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Study on Mechanism of Chemical Sulfate Attack on Reinforced Concrete Structures

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This paper studies four different cementitious materials including ordinary Portland cement paste and cement fly ash in closed environment based on previous study on characteristics of carbon sulphosilicate formation in single sulfate solution. As test paste, cement limestone paste and sulfate-resistant cement paste were put in a mixed solution of sodium sulfate and magnesium sulfate, the results of which show that solution pH value changes with time and the products change with pH values. Finally, the attack mechanism of carbon and sulfite in the embedded concrete is analyzed based on results of the concrete failure test.

1. Introduction

When the concrete is in soil and groundwater with dissolved sulfate, it will be destroyed by sulphate attack. The degree of damage depends on content of the sulfate in the environment, the movement of water, composition of the cement, properties of the concrete, and the transport mechanism of the solution in the concrete(Mouring et al.,2001). Under the sulphate attack, the hardened cement slurry continues to decompose and lose strength, eventually leading to the collapse of the entire concrete segment.

Concrete sulphate attack is an important factor that threatens the durability of concrete segment in railway of western China. It remains an urgent problem to be solved to improve the sulphate erosion resistance ability of concrete structures and to effectively repair the structures damaged by the sulphate attack already (Al-Rousan and Haddad,2013). This is a matter of safe operation in the whole railway system(Liang and Lan, 2005). If any safety accident occurs, the consequences will be disastrous. There have been more than 100-year history of sulfate attack, but there has formed no uniform attack. Some scholars believe that today's research on sulphate attack is still in a confusing state (Saetta, 2005).

It is well known that the main products of cement hydration are calcium silicate hydrate (CSH), calcium hydroxide (CH), calcium aluminate hydrate (CAH) and ettringite (AFT) (Castañeda et al.,2013). However, three of these hydration products is not stable in sulfate environment with products in chemical attack being formed under below chemical reactions:

$$Ca(OH)_2 + C-S-H + SO_4^{2-} + H_2O \rightarrow CaSO_4 \cdot 2H_2O \tag{1}$$

$$Ca(OH)_2 + C-S-H + MgSO_4 + H_2O \rightarrow CaSO_4 \cdot 2H_2O + Mg(OH)_2 + SiO_2 \cdot xH_2O \tag{2}$$

$$3CaO \cdot Al_2O_3Ca(OH)_2(12 \sim 18)H_2O + SO_4^{2-} \cdot 2H_2O + H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \tag{3}$$

$$Ca(OH)_2 + C-S-H + SO_4^{2-} + CO_3^{2-} + H_2O \rightarrow CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 2H_2O \tag{4}$$

The main products in the chemical reaction are gypsum, ettringite, carbon sulfosilicate, magnesium hydroxide and silica gel(Kamaitis, 2007; Tong et al., 2016). Gypsum and ettringite are the most common products of sulfate attack(Amin et al., 2008). Magnesium hydroxide and silica gel are the products of magnesium sulfate attack. If there is still CO_3^{2-} in the reaction process, thaumasite is also possible to be generated (Secco, 2014; Torkian et al., 2013).

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This paper studies the impact of mixed sulfate solution and high-concentration sulfate solution on products in attack. Based on previous research results in laboratory and actual engineering, the attack on carbon and sulfite in the embedded concrete is discussed in detail with focus on the conditions and attack mechanisms.

2. Experiments

2.1 Test Content on Concrete Sulfate Attack

In a stable external environment (temperature: 20 ± 2 ℃; relative humidity: 60 ± 5%), the test analyzed performance changes and products generated by the concrete which are semi-soaked in 5% Na_2SO_4 and 5% $MgSO_4$ solution. Meanwhile, the test studied the changes in sulfate attack resistance of the semi-soaking concrete cylinder under hydrostatic pressure and made a comparative study on the sulfate attack resistance between fly ash concrete (FAC) and sulphate-resistant cement concrete (SRC) as well as impact of different external relative humidity and external temperature on the sulfate attack to concrete.

2.2 Raw materials and equipment

This test mainly used the standard portland cement. Table 1 shows the chemical composition of the cement and the mineral composition of the clinker. The chemical component of fly ash and limestone flour is also shown in Table 1. Chemical reagents Na_2SO_4 and anhydrous $MgSO_4$ were used as sulphates in the tests. Table 2 shows the technical parameters of model LDM6119 acrylic admixture polymer emulsion from the Celanese company. Sulfate solution for semi-soak tests of the concrete cylinders was made with tap water, and that for the other tests was made with deionized water.

