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Interaction between sulfate and chloride solution attack of concretes with and without fly ash

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Abstract

In this paper, the two sets of concretes under attack of erosion solution of sulfate and chloride salt were investigated. The one set is the plain concrete without fly ash addition. The other set is the concrete with 20% and 30% of fly ash addition, respectively. The corrosion solution includes three types: 3.5%NaCl, 5% Na_2SO_4, and a composite solution of 3.5%NaCl and 5% Na_2SO_4. In addition, two corrosion regimes were employed in this study: naturally immersion (stored in corrosion solution for long duration), drying-immersion cycles. The damage process of the two sets of concretes was systematically investigated under the above three types of corrosion solutions and two corrosion regimes. The interaction between sulfate and chloride salt was also quantitatively determined. The experimental results shown that a presence of sulfate in the composite solution increased the resistance to chloride ingress into concretes at early exposure period, but the opposition was observed at latter exposure period. For the damage of concretes, a presence of chloride in the composite solution reduces the damage of concrete caused by sulfate. Addition of fly ash may significantly improve the resistance to chloride ingress into concretes and the resistance to sulfate erosion when a suitable amount of fly ash addition and low water-to-binder (W/B) was employed. Studies of the different corrosion regimes indicate that concretes stored in corrosion solution for about 850 d, the changes in relatively dynamic modulus of elastically (RDME) could be described by three stages: linearly increasing period, steady period, and declining period. Whereas for drying-immersion cycles, an accelerated trend could be found. The changes in RDME included an accelerated decreased stage, linearly increased stage, and then a slowly decreased stage, finally accelerating failure stage. In order to elucidate the above experimental results in a microscopic scale, the mechanism was also investigated by the modern microanalysis techniques.

Keywords: Concrete; Chloride; Sulfate; Composite salts; Damage

1. Introduction

The durability of concrete constructions is of a great major concern to the construction industry across the world. It is well known that the steel rebar erosions of the reinforced concrete caused by the ingress of chloride ions are the most severer problem affecting the durability of concrete constructions, especially in the saline environments. Once a sufficient quantity of chloride has been accumulated on the surface of the embedded steel rears, pitting corrosion will occur. Generally, the diffusion of chloride ion into concrete is very slowly if the concrete cover is not deteriorated. However, when the concrete cover is damaged by sulfate solution attack, which is commonly encountered in field constructions, chloride ion will rapidly access to the surface of steel rebar embedded in concrete. The attack of sulfates on concrete is due to two principal reactions: the reaction of Na_2SO_4 and $Ca(OH)_2$ to form gypsum and the reaction of the formed gypsum with calcium aluminate hydrates to form ettringite. In addition, it is noticed that $MgSO_4$ reacts with all cement compounds, including C–S–H, thus decomposing cement, and subsequently forming gypsum and ettringite [1].

At present there are more than 1000 salt lakes scattering in the Northwest of China, where many concrete constructions are severely deteriorated and lost its function only in several years, which is mainly caused by the concentrated salt solutions such

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Table 1
Chemical composition of OPC and fly ash

Constituent (wt.%)	SiO_2	Al_2O_3	CaO	MgO	SO_3	Fe_2O_3	Loss	C_3S	C_2S	C_3A	C_4AF
OPC	20.6	5.03	65.06	0.55	2.24	4.38	1.30	60.74	16.18	6.66	14.17
Fly ash	54.7	24.04	8.7	1.13	1.50	6.9	2.35				

as chloride and sulfate ions, and the badly climate. For example, in Chaierhan salt lake located in Qin Hai province of China, it is a typical salt lake with the Cl^- and SO_4^{2-} concentration of 220 g/l and 23 g/l respectively, the highest and low temperatures of 69 °C and −33.4 °C respectively, the RH of 40–60% and the average amount evaporation of 597 mm/month [2]. So investigation of the damage process of the concretes in these areas and its evaluation of service life are of great importance for a rapid development of the infrastructure in the northwest of china.

Many researches related to concrete deterioration and steel rebar corrosion are widely made in a sulfate solution or chloride solution [3–5]. However, little studies of the whole process of damage are done on concretes attacked by a composition salt solution of Cl^- and SO_4^{2-}. And it is in the little studies that different viewpoints were expressed. The role of chloride ions in the presence of sulfate and that of sulfate in the presence of chloride ions on the deterioration of concretes are not well known. Limited experimental data developed by Omar demonstrated that the damage caused in concrete by sulfate attack is reduced in a presence of chloride [6]. Feldman also reported that for the concrete stored in a composite solution for 12 months, the concurrent presence of sulfate and chloride ions in solution decreased the chloride ion ingress rate into plain concrete and concretes incorporating the partial replacement of cement with slag and silica fume [7]. Tumidajski showed a viewpoint similar to Feldman about the ordinary Portland cement concrete base on the experimental results, while he also proposed that a presence of sulfate ion increased the chloride penetration and diffusivity in the slag concrete [8]. Contrastly Dehwah considered that the presence of sulfate ions in the chloride solution did not influence the time to initiation of chloride-induced reinforcement corrosion, but the rate of corrosion increased with increasing sulfate concentration [9]. Obviously, chloride diffusion and deterioration of concretes would change with the different research circumstances. This study was conducted to assess the effect of sulfate on chloride penetration and diffusivity and effect of chloride on deterioration of concretes attacked by sulfate. And the damage process of concretes caused by mixed chloride and sulfate ions was also studied.

Table 2
The mix proportion and compressive strength of concretes (kg/m^3)

No.	kg/m3					Compressive strength(MPa)	
	Cement	Water	Fly ash	Sand	Aggregate	28 d	90 d
C30R	350	155	0	760	1140	47.8	58.0
C30F	245	155	126	740	1138	36.9	51.6
C50R	420	147	0	692	1127	70.1	78.2
C50F	336	147	100	644	1128	70.1	84.2

2. Materials

A Chinese standard 42.5 R(II) Portland cement similar to the ASTM type I ordinary Portland cement, with a compressive strength of 52.5 MPa at an age of 28 days was supplied by Jiangnan cement corporation in China. Class F fly ash, river sand with fineness modulus of 2.6, and coarse aggregate of crushed limestone with maximum size of 10 mm were used in the test. A naphthalene-type superplasticizer was used and the dosage was adjusted to keep the slump of fresh concrete in the range of 140 to 180 mm. The chemical composition of cement and fly ash is shown in Table 1.

Two sets of concretes were made in this investigation. The one set is the plain concrete without fly ash addition. The other set is the concrete with 20% and 30% replacements of cement with fly ash, respectively. Two W/B of 0.45 and 0.35 were employed. The mixture proportions and the corresponding compressive strengths of the concretes are given in Table 2.

