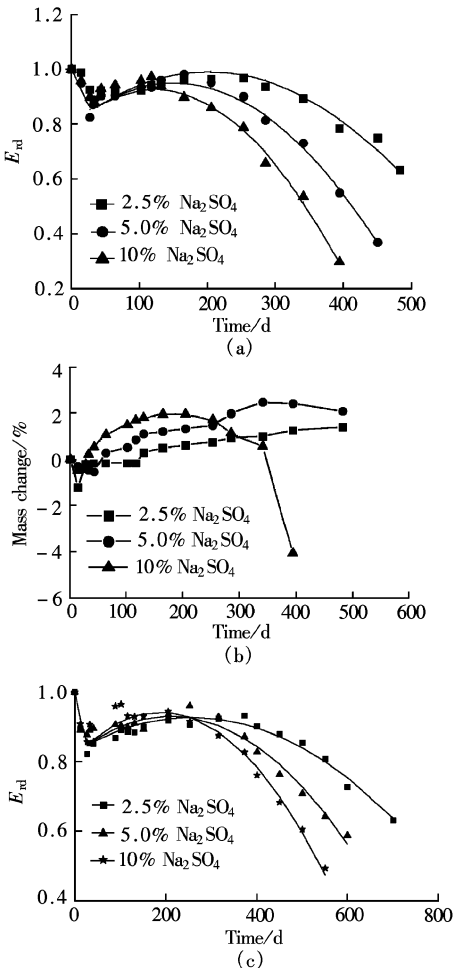


Fig. 1 Damage curves of OPC and HSC attacked by Na₂SO₄ with different concentrations and drying-immersion cycles. (a) E_{rd} of OPC; (b) Mass change of OPC; (c) E_{rd} of HSC

process curve can be described by three stages: an initial damaged stage, a performance improving stage, followed by a performance worsening stage. The initial damaged stage may be attributed to the fact that drying-immersion cycles lead to initial damage of concrete. The second and third stages may be clarified as follows: Initially, corrosion products (ettringite and gypsum) fill the matrix pores and then compact the concrete microstructure, which leads to the mass increasing, and the E_{rd} will, herein, increase with time. Subsequently, if the concrete pores are full of corrosion production and then expanded corrosion products split these pores, then cracks will extend from the matrix to the aggregate and form connected cracks in the concrete, which leads to the mass increasing and the E_{rd} decreasing with time until failure.

Based on the damage process of concrete in the sulfate solution with different concentrations, the failure time of the concrete is determined. The results indicate that the failure times of OPC and HSC decrease about 25% as the concentration of Na₂SO₄ increases from 2.5% to 5.0% in the corrosion solution, and about 40% as the concentration of Na₂SO₄ increases from 2.5% to 10%. That is, the service life of the concrete in a sulfate ion environment decreases due to the increased concentration of SO₄²⁻.

2.2 Loading effect on damage of concrete in sulfate environment

OPC and HSC are subjected to flexural loads with 25% and 50% levels of their initial strengths, and immersed in a 5% Na₂SO₄ solution. The E_{rd} vs. corrosion time can be seen from Fig. 2. The E_{rd} of HSC is about 1.11 after it is im-

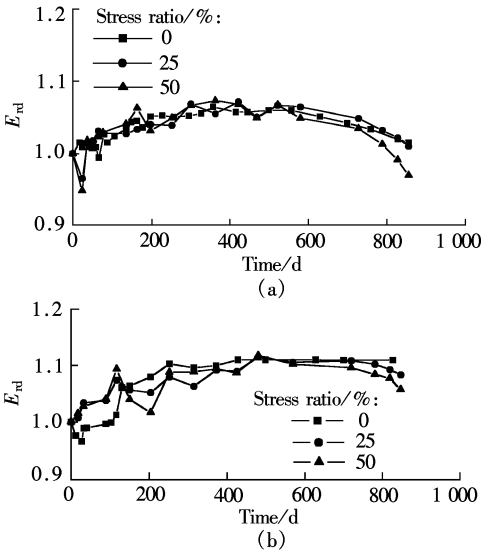


Fig. 2 Damage curves of OPC and HSC with different stress ratios immersed in 5% Na₂SO₄ solution. (a) OPC; (b) HSC

mersed in a 5% Na_2SO_4 solution for 830 d without the flexural load, but only 1.08 when the stress ratio is 25%, and 1.056 for a stress ratio of 50%. And a similar change is also observed for OPC. That is, the flexural load does not change the damage process but increases the deterioration degree when the concrete is attacked by sulfate ions, and its deterioration increases with the increase in the stress ratio.

The curves of the E_{rd} vs. corrosion time of the concrete, which is subjected to flexural loads with 25% and 50% levels of their initial strengths and with drying-immersion cycle regimes, are shown in Fig. 3. In comparison with natural immersion, drying-immersion cycles accelerate the change rate of E_{rd} , and the flexural load markedly reduces the sulfate resistance capacity of the concrete. The deterioration time of OPC and HSC decreases 15% as the stress ratio increases from 0 to 25%, and decreases 25% to 35% when the stress ratio increases up to 50%. Therefore, the flexural load shortens the service life of the concrete and it should be considered in structure design.