Table 1: Chemical component of P, SRC, FA and LP

Component (%)	52.5 cement (P)	sulphate-resistant cement concrete (SRC)	fly ash (FA)	limestone flour (LP)
SiO_2	19.6	19.94	53.21	0.86
Al_2O_3	4.9	3.13	26.43	0.08
CaO	63.1	61.56	4.46	56.3
Fe_2O_3	3.6	4.76	7.53	0.34
MgO	0.9	-	2.54	0.58
Na_2O	0.77	0.66	3.58	0.05
K_2O	0.41	0.24	1.15	0.08
SO_3	3.20	2.54	0.90	-
LOI	2.10	5.45	4.10	42.0

Table 2 : The technical parameters of LDM6119

Solid content (%)	minimum film formation temperature (°C)	pH value	particle size (μm)	Viscosity (MPas)	Compatibility with cement
50	0	7.0	0.13	2500±1500	fine

In order to avoid the effect from water or solution on the products produced by the specimen, after being removed from the solution the surface of the specimen was cleaned with a knife and a soft brush, since then it had been no longer in contact with the sulfate solution or washed with water. Before the microscopic analysis, all the specimens were vacuum dried in a container with silica gel.

2.3 Experimental process

Cement paste stirring process: put portland cement and fly ash or limestone powder into a 10-liter agitator, and stir at low speed for 30 seconds; during slow agitation, pour water into the mixing pot with a 400ml plastic cup one cup after another, leaving 2 cups of water behind the back Stir Slowly for 120 seconds, then at high speed for 120 seconds.

Put 5% Na_2SO_4 solution Into a PVC tube sized Φ 120*400 mm and seal the tube with a plastic film to avoid the impact of moisture evaporation; place 12 concrete specimens into a standard incubator with temperature at 20±2°C and relative humidity at 98±2%; place them into the refrigerator (Figure 1).

The total mass of concrete and PVC pipe was weighed each time the solution was replaced. After 3, 6, 9, 12 months respectively, three cylinders were taken out each time to cut into two parts as shown in Figure 2.

Part of the concrete was exposed to air while the other part was soaked in the solution. Completely soaked, its erosion environment is shown in Table 3.

Figure 1: The refrigerator used for putting concrete specimens

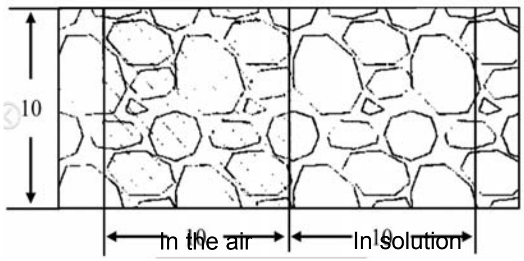

Figure 2: The longitudinal section of cylindrical concrete

Table 3: Na2SO4 solution concentration at 20, 30, 40℃

Temperature (°C) Water	Concentration (g/100g water)					
20	5	15	20			
30	5	15	20	30	40	
40	5	15	20	30	40	40

Compressive strength test method: use three specimens as a group for compressive strength of concrete and take six samples as a group for compressive strength of cement paste; Referring to the EN 196-1 Standard, measure the compressive strength of mortar by making two steel supports and fixing them in the fixture; Take the average of the three values with difference no more than 10% from the six compressive strength values as the intensity value of the test piece.

3. Discussion and analysis

3.1 Change in pH value of solution

In this study, the pH of the $MgSO_4$ solution was 12.5 after 3 moths of soaking and remained at 13.06 after 6 months of immersion. The concentration of SO_4^{2-} in 5% $MgSO_4$ solution (about 40,000 ppm SO_4^{2-}) was much higher than the maximum concentration level of aggressive agent specified in the national standards (about 10,000 ppm SO_4^{2-}).

Table 4: The pH value of the solution varies with the erosion time

	1 month		3 months		6 moths	
Na_2SO_4: $MgSO_4$	T (°C)	pH value	T (°C)	pH value	T (°C)	pH value
water	10.4	13.18	11.7	12.84	10.7	13.05
5:1	10.5	13.58	12.3	13.16	10.5	13.10
5:3	9.8	13.40	13	13.05	10.9	13.15
3:5	9.6	13.00	10.2	13.07	10.3	13.10
1:5	10.3	13.03	11.2	13.00	11.1	13.14
0:5	11.5	11.6	11.7	12.57	10.2	13.0

3.2 Changes in compressive strength

3.2.1 Effect of $MgSO_4$ and Na_2SO4 Solution Concentration on Compressive Strength of Different Concrete Materials

Figures 3 and 4 show the effect of different mixed sulphate solutions on the compressive strength of different gelling materials. Figure 2 shows that there was no significant difference in the compressive strength of the Portland cement paste in different mixed solutions of Na_2SO_4 and $MgSO_4$ differing in concentration with all data at the same intensity level. This indicates that concentration of the mixed sulfate solution has little effect on erosion and destruction of the Portland cement paste.