3. Experimental programs

Concrete specimens (40 × 40 × 160 mm^3) were cast and placed at room temperature with module. The mould was removed after 24 h. Then, all specimens were cured in a condition of 20 ± 3 °C and 95% of relative humidity for a period of 60 days. Two erosion regimes were used to investigate the damage process of concretes. One is naturally immersion regime and the other is accelerated regime. For naturally immersion regime, concrete specimens from each mixture were submerged in 21 g/l Cl^- solution (3.5% by mass of NaCl),

Fig. 1. Drilled concrete specimens for evaluation concentration of chloride at different depth intervals.

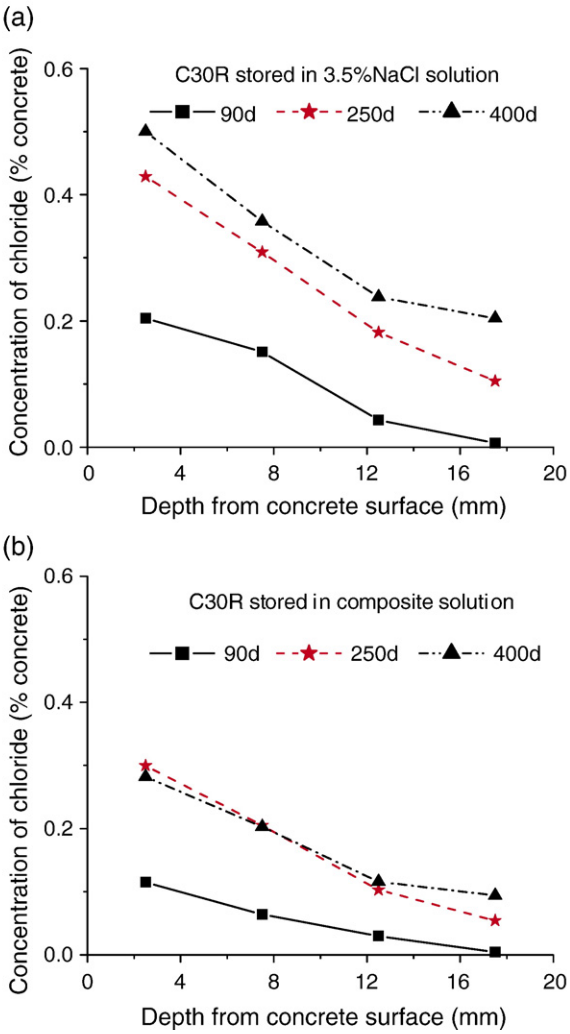

Fig. 2. Concentration of chloride of C30R concrete stored in 3.5%NaCl solution or in composite solution.

33.8 g/l SO_4^{2-} solution (5% by mass of Na_2SO_4) and a composite solution of 3.5%NaCl and 5% Na_2SO_4 at room temperature for about 800 d, respectively. For accelerated regime, concrete specimens were subjected to drying-immersion cycles: firstly concrete specimens dried at 60 °C for 24 h, then cooled in air at room temperature for 3 h, lastly submerged in above-mentioned solution at room temperature for 45 h.

The specimens are allowed to dry after subjecting to the two corrosion regimes mentioned above for 90 d, 250 d and 400 d, respectively. The surface of the dried specimens is cleaned with steel wire brusher until the salt crystals caused by corrosion test is completely removed. Then, each concrete specimen powder was collected from the exposed to chloride surface into the inner region of the specimens at regular intervals of 5 mm by drilling, which shown in Fig. 1. The powder taken from concrete specimens was dried at 105 °C for 2 h and passed through a 0.63-mm sieve, and the powder samples obtained were stored in airtight plastic bags. The chloride content of the powder samples was analyzed by means of water-soluble method [10,11]. And the powder samples were ground to pass through 0.08 mm sieve, used for X-ray diffraction (XRD) analysis.

For determining the content of water soluble chlorides at different depth intervals from the concrete surface to the inner section, about 3–5 g of the powder sample is weighted and digested using 50 ml deionized water for 24 h, and then filtered to remove the solid residues. The chloride content was measured using 0.02 mol/l silver nitrate and kalium chromate as indicator.

3.1. RDME measurement

Before placing the specimens in corrosion solution or exposing to drying-immersion cycles, their dynamic modulus of elasticity (DME), which was determined by Eq. (1), was measured by using a high-accuracy nonmetal ultrasonic analyzer as the initial value. The DME changes of specimens were then monitored at every 1 or 2 weeks at the first half years, and afterwards tested every one month. The relative dynamic modulus of elasticity (RDME), which was determined by Eq. (2), is the ratio of DME value to the initial DME value after a certain exposure age. According to the test procedure, the specimen was considered to be a failure if the

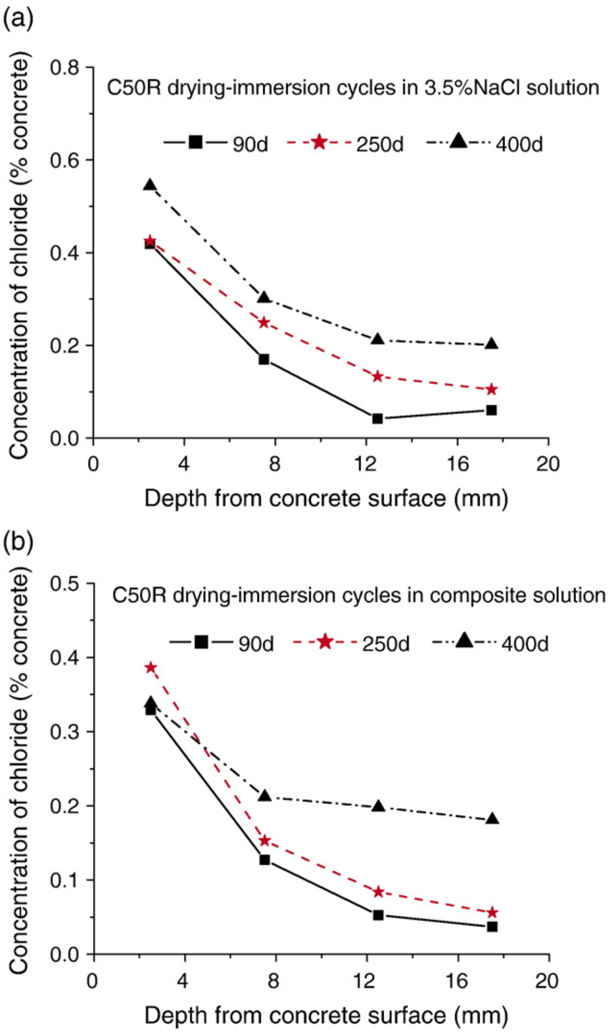

Fig. 3. Concentration of chloride of C50R concrete exposed to drying-immersion cycles in 3.5%NaCl solution or in composite solution.