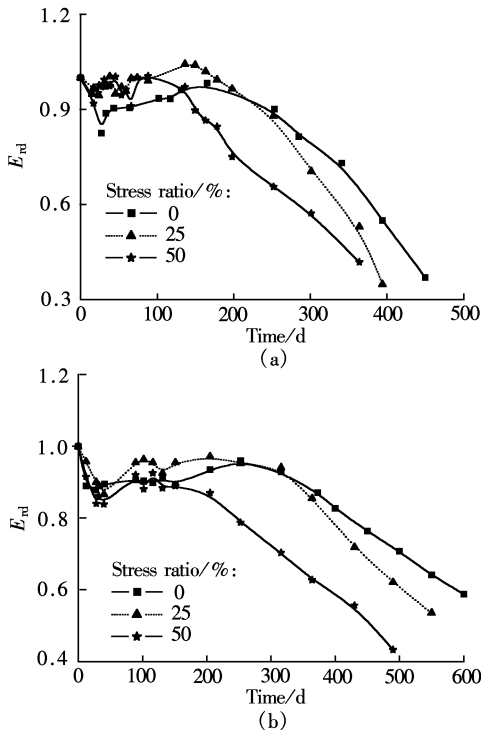


Fig. 3 Damage curves of OPC and HSC with different stress ratios in 5% Na_2SO_4 solution and drying-immersion cycles. (a) OPC; (b) HSC

2.3 Microstructure deterioration of concrete attacked by sulfate ions

The OPC specimen, which was in 5% Na_2SO_4 solution and drying-immersion cycles for 500 d, is used for SEM. The corroded specimen is embedded in a low-modulus epoxy first. Then it is polished using progressively finer grids, and then coated with a gold-palladium coating. Fig. 4 (a) shows a zone near the surface that gathers the corrosion product with reticulate continued microcracks, where the corrosion product is ettringite and thaumasite which are analyzed by EDS. Furthermore, gypsum crystal gathers in the interface zone between the matrix, and the aggregate is also shown in Fig. 4(b).

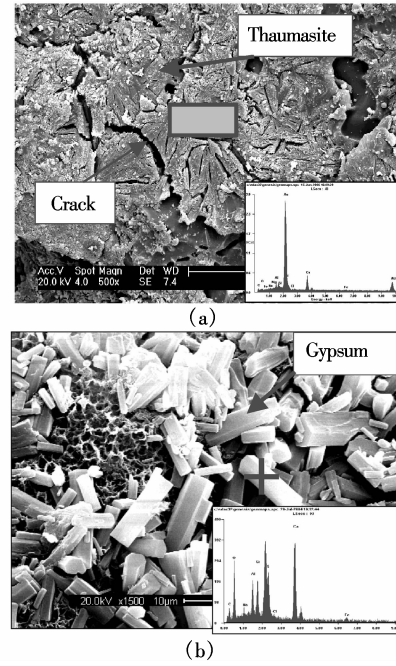


Fig. 4 Ettringite, thaumasite, gypsum and net cracks in concrete attacked by sulfate salt. (a) Ettringite, thaumasite and net cracks near the exposed surface; (b) Gypsum in the interface of paste and aggregate

Moreover, deterioration in the concrete shows a disintegrated surface zone, followed by a zone of deposition of corrosion products. From the surface to the interior of the concrete, microcracks extend from the matrix to the aggregate, and corrosion products with radioactive cracks fill up the pores in the concrete. Elements are distributed in gradients from the exterior to the interior, in which the amount of S, Al and Ca increase. According to the molar ratio of Al : S : Ca, it indicates that the corrosion crystal is ettringite. The details of the deterioration of the concrete are presented in Fig. 5.

Therefore, microstructural changes in the concrete attacked by sulfate ions can be described as follows: corrosion products, which are ettringite, gypsum and thaumasite, develop and congregate in pores and defection zones of the concrete. But as corrosion products fill up these zones, the microcracks extend from the matrix to the aggregate due to the expansion of corrosion products; continued cracking finally leads to the failure of the concrete.

2.4 Corrosion products of concrete with sulfate corrosion

Fig. 6 shows the XRD patterns for HSC concrete exposed to a 5% Na_2SO_4 solution and drying-immersion cycles for 100, 200, 400 and 500 d, respectively. In these diagrams, the peaks selected as qualitative analysis phases are ettringite at about 9.08° , gypsum at 11.59° , $\text{Ca}(\text{OH})_2$ at 18.04° , and CaCO_3 at 29.4° .