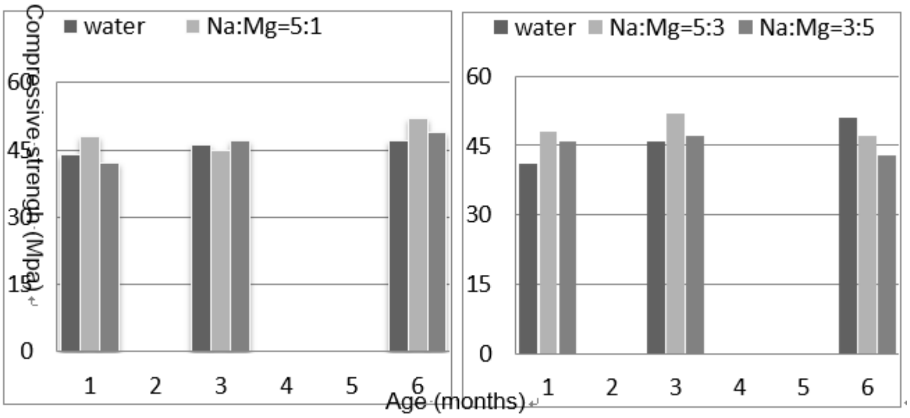

Figure 3: Compressive strength of portland cement paste in mixed sulfate solution

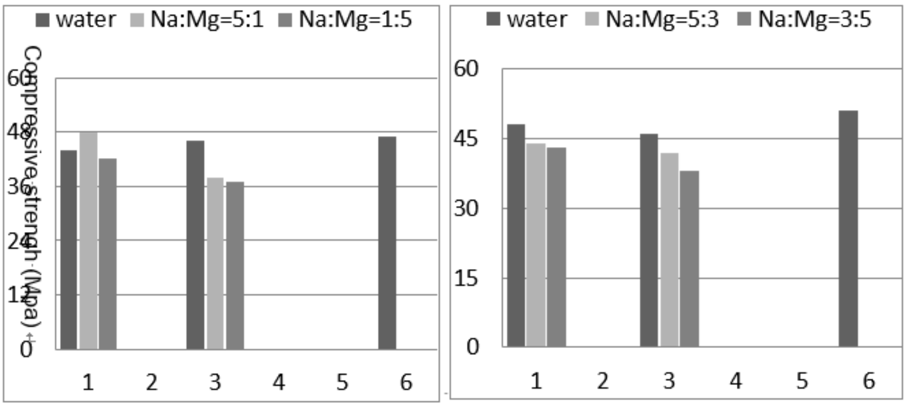

Figure 4: Compressive strength of cement limestone paste in mixed sulfate solution

As can be seen from Figure 4, cement fly ash is more sensitive to $MgSO_4$ solution. After 6 months of erosion, the compressive strength of the specimen in the mixed solution with more $MgSO_4$ was lower than that in the solution containing less $MgSO_4$. After 3 months of erosion, the specimen of cement limestone slurry had been severely damaged in the mixed solution. It is difficult to distinguish the impact between $MgSO_4$ and Na_2SO_4.

3.2.2 Effect of pH on compressive strength

As can be seen from Figure.5, after 3 months of immersion in saturated $MgSO_4$ and Na_2SO_4 mixed solution strength of the anti-sulfate cement paste was only 70% that of the specimen in water. After six months, the specimen was completely destroyed. However, after 6 months of erosion in the 5% $MgSO_4$ solution with high pH (pH = 13), the compressive strength of the specimen was still at the same level as that of the specimen in water.