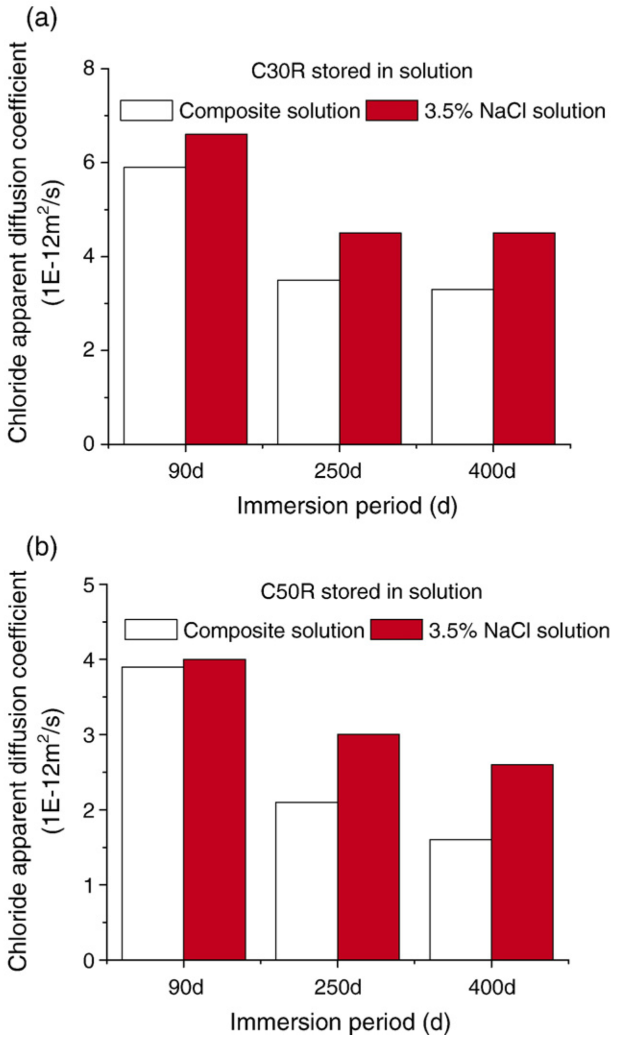

Fig. 4. Chloride apparent diffusion coefficient of concrete stored in 3.5%NaCl solution or in composite solution.

RDME dropped to 60% or less. Three specimens were measured for each concrete mix.

$$E_{\mathrm{d}} = \frac{(1+\upsilon)(1-2\upsilon)\rho V^2}{1-\upsilon} \tag{1}$$

$$\mathrm{RDME} = \frac{E_{\mathrm{d}t}}{E_{\mathrm{d}0}} = \frac{V_t^2}{V_0^2} = \left(\frac{T_0}{T_t}\right)^2 \tag{2}$$

Where E_{d} is Dynamic modulus of elasticity, V is ultrasonic speed (m/s), T_0 and T_t are the ultrasonic time of concrete specimens at an age of 60 days curing and at the exposure period of 't' (s), ρ is density of specimen (kg/m^3) and υ is Poisson's ratio.

XRD measurements were performed on D8 Advance X-ray using Cu radiation and operating at 40 kV and 20 mA. Step scanning was used with a scan speed of 2°/min and sampling interval of 0.08°2θ.

Table 3
Characteristic values of the age factor n for chloride ingress in 3.5%NaCl solution and composite solution

Concrete type	3.5%NaCl solution		Composite solution		Chloride solution (DuraCrete)
	C30R	C50R	C30R	C50R	OPC
n	0.3001	0.28605	0.43778	0.41733	0.30
Correlation	0.92	0.999	0.985	0.996	

4. Results

4.1. Chloride diffusion of concretes exposed to 3.5%NaCl solution and composite solution

Chloride concentration profiles at different depth intervals of C30R concretes submerged in 3.5%NaCl and composite solution after different immersion periods are shown in Fig. 2 (a) and (b) respectively. It is clear that the concentration of chloride decreased with the increase of specimen depth, and reached to a steady value at a depth of 15 mm to 20 mm. The amount of chloride, at a depth of 5 mm to 20 mm, increased with an increase of immersion period. Comparatively, the

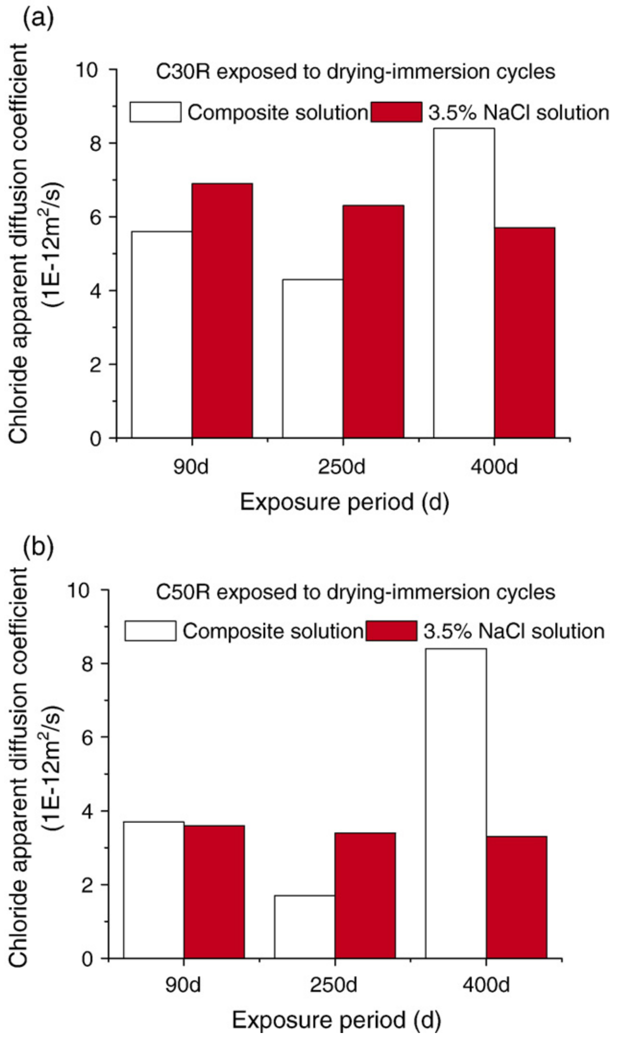

Fig. 5. Chloride apparent diffusion coefficient of concrete exposed to drying-immersion cycles and in 3.5%NaCl solution or in composite solution.

