

Durability of Cement Concrete under Chemical Erosion

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This paper launches the study on how the sulfate particle and chloride ions interact to impact the concrete durability. It is analyzed that there is a diffusion law of two particles in concrete, whether the concrete presents corrosion resistance and permeability as contacts with them. The findings reveal that the content of chloride ions decreases with the deepening of the concrete profile. The presence of sulfate ions does not break up the diffusion trend of chloride ions in concrete, but in the case when Cl^- and SO_4^{2-} act together, the content of chloride ions at a constant profile depth is less than that under the action of a single Cl^- . When sulfate ions permeate the cement, they will react with hydrate product of cement to generate new chemical substances that fill the inner pores of the cement, thereby suppressing the diffusion of chloride ions. The higher the concrete water-binder ratio, the lower the compression strength; the more inner pores, the weaker its resistance to chemical attack. When mineral admixtures are added to the concrete, the sulfate ions can react with the hydrate products of the cement and mineral admixtures to generate new crystals that largely fill the original pores in the concrete and make it more compact. In this way, the concrete corrosion resistance is built up. Concrete gets most vulnerable to sulfate attack at an ambient temperature of 21-24°C, and relieved at 30-35°C. Lower relative humidity, high temperature environment are the decisive factors that accelerate the concrete erosion.

1. Introduction

Cement concrete features high compression, low tensile and flexural strength (One, 2009). Due to its simple production process, superior mechanical properties, simple construction, and applicability to harsh conditions, it has been widely applied in bridges, highways, buildings, tunnels and other construction industries, etc. (Hueste, 2004; Ren, 2015; Konkov, 2013).

As concrete is susceptible to multiple factors such as construction methods and cement hydration, etc., plenty of voids and initial cracks are inevitable to appear inside the concrete. These defects in the concrete will not only weaken its mechanical properties (compression tensile and flexural strengths, etc.) but also impair its durability performance (Lu et al., 2016; Fahy et al., 2014). And worse, they also make the concrete more vulnerable to chemical attack (chlorine corrosion, sulfate attack, and carbonization), thus in turn seriously exacerbating the durability of the concrete structure (Lu et al., 2011; Busba, 2013; Chen and Mahadevan, 2008; Leung and Hou, 2012; Ormellese et al., 2015; Suwito and Xi, 2008; Shannag and Shaia, 2003).

Today, many scholars are obsessed with trying to bridge how chemical erosion has an effect on the durability of concrete. They have made some studies mainly on seawater corrosion, diffusion of sulfate particles and chloride ions, the impact of temperature on the diffusion rate of chloride ions, and the corrosion resistance of concrete under wet-dry alternating environment, the effect of admixtures on the durability of concrete, etc. (Thoft-Christensen, 2003; Zhang et al., 2010; Jang and Oh, 2010; Guzmán et al., 2011; Zhang, 2014).

Available literature focused more on how one chemical substance erodes concrete. There are relatively few studies on the effect of multiple chemical ions on the durability of concrete. In this paper, we aim to explore the co-effect of sulfate and chloride ions on the durability of concrete and analyze the diffusion law of the two particles in the concrete, as well as the corrosion resistance and the permeability of concrete (Sotiriadis et al., 2013; Peng et al., 2011; Sulikowski and Kozubal, 2016). The conclusions drawn in this paper can provide theoretical guidance for relevant construction projects.

2. Test material and method

Test materials: concrete, standard sand, gravel, deionized water, fly ash, polycarboxylic acid water reducer. The physical and chemical properties of the cement used are shown in Table 1 and Table 2.

Table 1: Chemical composition of cement %

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Loss of ignition
24.6	4.9	5.1	54.9	4.4	3.6	2.5

Table 2: Physical properties of cement

Density/ (g·cm ⁻³)	density		Strength/MPa			
	More than 80 μm cement content	Surface/(m ² ·kg ⁻¹)	Compressive strength		Flexural strength	
			3 d	28 d	3 d	28 d
3.08	3.7	382	22.4	49.5	4.88	9.83

Design three concrete mix ratios, see Table 3 for specific parameters. In the table, F_A represents fly ash and G is gravel.

