THE COMPETITIVE DIFFUSION PROCESS OF CHLORIDE INTO MORTAR IMMERSED IN CHLORIDE-SULFATE SOLUTION

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Abstract

The chloride and sulfate exist together in real environment, no matter marine or salts lakes, and the ratio of the chloride to sulfate is varied. To precisely predict the concrete durability under real environment, this paper mainly investigated the influence of sulfate on chloride ions diffuse into hardened cement paste. The Minitab software was used to calculate and design the content of compound impregnating solution in order to fully understand the effect of the concentration of chloride and sulfate on the chloride diffusion depth. The $AgNO_3$-based colorimetric method and acid-soluble chloride test were used to determine the chloride diffusion depth and the chloride penetration profile. The evolution phase distribution from the outer to the inner were characterized by SEM, EDS and XRD. The results showed that chloride diffusion generally increased with increasing concentration of chloride. The presence of sulfates promoted chloride diffusion initially, while it delayed the chloride diffusion in the later. Chloride ions diffused into mortar mainly through ITZ and pores, and reacted with the hydration products to produce Friedel's salt. Although the diffusion rate of sulfate ions is slow, it can alter the stability of the Friedel's salt and block the pores, which has a long-term effect on chloride ion diffusion.

Keywords: Chloride, Sulfate, Diffusion, Attack production

1. INTRODUCTION

Chloride-induced corrosion of steel reinforcement is a dominant factor on durability of concrete structures which exposed to marine and salts lake environments. Many studies have been focused on the chloride attack and simulated the process of chloride diffusion into the cement-based materials [1-5]. However, the real service environment is usually a combination with chloride and sulfate. For example, Maes [6] reported that the presence of sulfates decreased the chloride binding capacity and the effect of sulfate on the chloride diffusion depended on the exposure time.

As we all known, the formation of ettringite and gypsum causes the damage of concrete after sulfate ions ingress into the pore structure [7, 8]. However, the phase distribution in cement paste is a complicated problem when chloride-sulfate solution involved [9-12]. The penetrated chloride reacted with hydration products to produce Friedel's salt. However, sulfate can release the bound chloride easily [13-15]. In general, chloride ions penetrate much deeper in the mortar than sulfate ions. With the ingress of sulfate ions, the bound chloride will be decomposed into pore solution again. At this point, the diffusion process of chloride ions becomes complex and the laws of chloride diffusion will be broken by the presence of sulfate ions.

The purpose of this paper is to investigate the diffusion of chloride ions under combined exposure conditions of chloride and sulfate. The impact of sulfate on the entire chloride ion diffusion process is still unclear. Besides, the compound solution used in previous studies are limited into several groups, such as 165 g/l NaCl + 50 g/l Na_2SO_2 in [6] and 3.5% NaCl + 5% Na_2SO_4 in [16], or the simulation of sea water [9]. It is still unknown that the influence of sulfate concentration on the chloride diffusion. To reveal the effect of chloride and sulfate concentrations on the diffusion process, the Minitab was used to design a compound salt solution, in which the concentration range of the chloride salt was 0-25% and the sulfate was 0-5% in this study. This concentration range contains almost all of real chloride-sulfate environment.

2. MATERIALS AND METHODS

2.1 Materials

Cement (P II 52.5) was used to prepare the cement mortars and the detailed chemical composition of the cement is presented in **Table 1**. Combined chloride-sulfate corrosion was simulated under laboratory conditions by dissolve NaCl and Na_2SO_4 in designed concentrations.