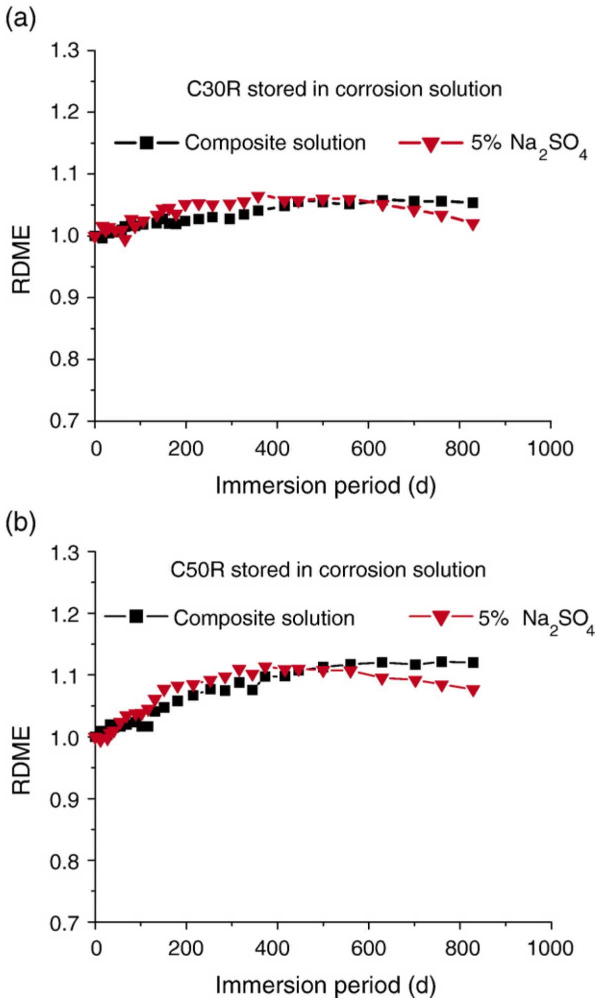

Fig. 6. RDME of concrete stored in composite solution or in 5%Na_2SO_4 solution.

exterior concrete at a depth of 0 mm to 5 mm, shows an increasing trend at an early immersion period, while becoming steady at the latter immersion period. This may be explained by the fact that the chloride will gradually become balance with the corrosion solution after a long immersion period. Additionally, it is clear that sulfate in composite solution has a pronounced effect on the chloride profiles. The presence of sulfate significantly increases the resistance of the concrete to chloride ion penetration in a period of 400 days immersion. Sulfate was very effective in reducing the chloride concentration at various depths, and the decreasing effects become more pronounced with an increase of depth. And a similar trend is also observed for C50R concretes.

C50R concrete is subjected to drying-immersion cycles. The chloride concentration at different depth interval profiles in 3.5%NaCl and composite solution is depicted in Fig. 3 (a) and (b). As compared with naturally immersion, drying-immersion cycles markedly accelerated the ingress of chloride, resulting in an increase of the concentration at various depths. It is interesting to note that sulfate in composite solution has a considerable effect on the profiles, which is largely different from naturally immersion test in the corresponding solution. For drying-immersion cycles, the chloride concentration of C50R concretes is reduced by 30 to 60% due to the presence of sulfate in composite solution at a period of 90 d and 250 d. While with a development of exposure period the chloride concentration in the composite solution gradually approaches to even exceed the concentration in only 3.5%NaCl. The above experimental results indicate that a presence of sulfate in composite solution will decrease the concentration of chloride at an early exposure period, while a reversible trend is right at a latter period.

The dominant mechanism for chloride ingress into concretes is diffusion. The simple non-steady state diffusion equation is then Eq. (3):

$$C_f = C_s\left(1-\mathrm{erf}\frac{x}{2\sqrt{Dt}}\right) \tag{3}$$

where C_f=chloride content at depth x and time t C_s=chloride content at the surface, x=depth, t=time, and D=free chloride diffusion coefficient.

Free chloride diffusion coefficient, which was calculated by Eq. (3), for C30R and C50R concretes stored in 3.5%NaCl and

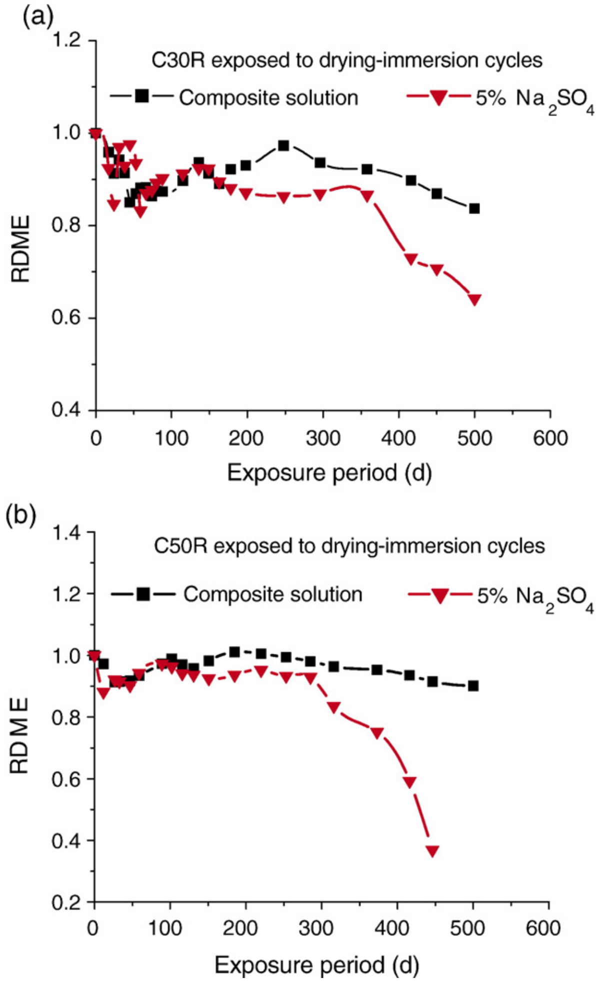

Fig. 7. RDME of concrete exposed to drying-immersion cycles and in composite solution or in 5%Na_2SO_4 solution.

