

# **Durability of concrete containing fly ash and silica fume against combined freezing-thawing and sulfate attack**

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## **Abstract:**

Durability of concrete containing fly ash (FA) and silica fume (SF) against combined freezing-thawing and sulfate attack was studied in this paper. Concretes with w/b of 0.38 and 0.33 containing FA (i.e. of 10%, 15% and 25% by weight) and SF (i.e. of 5%, 8% and 11% also by weight) as partial replacement of Portland cement (PC) were exposed to 5% and 10% sodium sulfate solution under freezing–thawing cycles. The performance, including deterioration resistant coefficient of compressive strength, relative dynamic elastic modulus (RDEM) and microstructure, of concretes were evaluated after being subjected to certain freezing-thawing cycles in sodium sulfate solution. It was found that when exposed to 5% sodium sulfate solution, both FA and SF can improve concrete's resistance to sulfate attack and in comparison SF performed better than FA. Concrete deterioration was attributed to the interaction

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between freezing-thawing and sulfate attack. As for concrete without any admixture, its resistance against combined freezing-thawing and sulfate attack increased up to 125 freezing-thawing cycles and then decreased. The replacement level of 25% FA and 5-8% SF both by weight led to significant improvements in the resistance of concrete against combined freezing-thawing and sulfate attack. 10% sodium sulfate solutions more obviously improved freezing-thawing resistance of concrete with 25% by weight FA replacing OPC than 5% sodium sulfate solutions, while 5% and 10% sodium sulfate solution had the similar improvements in freezing-thawing resistance of concrete with 8% by weight SF replacing OPC.

**Keywords:** concrete durability; deterioration resistance coefficient; fly ash; freezing-thawing; relative dynamic elastic modulus; silica fume; sulfate attack; interaction between freezing-thawing and sulfate attack; sodium sulfate concentration; microstructure

## **1. Introduction**

Durability and service life of concrete mainly depends on many environmental factors, such as carbonation, sulfate attack, alkali-aggregate expansion [1-5], heating-cooling cycles, freezing-thawing cycles, wetting-drying cycles, reinforcement corrosion etc. [6]. Sulfate attack is one of the most common and severe factors to concrete in service, which can be found at various regions throughout the world such as Northwest China, southern California in the USA, Arabian Gulf region, Japan, Australia and Alpine area [7-14]. Sulfate attack to concrete is a complicated physical and chemical process,

which includes physical salt attack due to salt crystallization and chemical sulfate attack by sulfate from certain sources external to concrete [15].

In the case of chemical sulfate attack, sulfates of sodium, potassium, calcium, or magnesium in soil or dissolved in groundwater or seawater in the vicinity of concrete structures enter concrete, attack the hardened cement paste and increase the potential of deterioration. Free lime ( $\text{Ca(OH)}_2$ ), calcium aluminate (C3A) and ferroaluminate phases in cement are the main determining compositions influencing sulfate resistance of concrete [16, 17]. As it is well known, the two recognized chemical reaction products of cement hydration are ettringite and gypsum. The formation of ettringite results in an increase in solid volume, leading to expansion and cracking if expansion is restrained. The formation of gypsum can lead to softening and loss of concrete mass and strength [15, 16, 18, 19].

The mechanism of physical salt attack is not fully understood and some discussions on it are presented in literature [20-22]. The ACI [15] considers that sodium sulfate, sodium carbonate and sodium chloride dissolved in groundwater transport through the moist concrete and then concentrate and precipitate at the exposed surface. Only salt crystallization such as thenardite and mirabilite rather than the chemical sulfate products such as ettringite and gypsum are identified in physical salt attack, which differs from the scenario of chemical sulfate attack. Cases of concrete damaged by physical sulfate attack are sometimes misinterpreted as by chemical sulfate attack [23].

As reported by Skalny [24], complete separation of physical and chemical sulfate attack is probably technically impossible and may cause more confusion. However, in

66 real environments, concrete durability is influenced by factors acting in a combined  
67 and possibly synergistic physical and chemical manner. Therefore, it is significant to  
68 study concrete performance under combined deteriorating factors to obtain sufficient  
69 information on concrete durability.

70 Yu et al. [25] investigated freezing-thawing durability of concretes under the attacks  
71 of a combination of external flexural stress and chemical solution. Their experimental  
72 results indicated that the freezing-thawing resistance of concrete was visibly reduced  
73 at the presence of flexural stress. Ganjian [26] revealed that different deterioration  
74 mechanisms make SF or GGBS cement to be more vulnerable in the magnesium  
75 sulfate bearing seawater particularly within tidal zone under wetting and drying cycles.