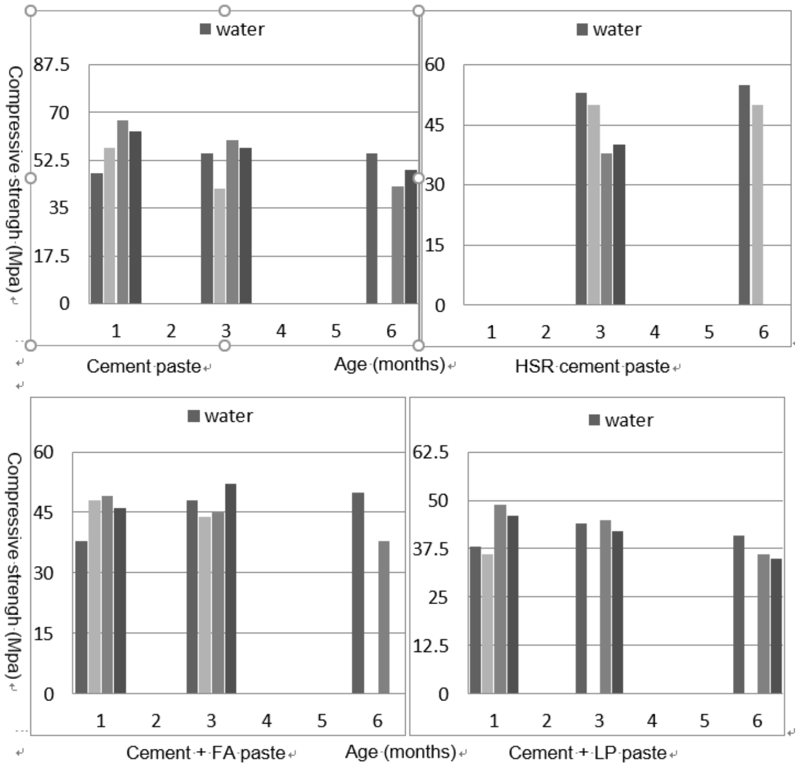

Figure 5: Effect of pH on compressive strength of different cement

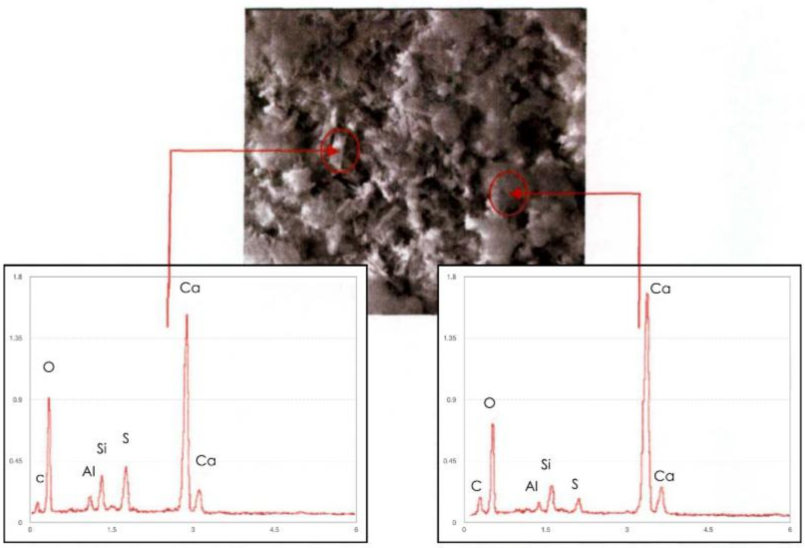

Figure 6: The SEM of the cement limestone slurry was immersed in solution for 1 month

According to the SEM analysis in Figure 6, carbon-sulfur-phlogite crystals were also formed on the surface of the cement limestone slurry. In contrast, Portland cement paste, cement fly ash pastes and cement limestone slurry showe better resistance to sulfate attack in low pH solutions, while in high pH sulfate solutions are vulnerable to erosion damage. In particular, the cement limestone slurry, when immersed in a 5% $MgSO_4$ solution, has been severely damaged after 3 months of erosion. But the specimens which are remained in saturated $MgSO_4$ solution have the 78% compressive strength relative to the specimen in water after 6 months of erosion.

4. Conclusion

In this paper, the test simulates the relationship between solution pH values and products in mixed sulfate solution in a closed environment. Carbon sulfosilicate may be generated in low pH (pH=9) solutions, but the main erosive product is gypsum. Carbothiite of large amount can only be produced in high pH (pH=13) sulfate solution. In a closed environment, high-concentration sulphate solution is lower at pH value. In closed high pH-value sulphate solution, compared with cement paste, cement fly ash slurry saw more ettringite generated due to more intense degradation and the sulfate-resistant cement paste owns the best resistance to sulfate attack while in saturated magnesium sulfate solution with low pH value, gypsum is the most important erosion product and anti-sulfate erosion of cement owns the worst resistance to sulfate attack.

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