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Study of Erosion Deterioration Mechanism and Influence Factors of Concrete under Combined Action of Sulphate and Chloride

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The article is synthetically revealed the erosion deterioration law of concrete under double-factor erosion condition in complex environment, research results indicate: within a short period of time, the combined action of double factors which are chlorine ion and sulphate ion changed the change laws of single factor effect of chloride ion or sulphate ion. Under the combined action of double factors, there does not appear simple superposition of concrete's erosion effect, while there appears drag effect each other in short time, crush resistance, fracture resistance and anti-erosion coefficient appear the change law of decreasing after increasing, at the early stage of being in erosion for the city underground structure, the role of double factors delayed the decreasing of erosion resistance coefficient.

1. Introduction

The erosion deterioration of concrete sulphate involves three associated processes of the transmission of erosion ion in concrete pore system, the chemical reaction of erosion ion and cement hydration products or seed out of erosion matter and expansible erosion products causing destroy on concrete structure (manifest as expanding, cracking, peeling off and loss of strength), therefore, it's a very complicated physical, chemical and mechanics changing process (Hernández et al., 2015; Liu et al, 2015; Zega et al., 2016; Zhang 2015; Zhang et al., 2016). Previously many studies were mainly focused on its erosion products (gypsum, ettringite, thaumasite and so on) when discuss the erosion deterioration mechanism of sulphate, so much more studies mainly lie in cement paste or mortar test specimen, even singleness cement mineral test specimen (like C3S, C2S), but for concrete, its pore structure occurs great change, cement paste or mortar test specimen has already can't reflect the dynamic procedure of erosion deterioration for sulphate (Zhang et al, 2011). In addition, at present, the studies about erosion deterioration of concrete sulphate are most restricted to single factor's effect, and the studies on recombination factor are rarely reported. In fact, concrete is always affected by other factors when suffered the erosion of sulphate, and all factors also mutually affect. Therefore, the research results with single factor hardly reflect the actual weather condition of concrete (Hime et al., 1986).
The background of this study is: when the underground water conveyance structure such as underground pipe laying, inverted siphon, closed conduit and other water areas are rich in humus matter, their structure lies in high humidity environment for long time, these matter would rot and resolve in room temperature, produce a large number of heat, thus result in the constant increasing of temperature in the enclosure space of structure interior, while when change draining off water, as the water outside in room temperature flow through, it will make the surface temperature decrease sharply, and in the water area, there always exists a large number of sulphate ion and chloride ion (Zheng et al., 2010). These concrete structure in specific work environment possess the characteristics of low work temperature, environment temperature being alternate changed and sulphate being alternate affected with chloride ion. In this article, based on the preliminary study, it takes the practical matching concrete as study object, synthetically reveals the deterioration mechanism of erosion under the action of sulphate and chlorine salt.

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2. Double-factor erosion experiment design n

2.1 Experiment design

This experiment was mainly studied the erosion mechanism of sulphate about underground concrete structure and its microstructure changing (Liu et al, 2012), the mix ratio of concrete and mortar design of experiment are shown in table 1, mixing ratio of mortars shown in table 2. Part of the experiment process photos are shown in figure 1 (Davies et al., 2001).

Table 1: Test specimen's proportions of concrete mix in test

Number	W/C	Binding Material /%			Sand percentage/%	Water Reducing Agent /%
		C	FA	SF		
A22 (C1)	0.35	100	0	0	37.5	0.6
A23 (C2)	0.42	100	0	0	37.5	0.6
A24 (C3)	0.65	100	0	0	37.5	0

Table 2: Mortar Mix Ratio in Test

Number	W/C	Binding Material /%		
		C	FA	SF
M18	0.35	100	0	0
M19	0.42	100	0	0
M20	0.65	100	0	0

2.2 Experimentation

The test was adopted spray dry-wet cycle and immersion method, immersion and spraying were adopted mixed solution of 3.5% NaCl and 5% Na_2SO_4 solution, spray dry-wet cycle and immersion treatment are same with the former method (Bakharev and Struble, 1997). The fashioned concrete and mortar specimens were put in the mixed solution of 3.5% NaCl and 5% Na_2SO_4 solution (volume ratio 1:1) and conducted complete and half immersion test, then took the specimens out when reached the target immersion time (60 d, 90 d, 120 d, 150 d), then conducted stratified measurement for ion content, stratified sampling method was adopted for the measurement of ion content, in which sulphate ion content was measured by barium sulphate turbidimetry. The well prepared sample was put in a beaker, and made it fully dissolved in the distilled water with 100°C, then added barium nitrate into defined amount of clarified solution, measured its absorbency with type 72 spectrophotometer and colorimetric determination and compared with standard curve, took the sulfate ion content average of two test specimens as the final value. At the same time, the quality change, exterior appearance, compressive strength, dynamic elastic modulus, breaking strength changes and the change of microstructure with corrosion products generated from test specimen were measured.