Table 1: Chemical composition of the cement (%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	LOI
20.87	4.87	3.59	64.47	2.13	2.52	0.65	0.11	0.77

2.2 The design of compound salts solution

The Minitab is helpful to intuitively understand the relationship between the factors and the response, and it was usually used to optimize the mix design for desired responses and to find the synergistic effect between factors since it provided continuous features of the image analysis

[17-19]. In this study, chloride and sulfate in the compound salts solution are equivalent attack factors which should satisfy the equation (1):

$NaCl$ (wt/%)+ Na_2SO_4 (wt/%)+ H_2O (wt/%)= 1 (1)

The detail of the compound ratio is shown in Table 2. 25% NaCl (Cl25) was selected as single chloride solution, while 25% NaCl+5% Na_2SO_4 (Cl25S5) was the chloride-sulfate compound salts solution.

Table 2: The proportion of compound salt solutions (wt/%)

Number	H_2O	NaCl	Na_2SO_4
Cl25	75	25	0
S5	95	0	5
Cl6S3	89.375	6.875	3.75
Cl19S1	79.375	19.375	1.25
Cl25S5	70	25	5
Cl5	95	5	0
Cl19S3	76.875	19.375	3.75
Cl9S1	89.375	9.375	1.25
Cl13S2	83.75	13.75	2.5

2.3 Test methods

The mortars with dimension of 40*40*160 mm were prepared at water-to-cement of 0.48. The sand to binder ratio was maintained at 1.5 by weight. After standard curing for 28 days, the specimens were sealed with epoxy on around to ensure one-dimensional diffusion. Then, the specimens were immersed in the compound salts solution above.

The $AgNO_3$-based colorimetric method was used to determine the depth of chloride diffusion [20]. After immersing for different times, the specimens are split and sprayed with $AgNO_3$.

The total chloride content (acid-soluble chloride) along the depth of the specimen was test according to Chinese standard (JTJ 270-1998). The chloride content at each depth of the specimen and various designated time was tested in order to determine the chloride profile according to the depth and the time.

3. RESULTS AND DISCUSSION

3.1 Chloride penetration depth

Fig. 1 demonstrates the chloride diffusion depth immersed in chloride and chloride-sulfate, respectively. For immersion periods before 120 d, chloride diffusion depth in chloride solution was shorter than that in the compound salts solution. After 120 d immersion, the chloride penetration depth immersed in chloride-sulfate solution was less than that in single chloride environment. The results revealed that the presence of sulfate promoted chloride diffusion initially, with the prolongation of immersion time, the sulfate has an inhibitory effect on chloride ion diffusion. Therefore, the influence of sulfate on the chloride diffusion mechanism changes in a function of the exposure time.

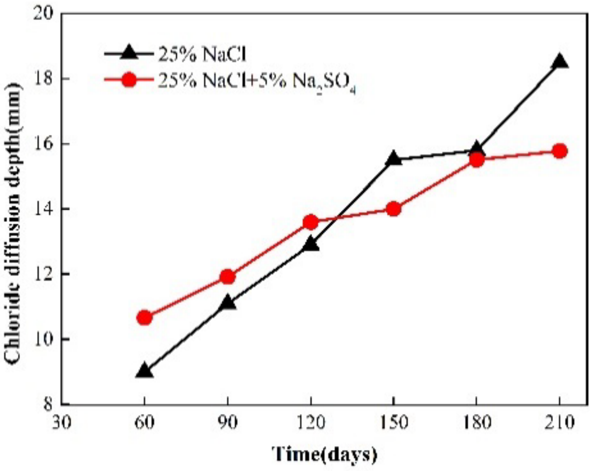

Figure 1: Chloride diffusion depth for exposure to Cl25 and Cl25S5 solution

3.2 Chloride penetration profile

The chloride content in the mortars at different depth when subjected to chloride and chloride-sulfate are shown in Fig. 2. In the outermost layer, when immersed in 25% NaCl for 60 d, the chloride content was 1%, and it had reached up to 1.55% after 210 d. For immersion time from 60 d to 210 d, the longer immersion time, the more chloride contents diffusion into the mortars. The presence of sulfate can promote more chloride ions into the mortars at every depth, when the immersion time was 60 d. However, after immersion time up to 210 d, the chloride contents of mortars immersed in single chloride environment were more than that immersed in chloride-sulfate solution, especially in the outmost layer.