Table 3: Three mix ratios of concrete

Numbering	Concrete	F _A	Water	Sand	Gravel	Water reducer/%
1	1	0	0.35	1.57	2.32	0.9
2	1	0	0.65	1.57	2.32	0.0
3	0.9	0.3	0.41	1.44	2.65	1.5

As shown in Figure 1, it is a device for testing chemical erosion resistance of concrete. The sulfate liquor consists of NaCl and Na₂SO₄. The concrete test blocks are treated by spraying and soaking liquor, and erosion time lasts for 60-150d.

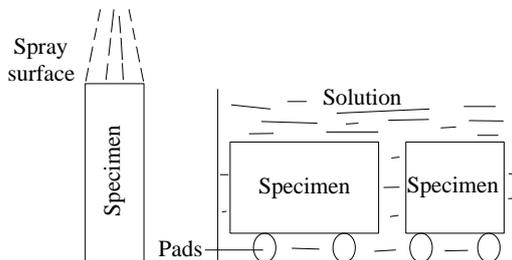


Figure 1: Test device

As shown in Figure 2, the electrochemical method is used to accelerate the diffusion of Cl⁻ and SO₄²⁻ in the liquor, test the diffusion of the two ions after energizing for 6 h, 12 h, and 18 h.

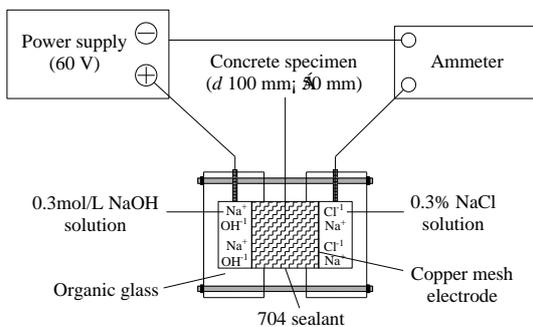


Figure 2: System for testing diffusion of test block electrochemical ion

3. Test results and analysis

3.1 Diffusion effects of Cl⁻ and SO₄²⁻ in concrete

As shown in Figure 3, the chloride ions diffuse in two types of concretes (concrete blocks 1 and 2 in Table 3) under the attack of a mixed solution containing NaCl and Na₂SO₄; as shown in Figure 4, the chloride ions diffuse in the two concretes eroded by a single NaCl solution; as shown in Figure 5, sulfate ions diffuse in two concretes under erosion of mixed solution. In three cases, the concrete should be soaked for 150 days. In Figure 3 ~ 5, we can observe that the content of chloride ion decreases with the deepening of the concrete profile in each case. Comparing Figure 3 and 4, Figure 3 and 5, the presence of sulfate ions does not break up the diffusion trend of chloride ions in concrete. However, under the erosion of mixed solution, the content of chloride ions in different profile is less than that under the attack of single element, and this case presents even more pronounced when water-cement ratio is relatively high (0.65). This is due to the fact that sulfate ions enter the cement and react with the hydrate product of cement to produce new chemicals that fill the inner pores of the cement.

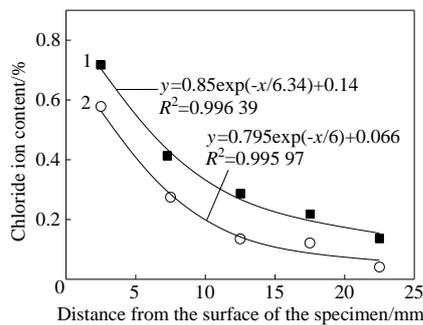


Figure 3: Curves of chloride diffusion in two types of concrete blocks under attack of mixed solution

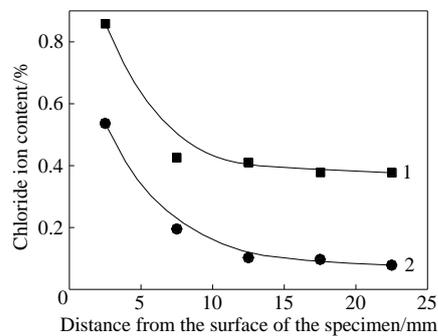


Figure 4: Curves of chloride diffusion in two types of concrete blocks under immersion of NaCl solution