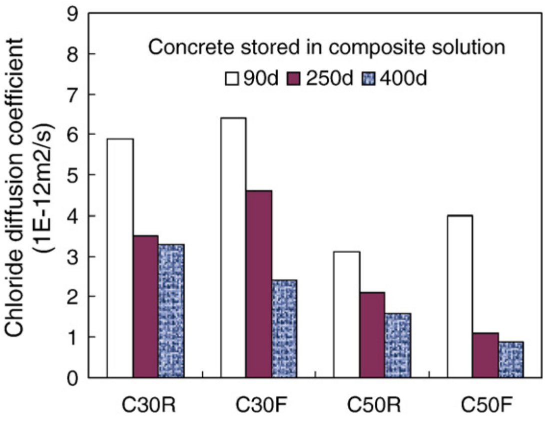

Fig. 8. Chloride apparent diffusion coefficient of concrete with and without fly ash stored in composite solution.

composite solution was shown in Fig. 4 (a) and (b), respectively. It is obvious that chloride diffusion coefficient decreased with immersion time in a period of 400 days. Considering the chloride diffusion coefficient varied with exposure period, the value of the time dependent chloride diffusion is as Eq. (4). In our testing, as concretes stored in 3.5%NaCl and composite solution, the age factor *n* was presented in Table 3

$$R(t) = R_0 / \left(\frac{T_0}{t}\right)^n. \tag{4}$$

Where

R_0 Resistance with respect to chloride ingress determined on the basis of compliance tests, which equal to the reciprocal of chloride diffusion coefficient ($1/D_0$).

$R(t)$ Value of the chloride resistance at the age of 't', year/mm^2. n, age factor.

As shown in Table 3, the calculated age factor '*n*' was 0.3 and 0.286 for C30R and C50R concretes respectively when concretes are naturally stored in 3.5%NaCl for a period of 400 days. But in composite solution, the age factor '*n*' increased by 0.138 and 0.131 respectively. This means that a presence of sulfate in composite solution decreased the diffusion coefficient of chloride, and reduced the ingress of chloride into concretes at early exposure age.

Free chloride diffusion coefficient, which was calculated by Eq. (3), for C30R and C50R concretes exposed to drying-immersion cycles in 3.5%NaCl and composite solution was shown in Fig. 5 (a) and (b). It is clear that chloride diffusion coefficient decreased with exposure period and gradually approached to steady state as concretes stored in 3.5%NaCl solution. But as for concretes in composite solution from 90 d to 250 d, the chloride diffusion coefficient decreased with exposure period, and then increased sharply from 250 d to 400 d. So a presence of sulfate in composite solution reduced the ingress of chloride into concretes in early exposure period but the opposite is observed in the latter exposure period considering the drying-immersion cycles an accelerated regime.

4.2. Deterioration of plain concretes in 5%Na2SO4 and in composite solution

RDME of C30R concrete stored in 5%$NaSO_4$ and in composite solution was recorded and shown in Fig. 6 (a). The RDME of C30R in 5%$NaSO_4$ exhibits three distinct stages. In Stage I, from the initial immersion to 316 d, the RDME increases linearly with immersion period, thus calling the 'linearly increased period'. In Stage II, from 316 d to 560 d, the RDME keeps steady in the period, denoting 'steady period'. In Stage III, from 560 d to 830 d, the RDME decreases from 1.107 to 1.077 and this stage denoted as 'declining period'. Comparatively, in concrete specimen in composite solution for 830 d, only Stage I and II occurred, and Stage III didn't occur due to the short immersion period. The RDME for C50R concrete was also plotted in Fig. 6 (b). Careful observation shows a trend similar to C30R concrete.

Based on the above experimental results, the presence of chloride in composite solution prolongs the duration of each period. That is, the presence of chloride delays the deterioration of concrete attacked by sulfate. For example, the period of Stage I is 316 days for C50R in 5%$NaSO_4$, while it is about 560 days in composite solution.

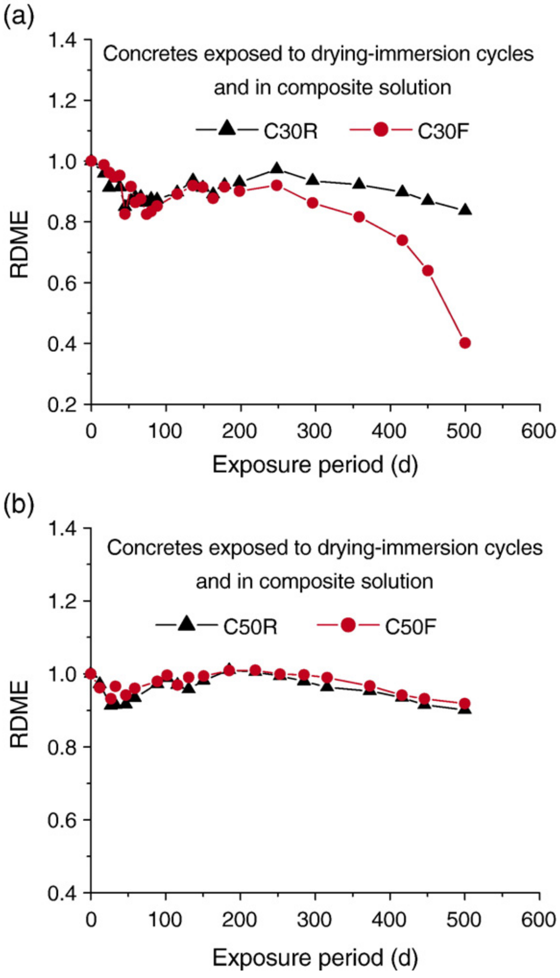

Fig. 9. RDME of concretes with and without fly ash exposed to drying-immersion cycles and in composite solution.

The RDME of C30R and C50R exposed to drying-immersion cycles in 5%Na_2SO_4 and in composite solution was shown in Fig. 7 (a) and (b), respectively. Compared to naturally immersion, drying-immersion showed a low value of RDME. Moreover, the RDME of specimens in 5%Na_2SO_4 was compared with that in composite solution. The RDME in C30R concrete was 0.63 in 5% Na_2SO_4, 0.84 in composite solution after an exposure period of 500 days. The C50R concrete also shows a similar trend, that the RDME in C50R was 0.35 in 5% Na_2SO_4, 0.89 in composite solution after an exposure period of 450 days. This indicates that the presence of chloride in composite solution delays the deterioration of concretes caused by sulfate attack.