(a) Concrete stratified sampler (b) Concrete sample with sealing wax on surface

Figure 1: Part of test photos

2.3 Experimental design

It was conducted test according to the predetermined experimental conditions and process, the experimental data after tidied are shown in table 3 ~ 4

Table 3: Experimental data (1)

Number	Environmental conditions	Time/h	Water loss /g	Environmental conditions	Water loss /g	Environmental conditions	Water loss /g
A22 Group w/c=0.35	5°C, relative humidity 90%	0	0	5°C, relative humidity 25%	0	25°C, relative humidity 25%	0
		12	2		5		4
		24	3.8		6		6
		36	4.2		6		7.5
		48	5		6		9
		60	5.1		6.5		9
		72	5.5		7		9
		84	5.6		7.5		9.5
		96	5.8		8		10
		108	5.9		8		11
		120	6.2		8		11

Table 4: Experimental data (2)

Number	Environmental conditions	Time/h	Water loss /g	Environmental conditions	Water loss /g	Environmental conditions	Water loss /g
A23 Group w/c=0.42	5°C, relative humidity 90%	0	0	5°C, relative humidity 25%	0	25°C, relative humidity 25%	0
		12	2.3		5.5		4.5
		24	4		6.5		5
		36	4.5		7		7
		48	5.5		7		10
		60	5.6		7.5		10
		72	5.7		8		10
		84	5.9		8.3		10.5
		96	6.2		8.5		11
		108	6.6		8.5		11.5
		120	6.8		9		12

3. Experimental results and analysis

3.1 Ion diffusion concentration

Under the combined action of erosion factors from sulfate ion and chloride ion, the erosion ion diffusion concentration distribution of concrete specimen was tested, the experimental data are shown in table 5.

Table 5: Test data for erosion ion diffusion concentration distribution

Number	Distance to concrete surface/mm	Cl- Content test result/%	SO42- Content test result/%
A1 (w/c=0.35 Immerse for 120d)	2.5	0.59	0.92
	7.5	0.29	0.72
	12.5	0.16	0.67
	17.5	0.13	0.66
	22.5	0.07	0.66
A3 (w/c=0.65 Immerse for 120d)	2.5	0.72	1.34
	7.5	0.39	1.04
	12.5	0.27	1.01
	17.5	0.21	0.91
	22.5	0.15	0.85

Figure 2 shows the chlorine ion content in different positions after immersing test specimens with water cement ratio 0.65 and 0.35 in the mixture solution of 3.5% NaCl and 5% Na_2SO_4 for 120 days. From Figure 2, it can be seen that after immersing for 120 days, the chlorine ion content decreased with increased depth, and the effect of water cement ratio was obvious. When the test specimen was immersed in mixture solution of sulfate and chlorine salt, two kinds of solution entered into concrete interior at the same time, while the SO42- would happen chemical reaction with hydration products of cement after entering into concrete interior, the new products generated would block pores which influence the diffusion velocity of Cl-. The Figure 3 shows the influence result of chloride ion on sulfate ion content. From the result, it can be seen that after immersing for 120 days, sulfate ion contents in different position were all decreasing with increased depth, in which the erosion and diffusing capacity influence of water cement ratio on sulfate ion was obvious. When immersed in mixed solution, the sulfate ion capacity in different positions of mortar interior reduced obviously. The experiment result indicates that under the action of double factors, the chloride ion concentration in test specimen interior was similar with it in single sodium chloride solution soaking condition, which all conform to Fick's Second Law, which explains the existing of sulfate ion don't affect the diffusion rule of chloride ion, but it can decrease diffusion content of chloride ion.