3.2 Change in mechanical properties of concrete under chemical attack

As shown in Figure 6, they are the curves of the erosion resistance factor of different types of concrete (No. 1 - 3 respectively represent the water-cement ratio of 0.35, fly ash yields 0.2, 0.6, 0.4 once; No. 4 - 6 represent the water-cement ratios 0.35, 0.42, 0.65 respectively, no fly ash added) soaked into pure Na₂SO₄ solution and concrete cured in clean water.

As shown in Figure 6, the corrosion resistance factor of concrete swoops during the first 60 days, but slowly decreases after 60 days. The higher the water-cement ratio, the lower the compression strength; the more the inner pores, the weaker its resistance to chemical attack. When mineral admixtures are added to the concrete, the sulfate ions react with the hydrate products of the cement and mineral admixtures to generate new crystals that can fill up the original pores of the concrete to a great degree, so that the concrete gets denser, improving its anti-corrosion performance. When the concentration of sulfate ions is too high, too much crystals generated make the concrete swelling and degrading in the interior, so that the mechanical properties of the concrete will be worsened once again.

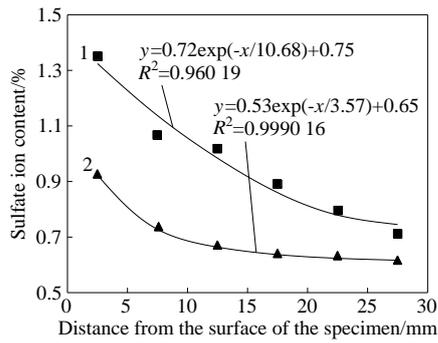


Figure 5: Curve of sulfate ion diffusion in two concrete blocks under attack of mixed solution

As shown in Figure 7, there are erosion resistance factors of different concretes soaked in mixed solution. Comparing Figure 6 and 7, it can be seen that the erosion resistance factor of concrete soaked into mixed solution within 60 days increases at different degrees, but swoops after 60 d due to the fact that salt compound produced from the reaction between the two solutions and the hydrate products of the cement makes the Cl^- and SO_4^{2-} in the solution disappear, thereby reducing the erosion rate of the two ions on the concrete.

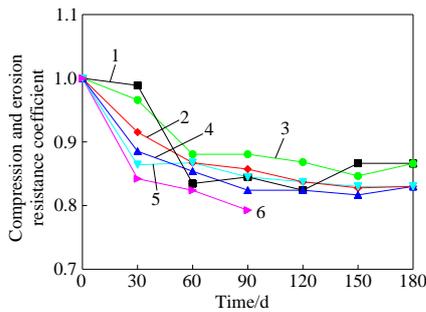


Figure 6: Erosion resistance factor of different concrete blocks soaked in Na_2SO_4 solution

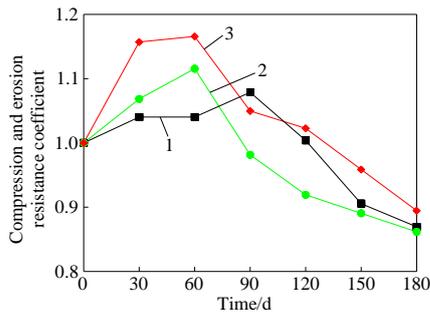


Figure 7: Erosion resistance factor of different concrete blocks soaked into mixed solution

3.3 Analysis of electric flux and crystallization temperature of concrete

As shown in Figure 8, different concrete blocks (water-cement ratios 0.35, 0.65 and 0.35+20% fly ash) change in electric flux after the test using the device shown in Figure 2, where the electrolyte takes NaCl and Na_2SO_4 mixed solution. It can be seen that the electric fluxes of the three types of concrete blocks after being subjected to erosion of 90d and 120d are significantly lower than those of 28d, while the electric flux after 150d erosion is higher than that of 28d. The test results shown in Figure 8 reveal that the concrete has a lower permeability, but gradually builds up as the corrosion time extends.