The distribution of chloride content in the mortar are present in Fig. 3, from which it can draw the conclusion that the interaction effect between chloride and sulfate on chloride diffusion. The abscissa is the concentration of the chloride salt, and the ordinate is the concentration of the sulfate. The most obvious rule was that the higher the concentration of the chloride salt, the more chloride content entered into the mortar. After immersion for 210 d, the change trend of counter was upward as shown in Fig. 3(a), which demonstrated that the presence of sulfate reduced the amount of chloride content within 0-5 mm. In the range from 5 to 10 mm, the effect of the sulfate was not obvious shown in Fig. 3(b), but, this level can be considered as the region where the role of sulfate begin to transform. From Fig. 3(c) and Fig. 3 (d), it can be found that sulfate was helpful to increase the chloride content in the range of 10-20 mm, which was different from Fig. 3(a).

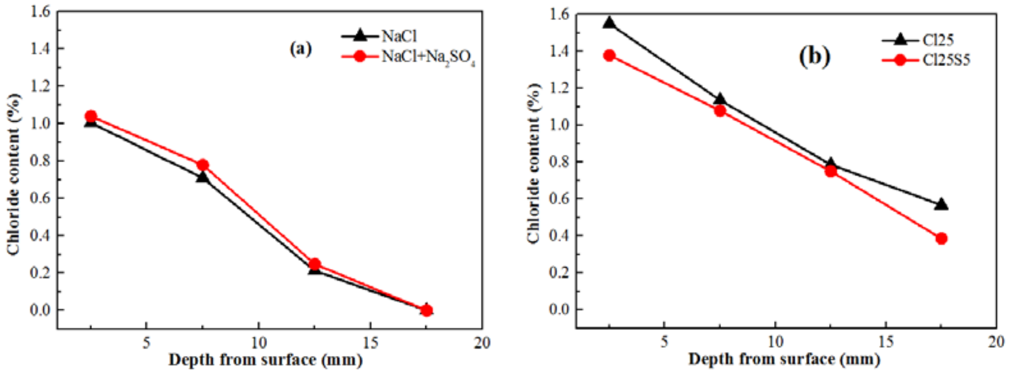

Figure 2: Chloride penetration profile along the depth at: (a) 60 d and (b) 210 d