76 Zivica [3] studied the influence of compression stress on sulfate corrosion rate of  
77 cement mortar and confirmed that the applied compression stress up to 60% of  
78 ultimate strength of mortar significantly slowed down this rate and the inhibition  
79 effect by decreasing bound  $\text{SO}_3$  content and the destructive phases, as ettringite and  
80 gypsum generated in concrete/cement paste attacked was connected. Mathias [27]  
81 pointed out that chloride penetration increased when the sulfate content increased at  
82 short immersion periods for OPC concrete and the presence of chlorides had a  
83 mitigating effect on the sulfate attack. According to Jiang [28], freezing-thawing  
84 cycles and sulfate attack affected each other and the deterioration of concrete with  
85 20% by weight FA replacing OPC attacked by magnesium sulfate led to the most  
86 aggressive deterioration subjected to freezing-thawing cycles. The shotcrete durability  
87 under combined frost and sulfate attack was investigated [29] and the results revealed

that ordinary shotcrete was more durable under the combined action of freezing-thawing cycles and sulfate ion attack than that of the ordinary concrete with the same mixture. Steel fiber reinforced shotcrete had the best durability performance in frost and sulfate resistance.

Investigations on frost and sulfate resistance of concrete had also been conducted in concrete science and engineering community, but the effects of sodium sulfate on the deterioration of concrete with FA and SF under combined freezing-thawing and sulfate attack was limited in literature. In this research, deterioration resistant coefficient of compressive strength, relative dynamic elastic modulus (RDEM) and Scanning Electron Microscopy analysis (SEM) of concrete subjected to sulfate attack and freezing-thawing cycles in water and in the sulfate solutions were conducted. The influence of FA and SF replacement level and sodium sulfate concentration under the combined action of freezing-thawing and sulfate attack was also analyzed.

## **2. Experimental program**

### **2.1 Materials**

P.O.42.5R OPC conforming to Chinese standard GB175-2007 and similar to the 42.5 R Portland cement conforming to EN197-1:2009, was used for preparing concrete in this research. The physical and mechanical properties of the cement are listed in Table 1. Table 2 presents the chemical composition of FA and Table 3 the performance index of SF used in this study as partial replacement of OPC. Crushed limestone aggregates were used as coarse aggregates and washed mountain sand as fine aggregates. The

fineness modulus of fine aggregates was tested according to Chinese standard JGJ52-2006 (similar to ASTM C136-01) and the results are tabulated in Table 4. Tap water was used for mixing concrete. A commercially available water reducer (i.e. SM) was used to keep concrete slump between 80 and 100 mm. Sodium sulfate anhydrous with 99% purity were used for making sulfate solutions as the sulfate attack source.

Table 1

Physical and mechanical properties of OPC used for this research

	80μm sieving residue (%)	Water requirement of normal consistency (%)	Initial setting time (min)	Final setting time (min)	Compressive strength (MPa)		Flexural strength (MPa)		soundness
					3	28	3	28	
					days	days	days	days	
Experimental result	1.50	27.5	96	146	36.8	48.9	5.3	8.9	qualified

Table 2

Chemical composition of fly ash (FA)

Chemical composition	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O+K <sub>2</sub> O
Weight percent/%	31.93	8.98	5.2	43.87	2.14	0.2	1.96

Table 3

Performance index of silica fume (SF)

Performance index	Loss on ignition(%)	Moisture content(%)	Water Requirement Ratio(%)	Specific surface area(m <sup>2</sup> /kg)
measured result	2.4	1.0	110	18000

Table 4

Physical characteristics of aggregates

	Apparent density (kg/m <sup>3</sup> )	Bulk density (kg/m <sup>3</sup> )	Crushing value index (%)	Maximum size(mm)	Fineness modulus	Dust content (%)
Fine aggregates	2735	1566	--	5	2.78	0.85
Coarse aggregates	2684	1470	7.8	25	--	0.12

## 2.2 Mix proportion and specimen preparation

The actual mix proportions in terms of 1 m<sup>3</sup> concrete for the mixtures investigated in this study are given in Table 5. In order to investigate the effect of FA and SF on the resistance of concrete to sulfate and freezing-thawing attack, two groups of concrete mixtures were prepared with w/b ratios of 0.38 and 0.33, respectively. In each group, concrete mixtures with three different FA contents (i.e. of 10%, 15% and 25% by weight of cementitious materials (i.e. OPC + FA + SF)), three different silica fume contents (i.e. of 5%, 8% and 11% also by weight of cementitious materials) as partial replacement of OPC were prepared and tested.

Concrete mixtures were prepared by a single horizontal-axis forced mixer. After moulded, concrete specimens were placed in the curing room with temperature of (20±5)°C for 24 hours. Then they were demoulded and immersed in limewater with temperature of (20±2)°C for another 27 days. For each mix, a total of 24 specimens were prepared, among which 15 specimens had the dimensions of 100 ×100 ×100 mm<sup>3</sup> for measuring compressive strength and resistance to sulfate attack, while the remaining 9 specimens with the dimensions of 100 ×100 ×400 mm<sup>3</sup> were prepared for assessing freezing-thawing resistance. For each test, the results presented were the average of the values obtained from three specimens under identical conditions.