Additionally, it can been seen from Fig. 7 (a) and (b) that the RDME of specimens in 5%$NaSO_4$ occurs in 4 stages: (I) the decreased stage, (II) linearly increased stage, (III) slowly decreased stage, and (IV) the accelerating failure stage. But in composite solution, the RDME only experiences Stage I to Stage III for 500 days of drying-immersion cycles. Stage I corresponds to 0–55 d for specimens in 5%$NaSO_4$ and in composite solution, and the decreased value of RDME is similar for two corrosion solutions. In Stage II and stage III, their period prolongs about 100 days in composite solution in comparison with that in 5%$NaSO_4$, respectively. And Stage IV just occurs in 5%$NaSO_4$.That is, the presence of chloride in composite solution prolonged the interval of each stage, and decreased the deterioration of concretes attacked by sulfate.

4.3. Deterioration of concretes with fly ash in 5%Na2SO4 and composite solution

Free chloride diffusion coefficient of the concretes with and without fly ash (denoted as C30R, C30F, C50R and C50F), when submerged in composite solution, is shown in Fig. 8. The chloride

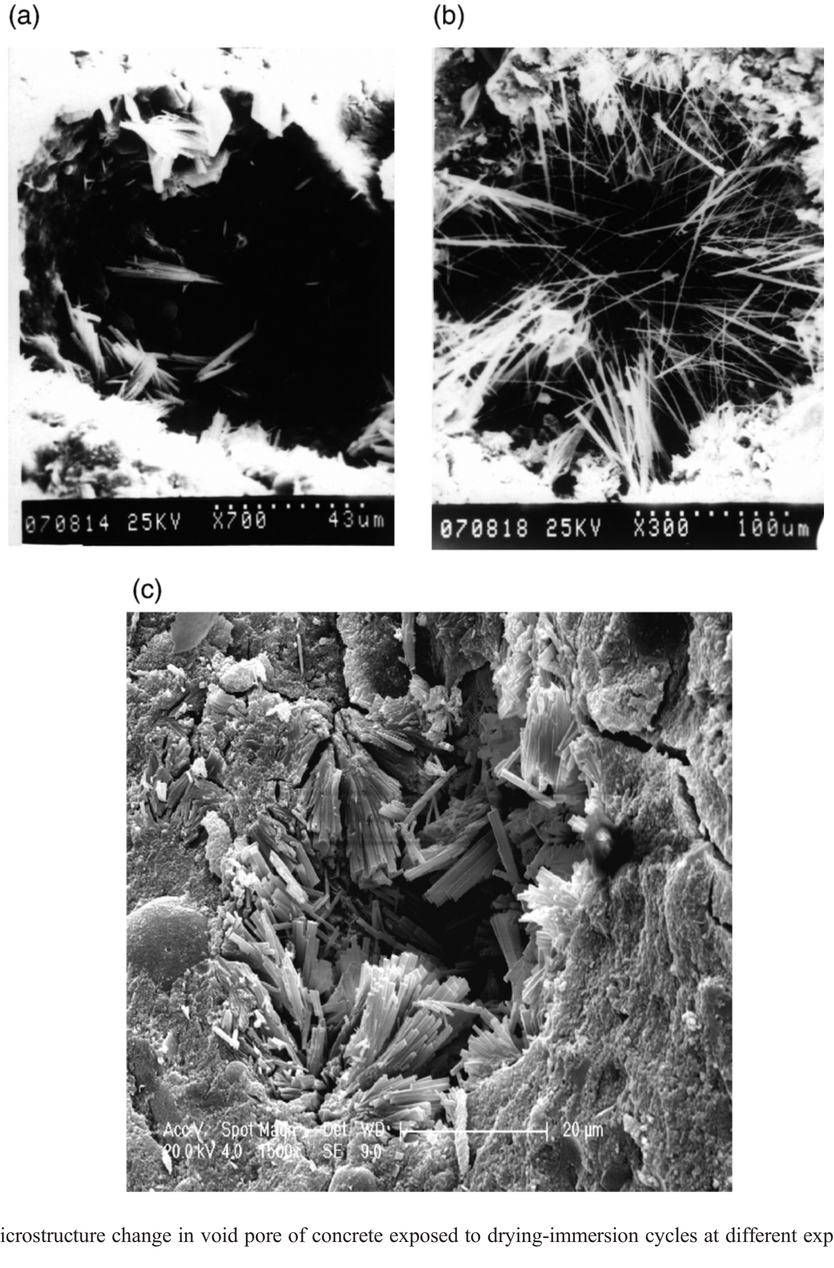

Fig. 10. The microstructure change in void pore of concrete exposed to drying-immersion cycles at different exposure periods.

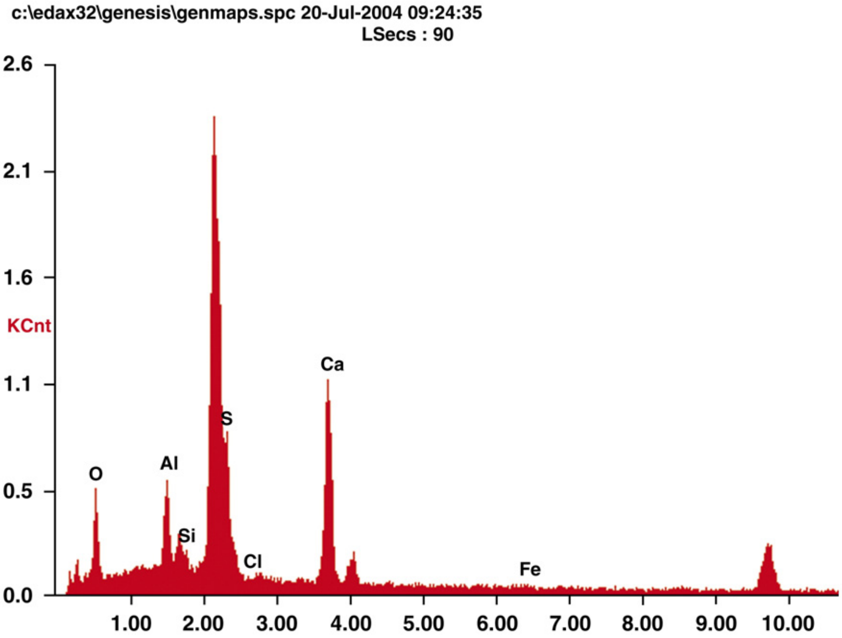

Fig. 11. EDS of needle crystal in void pore of concrete exposed to drying-immersion cycles.