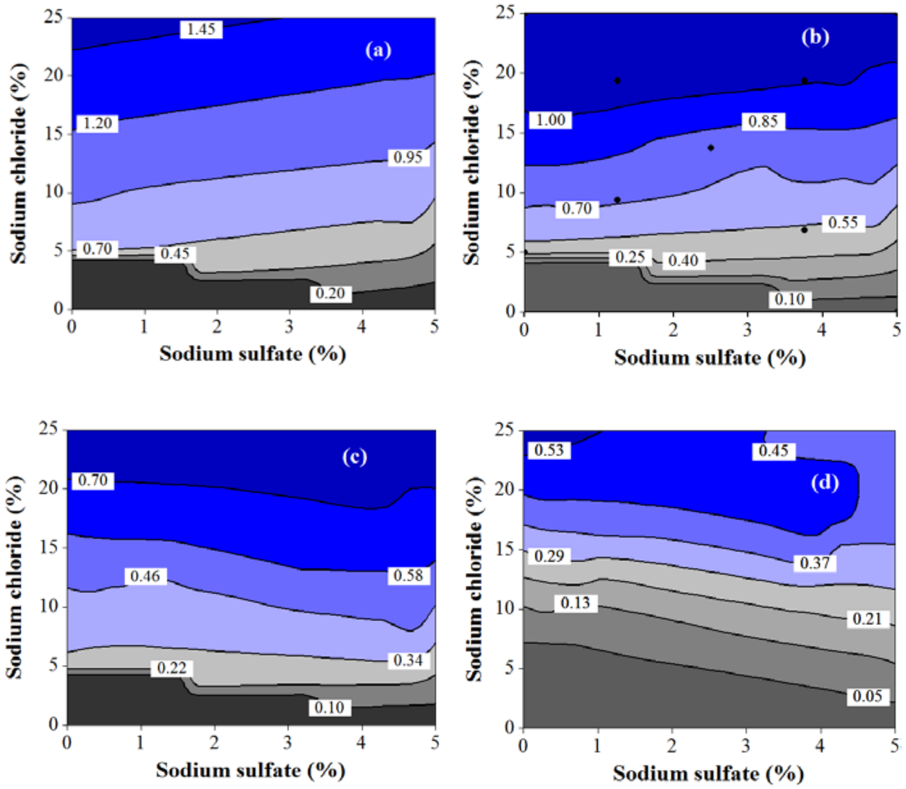

Figure 3: The distribution of chloride content in the mortar (a) 0-5 mm; (b) 5-10 mm; (c) 10-15 mm; (d) 15-20 mm

3.3 XRD analysis

The phase distribution inner the mortar is shown in **Fig. 4**. There are two hydration products which are best known to bind chloride ions, the CSH phase and AFm phase. When immersed in 25% NaCl+5% Na_2SO_4 for 60 d, Friedel's salt was still present at the outmost layer. However, it disappeared after 210 d immersion because of sulfate invasion. It is reported that the SO_4^{2-}

can replace the Cl^- in Friedel's salt to form ettringite, which can also be confirmed by **Fig. 4**. At the same immersion time for 60 d, the Friedel's salt subjected to 25% 25% NaCl + 5% Na_2SO_4 was more than that subjected to NaCl at the depth of 15 mm to 20 mm. It can be considered that the sulfate can promote the chloride diffusion before 60 d. On the contrary, the rule was reversed when the immersion time was up to 210 d.

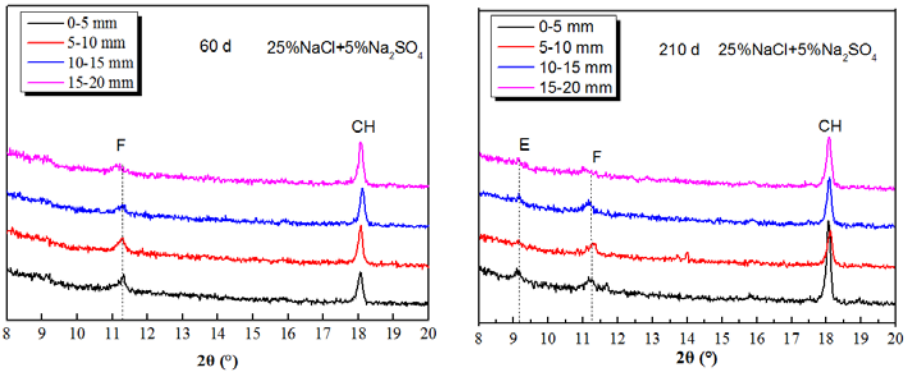

Figure 4: XRD pattern of mortar immersed in NaCl and NaCl + Na_2SO_4 for different immersion age (E: ettringite, F: Friedel's salt, CH: $Ca(OH)_2$)

3.4 SEM analysis

Fig. 5 gives the distribution of sodium chloride inner mortar by SEM analysis. There was a large amount of sodium chloride crystals, determined by EDS analysis, in the vicinity of the sands. The diffusion properties of the ITZ has a significant impact on chloride ingress in concrete [21]. Therefore, the ITZ and pores are the main paths for chloride diffusion. **Fig. 6** is the SEM images of ettringite crystals after 210d immersion in 25% NaCl+5% Na_2SO_4. The ettringite crystals have perfect needle-shape with hexagonal cross section [22] and usually form in cracks.