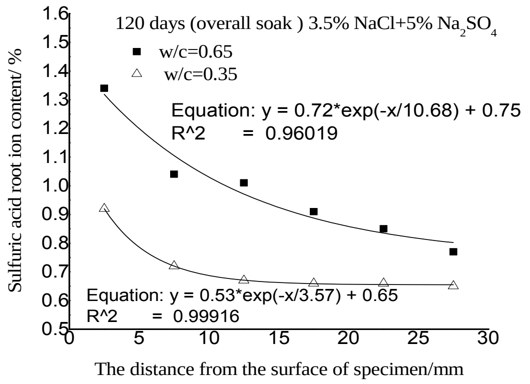


Figure 2: The change law of sulfate ion content with changes of distance to specimen surface

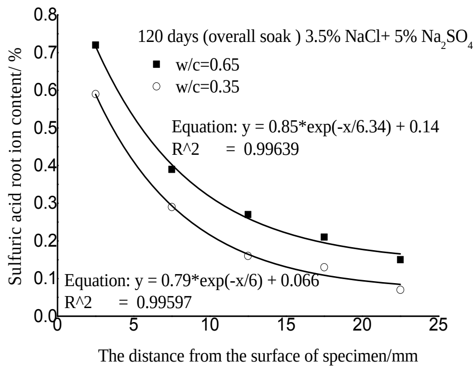


Figure 3: The change law of chlorine ion content with changes of distance to specimen surface

3.2 Anti-erosion performance analysis

Figure 4 shows the changing of compressive resistance erosion coefficient of mortar under complete immersion condition in mixture solution of 3.5% NaCl with 5% Na_2SO_4(Mixed volume ratio is1:1).

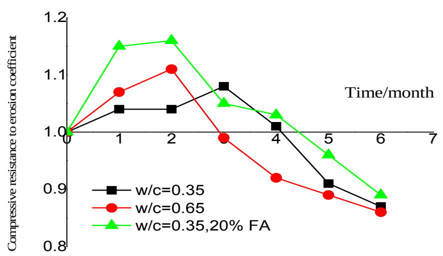


Figure 4: The compressive resistance erosion coefficient of mortar under complete immersion condition

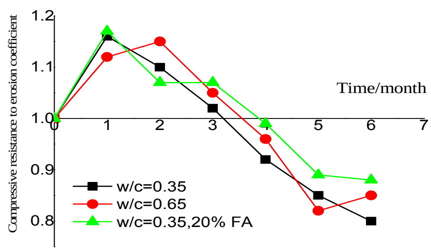


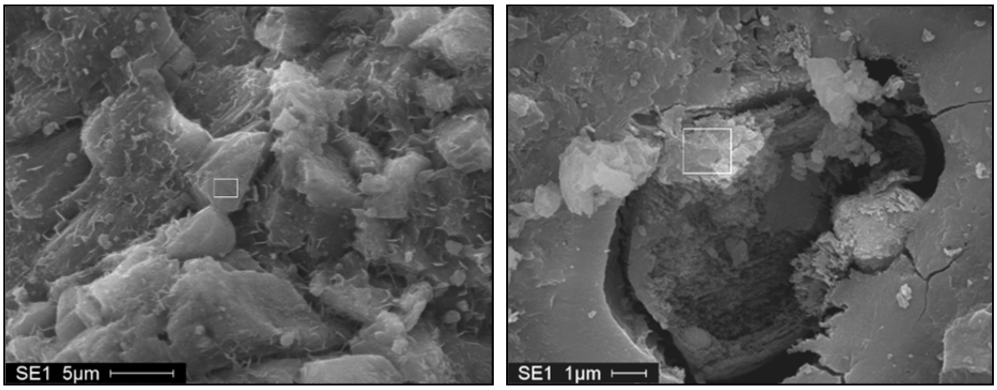
Figure 5: Theanti-erosion coefficient under half immersion condition

From Figure 4, it can be seen that unlike single 3.5% NaCl erosion solution(anti-erosion coefficient was less than 1.0), under the complete immersion condition of 3.5% NaCl with 5% Na_2SO_4 mixture solution, in the early time, anti-erosion coefficient increased gradually(greater than 1.0), with the erosion time lengthened, anti-erosion coefficient decreased gradually (less than 1.0). Among them, when the erosion time reached 3 months, the anti-erosion coefficient of mortar with water cement ratio being 0.65 firstly decreased to less than 1.0, the anti-erosion coefficient of the rest groups was still greater than 1.0 after 3 months.