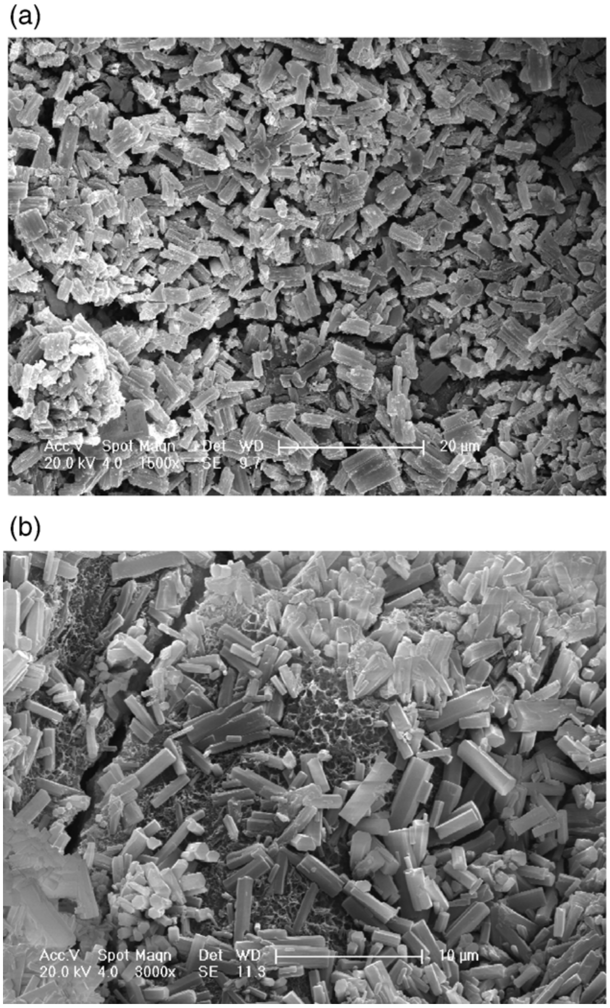

Fig. 12. Short columniation shape crystal and cracks in interface of paste-aggregate.

diffusion coefficient of C30R concrete is 5.9E$E-12$ m^2/s and 3.5$E-12$ m^2/s at 90 d and 250 d, respectively. When fly ash is introduce, the chloride diffusion coefficient of the concrete (C30F) increases to 6.4$E-12$ m^2/s and 4.6$E-12$ m^2/s at 90 d and 250 d. Whereas, a different phenomena is seen at 400 days, that the chloride diffusion coefficient of C30R (3.3$E-12$ m^2/s) is higher than that of C30F (2.4$E-12$ m^2/s). A similar change in chloride diffusion coefficient is also observed for the C50R and C50F. That is, chloride can more rapidly ingress the interior of concretes with fly ash compared to plain concretes at the early exposure period, while the opposite is right at the latter exposure period.

Fig. 9 (a) and (b) shows the RDME of concrete with and without fly ash exposed to drying-immersion cycles in composite solution. The RDME of C30R concrete is 0.84 after an exposure period of 500 days, which is higher than that of C30F (0.4). However, C50R concrete exposed to drying-immersion cycles didn't show significant difference in RDME from C50F. The RDME of C50R is 0.91 compared with a value of 0.93 noted in

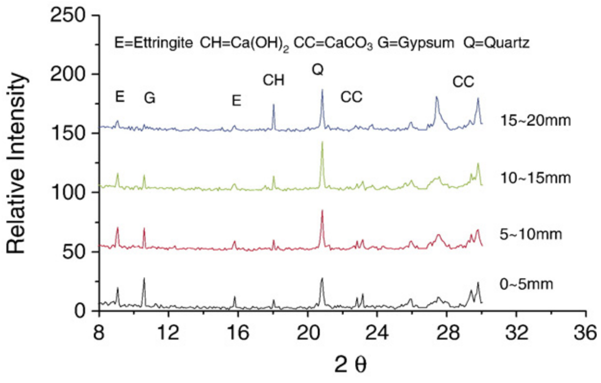

Fig. 13. XRD patterns for C50R exposed to 5% Na_2SO_4 and drying-immersion cycles at 400 d.

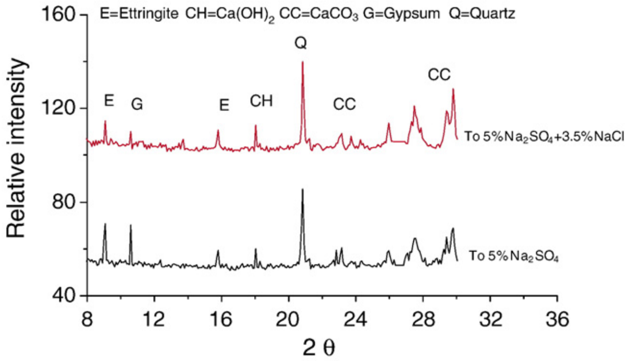

Fig. 14. The XRD patterns of C50R concrete (in 5–10 mm depth) to different solutions.

C50F after an exposure period of 500 days. The above experimental results well imply that the decrease of W/B and a suitable amount of fly ash addition could greatly increase the resistance to sulfate attack, but the opposite is for concrete with high content of fly ash and W/B.

4.4. Microstructure change of concretes exposed to composite solution

For concrete specimens exposed to drying-immersion cycles for a period of 90 d, 250 d and 400 d, the microstructure change in void pore was shown in Fig. 10 (a), (b), (c). As can be seen from Fig. 10, needle-like crystals can be seen in the pores and its amount continuously increases with exposure period. After 400 days of exposure, these pores are almost completely filled up by needle-like crystals, and with the further development of exposure period, the crystals continuously produced in pores, resulting in occurrence of cracking. To characterize the chemical compositions of the needle crystals, EDS technique is utilized and the results were shown in Fig. 11. Careful observation of EDS spectra showed that needle crystals consist of aluminum, sulfate, calcium and silicon elements, and the molar ratio of Al:S:Ca is about 1:3:6, which indicated the needle crystals were ettringite crystals. Fig. 12 displayed the SEM images of the interface zone (ITZ) between paste and aggregate of concrete specimens exposed to drying-immersion cycles for a period of 500 days. SEM observation shows that there exists a large amount of crystals and cracks in ITZ. The EDS spectra of these crystals indicate that they are gypsum.

Fig. 13 shows the XRD patterns for C50R concrete exposed to 5% Na_2SO_4 solution and drying-immersion cycles at 400 d. In these diagrams, the quartz first peaks were reduced using software to clearly show the compounds formed by sulfate attack. The peaks selected for the qualitative analysis of these phases were ettringite at about 9.08°2θ, gypsum at 11.59°2θ, CH at 18.04°2θ, and $CaCO_3$ at 29.4°2θ.