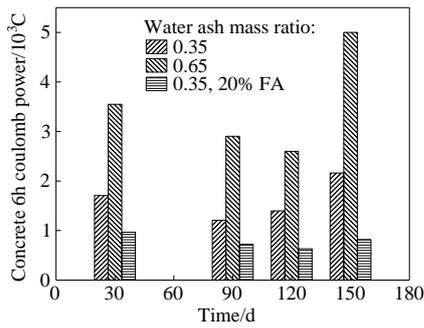


Figure 8: Electric fluxes of different concrete blocks

As shown in Figure 9, the Na₂SO₄ crystallization plays an effect on the internal concrete at different temperatures. The erosion solutions of curves 1 ~ 3 are respectively 30%, 20%, and 10% Na₂SO₄ solutions. As can be seen from the figure, when the temperature drops from 24°C to 21°C, the crystallization rate inside the concrete containing 30% Na₂SO₄ solution jumps sharply from 0 to 0.083 ml/s. As the temperature further drops, the Na₂SO₄ crystallization rate in the concrete declines to zero. When the solution temperature gradually increases from low to high, the crystal volume of Na₂SO₄ inside the concrete with high concentration (30% and 20% Na₂SO₄) gradually decreased. The crystal gradually dissolves inside the concrete. We conclude from Figure 9(a) and (b) that the concrete is most susceptible to sulfate attack at 21-24°C, and relieved at 30-35°C. Lower relative humidity and high temperature environment are the main factors that accelerate the concrete corrosion.

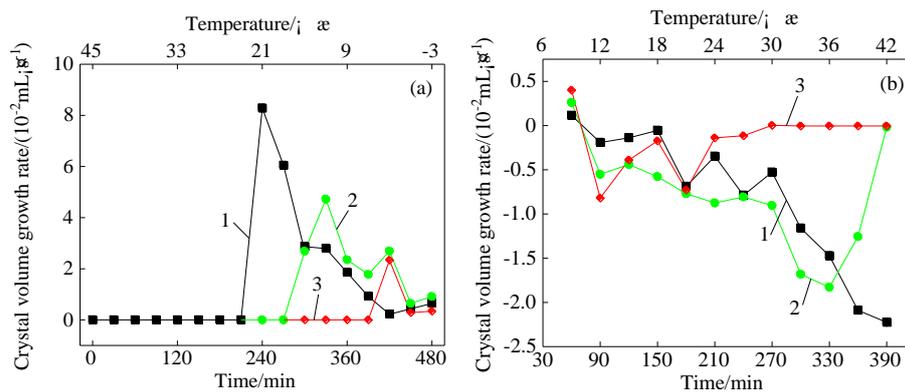


Figure 9: Impact of temp on Na₂SO₄ crystals

4. Conclusions

In this paper, we study how the interaction of sulfate and chloride ions affects the concrete durability. The diffusion law of two types of particles in concrete and the changes in corrosion resistance and permeability of concrete are also analyzed here. The findings come here as follows: Chloride ion content decreases as the concrete profile depth increases. The presence of sulfate ions does not change the diffusion tendency of chloride ions in concrete, but under the interaction of Cl⁻ and SO₄²⁻, the content of chloride ions is less than that under the action of single chloride ion. When sulfate ions enter the cement, they react with the hydrate product of the cement to produce new chemical substances that fill the inner pores of the cement, thereby repressing the diffusion of chloride ions. The higher the concrete water-cement ratio, the lower the compression strength, and the more the inner pores, the weaker its resistance to chemical attack. When mineral admixtures are added to the concrete, the sulfate ions react with the hydrate products of the cement and mineral admixtures. The new crystals produced can fill up the original pores of the concrete to a great degree, and make the concrete more compact, thereby improving its corrosion resistance.

Concrete is most susceptible to sulfate attack at an ambient temperature of 21-24°C, and mild at 30-35°C. Lower relative humidity, high temperature environment is the dominant factor to accelerate the concrete corrosion.

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