Test results indicate that, when the city underground concrete structure was jointly eroded by sulfate and chlorine salt, as concrete's hydration products would combine with $Cl^-$and generate F salt, therefore it reduced the reactant used for chemical reactions with sulfate, so it postponed sulfate erosion on concrete. In the short time, the combined action of double factors from chloride ion with sulfate ion changed the change law of single factor action from chloride ion or sulfate ion, in the combined action of double factors, there didn't appear the simple superposition of erosion effect concrete, while there appear drag effects each other in short time. Test results reflect that, the compressive, flexural and erosion resistance coefficients presented obvious change law of decreasing after increasing, in the earlier stage of city underground structure erosion, the action of double factors postponed the decreasing time of erosion resistance coefficient.

3.3 Micro-Structure Analysis

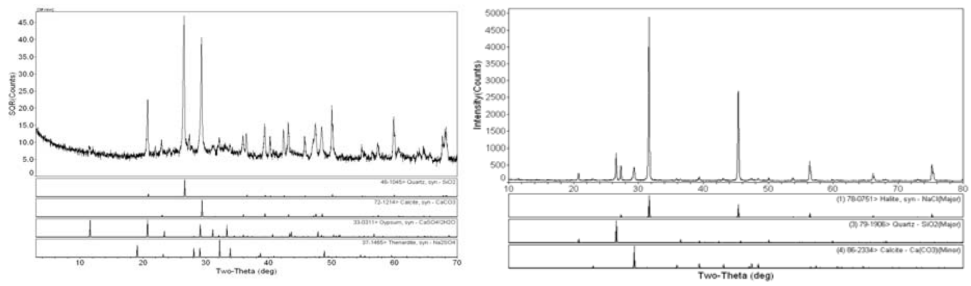
The Figure 6 shows microstructure SEM test for concrete interior under combined erosion action of 3.5% NaCl with 5% Na2SO4. Under the combined action of sulfate and chlorine salt, in the area which freed from erosion, cement hydration condition is well, there were a large number of hydration products to be generated, as shown in Figure 6(a). In the area being eroded which shown in Figure 6(d), the structure of concrete interior was loose, which had big holes and many suspicious needle-like matter generated, this indicates that concrete had been eroded seriously.



(a) (b)

Figure 6: The microstructure of concrete interior under combined action of 3.5% NaCl with 5% Na2SO4 (A24)

It adopted EDS to analyze the suspicious matter generated from concrete interior, which is shown in Figure 7, it is found that the Ca and Si contained in the suspicious matter mainly come from concrete its own matter CaCO3 and SiO2, while Na, S, Cl^- etc are derived from sodium chloride and sodium sulfate which intrude into concrete interior, which proved erosion is obvious under double-factor’s combined action.



(a) (b)

Figure 7: The XRD analysis of suspicious matter in concrete interior Conclusions

4. Conclusion

The conclusions can be drawn as follows:

1. Through the erosion experiment of sulfate with chlorine salt, the article is put forward diffusion rule that sulfate ion won’t influence chloride ion under the action of double factors in city underground structure, but chloride ion diffusion content decreased. As hydration products of concrete would combine with $Cl^-$and generate F salt, therefore it reduced the reactant used for chemical reactions with sulfate, so it postponed sulfate erosion on concrete.
2. In the short time, the combined action of double factors chloride ion with sulfate ion changed the change law of single factor action by chloride ion or sulfate ion, in the combined action of double factors, there didn’t appear the simple superposition of erosion effects from concrete, while there appeared drag effect each other in short time. Test results reflect that, the compressive, flexural and erosion resistance coefficient present obvious change law of decreasing after increasing, in the earlier stage of city underground structure erosion, the action of double factors postponed the decreasing time of erosion resistance coefficient.
3. It was adopted EDS to analyze the suspicious matter generated from concrete interior, it was found that the Ca and Si contained in the suspicious matter mainly come from concrete its own matter CaCO3 and SiO2,

while Na, S, Cl etc are derived from sodium chloride and sodium sulfate which intrude into concrete interior, which proved erosion is obvious under the combined action of double factors.

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