The XRD trace indicates that gypsum, ettringite and $Ca(OH)_2$ were only crystalline phases present in the different depths of concrete in addition to quartz and calcite. The gypsum and ettringite peaks in each depth of concrete were strong, indicating that the gypsum and ettringite were main corrosion products. Moreover, the concentrations of gypsum and ettringite were higher than in the core, showing that surface layer of concrete is more damaged than in the core. The concentration of $Ca(OH)_2$ in the surface layer was lower than in the core for two reasons: Firstly, higher concentrations of gypsum in surface layer of concrete will consume more $Ca(OH)_2$. Secondly, carbonation in concrete surface changes more $Ca(OH)_2$ to calcite, and indicated by change of concentration of calcite in different depths.

The XRD patterns of C50R concrete (in 5–10 mm depth) exposed to 5% Na_2SO_4 solution and to 5% Na_2SO_4+3.5%NaCl composite solution and drying-immersion cycles at 400 d are shown in Fig. 14. Obviously, gypsum and ettringite are only corrosion crystalline whether concrete exposed to sulfate solution or to composite solution. But the concentrations of gypsum and ettringite as concrete to 5% Na_2SO_4 solution are higher than that to composite solution, indicating more damage of concrete to 5% Na_2SO_4 solution than that of composite solution.

5. Discussions

The experimental results presented in this paper indicate that sulfate has a significant effect on ingress of chloride into concretes. The presence of sulfate in composite solution will decrease the ingress of chloride into concretes at early exposure period. This behavior was observed in both plain and fly ash concretes. This may be attributed to two respects. (1) Each diffusion rate of anion in co-diffusion of sulfate and chloride was less than that in single-diffusion for concretes subjected to natural immersion or drying-immersion cycles according to charges-equilibrium and mass-equilibrium principle. (2) Gradual formation of ettringite crystal in early exposure period leads to compacted microstructure of concretes, which decreases the ingress of chloride into concretes to some extent.

The experimental results that also indicated a presence of sulfate in composite solution would increase ingress of chloride into concretes at the latter exposure period. This may be attributed to the fact that too much expansive ettringite crystals produce in pores and ITZ cause new crack occurrence and prorogation of old cracks, which become rapid access to ingress of chloride into concretes, as shown in Figs. 10 (c) and 12.

The RDME of specimens (Figs. 6 and 7) that indicated a presence of chloride in composite solution prolonged the interval of each stage, and delayed the deterioration of concretes caused by sulfate attack. This may be explained from 3 respects: (I) The rate of sulfate diffusion in composite solution was less than that in 5% Na_2SO_4, which is similar as explained in the role of sulfate to chloride diffusion. (II) The higher rate of chloride diffusion than sulfate ions allows the chloride ions to react firstly with C3 A to form Friedel's salt, which will reduce the formation of either gypsum or expansive ettringite on the other hand. (III) Three times greater solubility of ettringite in chloride solution than that in water [6] reduced the formation of ettringite.

The effect of fly ash on chloride diffusion was shown in Fig. 8. The results indicated that the introduction of fly ash increased the ingress of chloride into concretes at early exposure period but the opposite is at the latter period. This maybe attributed to the fact that less hydrated products of fly ash concrete than plain concrete at early age will result in a loose structure due to a slow pozzolanic reactivity of fly ash. However, at latter age, fly ash would react with $Ca(OH)_2$ to produce the sub-silicate gel which can improve the compaction of concretes, decreasing the chloride diffusion. In addition, sub-silicate gel can also chemically bind chloride ions, resulting in a decrease of water-soluble chloride concentration. Moreover, the reactive aluminium phases in fly ash may react with chloride to produce Friedel's salt ($Ca_3Al_2O_6CaCl_2(NaCl)\cdot 10H_2O$), which can improve the binding capacity of chloride, and reduce the amount of water-soluble chloride. The reaction can be schematically expressed as follows:

$$\begin{aligned}&2NaCl + Ca_3Al_2O_6\cdot 6H_2O + CaCl_2 + 4H_2O\\&\quad = Ca_3Al_2O_6\cdot CaCl_2\cdot 10H_2O + 2NaOH\end{aligned}$$

$$\begin{aligned}&CaCl_2 + Ca_3Al_2O_6\cdot 6H_2O + 4H_2O\\&\quad = Ca_3Al_2O_6\cdot CaCl_2\cdot 10H_2O\end{aligned}$$

The effect of fly ash on damage of concrete in composite solution was shown in Fig. 9. Experimental results show that concrete with low W/B and suitable content of fly ash could reduce the deterioration of concretes caused by sulfate attack. This maybe attributed to the fact that the pozzolanic reaction in fly ash consumed the $Ca(OH)_2$, which the less amount of $Ca(OH)_2$ decreased the gypsum and ettringite formation. Moreover, the sub-silicate gel improved the compaction of concrete and reduced the rate of sulfate diffusion.

6. Conclusions

The synergistic effect of sulfate on chloride diffusion at early exposure period is different from that at latter exposure period. In the former, a presence of sulfate will decrease the concentration of chloride by 30–60%, increasing the age factor of chloride diffusion coefficient by about 0.13–0.14 for plain concretes; and reducing the chloride diffusion coefficient. But in the latter, a presence of sulfate in composite solution increased the ingress of chloride.

The damage process of concretes naturally submerged in 5% $NaSO_4$ for a period of 830 days can be classified to three periods according to the RDME: (I) 'linearly increased period'. (II) 'steady period', and (III) 'declining stage'. Comparatively only pro-Stage II occurred in composite solution. This well indicated presence of chloride in composite solution will reduce the number of stages at the same exposure period, and will prolong the interval of each stage.

The damage process of concretes exposed to drying-immersion cycles in 5%$NaSO_4$ for a period of 500 days can be classified to four stages: (I) the firstly decreased stage, (II) linearly increased stage, (III) slowly decreased stage, and (IV) the accelerating failure stage. For the composite solution, only pro-Stage III occurs for 500 days of accelerated corrosion periods. And the deterioration was found to be severer in the 5% $NaSO_4$ compared with that in composite solution. This indicates that a presence of chloride in composite solution prolonged the interval of each stage and the deterioration due to sulfate ions is retarded.

Fly ash increased the ingress of chloride into concretes at the early exposure period but reduced it at latter period. Concrete with low W/B and suitable content of fly ash could retard the deterioration due to sulfate ions, and the opposite is for concrete with high content of fly ash and W/B. And concretes with low W/B and suitable content of fly ash can service in Northwest of China with high concentration of sulfate and chloride.

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