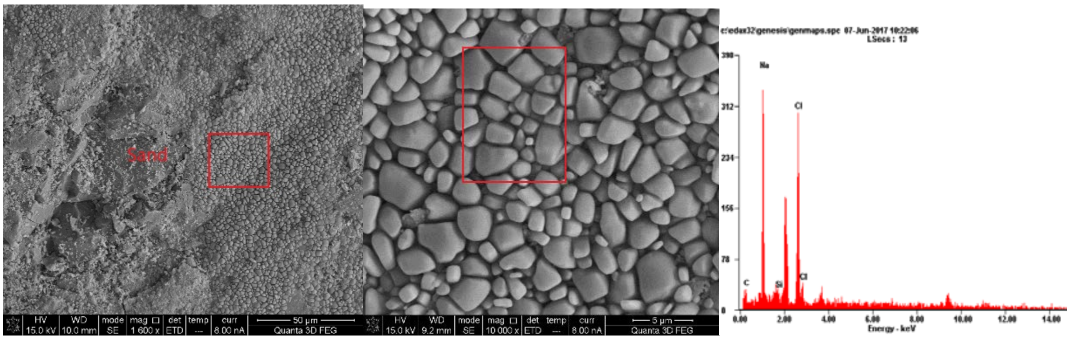

Figure 5: SEM images of NaCl crystals growing inside pores and ITZ after 210d immersion in NaCl

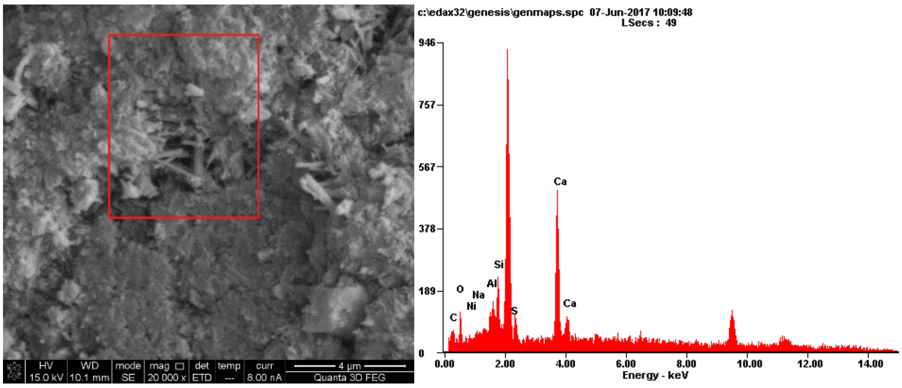

Figure 6: SEM images of ettringite crystals after 210 d immersion in 25% NaCl+ 5%Na_2SO_4

When the mortar was immersed in chloride-sulfate solution, chloride and sulfate ions diffused into the interior of the mortar simultaneously. Because of the fast diffusion rate of chloride, it can be considered that hydration products have reacted with chloride completely. However, the sulfate has a significant effect on the stability of the Friedel’s salt, which can convert the Friedel’s salt into ettringite. It is also reported that there is a binding competition between chloride and sulfate and the competition should start from the outmost layers [6]. This implies that the presence of sulfate will decrease the amount of chloride bound by hydration products and accelerate the chloride diffusion. After immersion for 210 d, the sulfate also entered into the mortar and filled in the pores and ITZ as the sodium chloride shown in **Fig. 4**. In other words, sulfate ions maybe an unfavorable factor for chloride diffusion for a long term.

4 CONCLUSIONS

(1) The influence of sulfates on the chloride diffusion in function of not only the exposure time, but also the concentration.

(2) The stability of bound chlorides is susceptible to Na_2SO_4 attack, so the presence of sodium sulfate in a chloride solution aggravates the diffusion of free chlorides at early/short exposure.

(3) The ITZ and pores are main paths for chloride and sulfate diffusion. The formation of ettringite and gypsum caused by sulfate act as a favorable factor to delay chloride diffusion in the long term.

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