The XRD trace indicates that the gypsum, ettringite and $\text{Ca}(\text{OH})_2$ are the only crystalline phases of the concrete. These are attacked by sulfate ions, presented in the different exposure times and include quartz and calcite. The gypsum and ettringite peaks at all corrosion times were strong, indicating that gypsum and ettringite were the main corrosion products. Furthermore, the concentrations of gypsum and

ettringite increase with exposure time, showing that the degree of concrete deterioration increases with exposure time. The concentration of $\text{Ca}(\text{OH})_2$ in earlier phases is higher than that in later phases for two reasons: First, higher concentrations of gypsum in later phases consume more $\text{Ca}(\text{OH})_2$. Secondly, carbonation in the concrete transforms more $\text{Ca}(\text{OH})_2$ to calcite, and it is indicated by the variations in the concentrations of calcite at different exposure times.

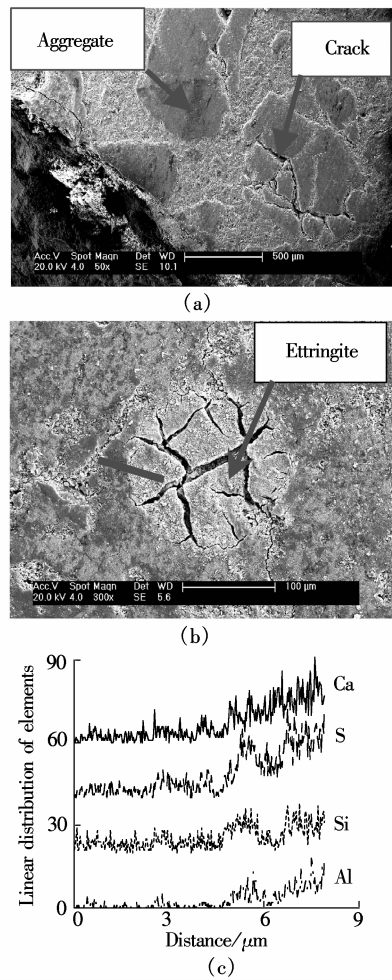


Fig. 5 Cracks in paste and aggregate, ettringite, cracks in void of concrete, and the linear distribution of corrosion elements. (a) Cracks in paste and aggregate; (b) Ettringite in air voids; (c) Corrosion products

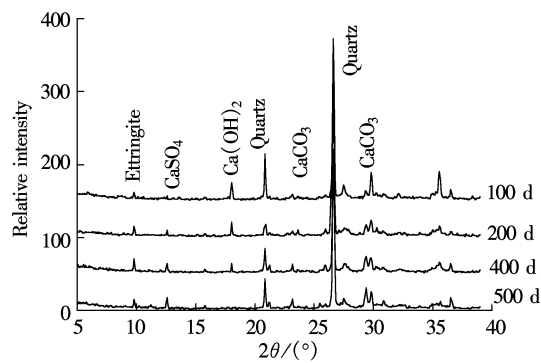


Fig. 6 XRD curve of HSC in 5% Na_2SO_4 solution for different periods of drying-immersion cycles

3 Conclusions

- 1) The damage process of concrete attacked by sulfate ions can be described by three stages: an initial damaged stage, a performance improving stage, followed by a performance worsening stage.
- 2) The degree of concrete deterioration increases with the concentrations of SO_4^{2-} in its service environment. And the failure time of the concrete decreases about 25% when concentrations of Na_2SO_4 increase from 2.5% to 5% in corrosion solutions, and decreases about 40% if concentrations of Na_2SO_4 increase from 2.5% to 10%.
- 3) Flexural load significantly decreases the sulfate resistance capacity of the concrete and shortens its service life. The deterioration time of OPC and HSC decreases 15% as the stress ratio increases up to 25%, and decreases between 25% and 35% if the stress ratio rises to 50%.
- 4) Ettringite, gypsum and thaumasite are the main corrosion products, and the amounts increase with exposure time. Corrosion products develop, congregate and fill up in pores and defection zones of the concrete. The microcracks extend from the matrix to the aggregate due to the expansion of the corrosion products, and then the continued cracks finally lead to the failure of the concrete.

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持续荷载下混凝土的硫酸盐腐蚀研究

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摘要:研究了普通混凝土和高强混凝土在 2.5%、5.0% 和 10% Na_2SO_4 溶液(质量分数),以及承受不同应力比(0、25% 和 50%)弯曲荷载作用下的损伤失效规律、特点.结果表明:混凝土在硫酸盐溶液中腐蚀,其损伤劣化包括初始劣化段、性能改善段和性能劣化段.腐蚀溶液中 Na_2SO_4 浓度从 2.5% 增加到 5.0%,混凝土失效时间缩短了 25% 左右; Na_2SO_4 浓度增加到 10%,失效时间缩短了 40%.弯曲荷载在腐蚀后期加速混凝土的损伤劣化速度,应力比由 0 增加到 25%,混凝土破坏时间降低 15%;应力比增加到 50%,其破坏时间降低 25% ~ 35%.此外,用 SEM、能谱和 XRD 分析了混凝土在硫酸盐腐蚀作用下的腐蚀产物.

关键词:混凝土;硫酸盐;弯曲荷载;微观结构

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