Table 5

Mix proportions in kg/m<sup>3</sup> (except w/b) of concretes investigated in this study

		w/b	Fly ash	Silica fume	OPC	Coarse aggregates	Fine aggregates	Water
C	C-8	0.38	0	0	500	1094	616	190
	FA10-8	0.38	50	0	450	1094	616	190
FA	FA15-8	0.38	75	0	425	1094	616	190
	FA25-8	0.38	125	0	375	1094	616	190
	SF5-8	0.38	0	25	475	1094	616	190
SF	SF8-8	0.38	0	40	460	1094	616	190
	SF11-8	0.38	0	55	445	1094	616	190
C	C-3	0.33	0	0	500	1145	590	165
	FA10-3	0.33	50	0	450	1145	590	165
FA	FA15-3	0.33	75	0	425	1145	590	165
	FA25-3	0.33	125	0	375	1145	590	165
	SF5-3	0.33	0	25	475	1145	590	165
SF	SF8-3	0.33	0	40	460	1145	590	165
	SF11-3	0.33	0	55	445	1145	590	165

### 2.3 Sulfate resistance assessment

For assessing sulfate resistance of concrete, cubic specimens with the dimensions of 100×100 ×100 mm<sup>3</sup> cured standardly for 28 days were immersed in designated solution (i.e. 5% sodium sulfate by wt.%). Conforming to Chinese standard GB/T 50082-2009, which is similar to ASTM C1012-04 but it should be noted here that ASTM C1012-04 protocol only includes immersion but does not have drying-immersion cycle, a standard drying-immersion cycle lasted for 24 hours and was proceeded as following: first the cubic specimens were immersed in the designated sodium sulfate solution for 15 hours at (25~30)°C; then they were taken out from the solution and dried in air for 1 hour; subsequently the cubic samples were heated up to (80±5)°C to dry for 6 hours and followed by cooling down in air at



(25~30)°C for another 2 hours. PH value of the solution was measured once every 15 cycles and it was found it remained stable at the level of 6-8 as designed. Deterioration resistant coefficient of compressive strength (DRCCS) was measured and calculated via Equation (1) after 30 and 60 drying-immersion cycles.

$$K_f = \frac{f_{cn}}{f_{c0}} \times 100 \quad (1)$$

where  $K_f$  in % is the deterioration resistant coefficient of compressive strength;  $f_{cn}$  in MPa compressive strength after  $n$  drying-immersion cycles;  $f_{c0}$  in MPa the  $(n+28)$  days compressive strength of concrete subjected to standard curing without subjected to drying-immersion cycles.

## 2.4 Freezing-thawing resistance assessment

Rapid freezing-thawing test was conducted on the 100×100×400 mm<sup>3</sup> prismatic specimens cured standardly for 28 days. To do so, the prismatic specimens were immersed in clean water, 5% sodium sulfate solution and 10% sodium sulfate solution (by wt.%) respectively to investigate their resistance to the combined freezing-thawing and sulfate attack. Conforming to Chinese standard GB/T 50082-2009 (similar to ASTM C666/C666M-03), a standard freezing-thawing cycle lasted for 6 hours and was proceeded as following: first the prismatic specimens were froze in the designated sodium sulfate solution for 3 hours at (-18±2)°C, and subsequently they were thawed for 3 hours in water at (5±2)°C. All prismatic specimens were subjected to 175 freezing-thawing cycles. Frequency and mass of the prismatic specimens after every 25 freezing-thawing cycles were measured using a

dynamic elastic modulus tester and a scale, respectively. The relative dynamic elastic modulus (RDEM) and the deterioration resistant coefficient of dynamic elastic modulus ( $\lambda$ ) were calculated via Equation (2) and Equation (3).

$$RDEM = \frac{f_N^2}{f_0^2} \times 100 \quad (2)$$

$$\lambda = \frac{RDEM_{dc}}{RDEM_{ds}} \quad (3)$$

Where  $RDEM$  in % is the relative dynamic elastic modulus of concrete;  $\lambda$  in % the deterioration resistant coefficient of dynamic elastic modulus;  $f_0$  the initial transverse frequency in Hz;  $f_N$  the transverse frequency in Hz of a concrete prismatic specimen after subjected to  $N$  freezing-thawing cycles;  $RDEM_{dc}$  and  $RDEM_{ds}$  in % the relative dynamic elastic modulus of a concrete prismatic specimen after subjected to combined freezing-thawing and sulfate attack and to solely freezing-thawing attack in clean water, respectively.

To determine the elastic modulus of the specimens, the transverse frequency test method adapted from ASTM C215-02, was employed. First, the mass and the average length of the specimens were measured. The specimens were then placed on a 20mm thickness Polystyrene board. A driving unit was attached at the middle of the specimen's lateral surface, followed by a pickup unit 5mm away from the end of the specimen on the midline of the lateral surface. The transverse frequency was recorded by means of a concrete dynamic elastic modulus testing apparatus. The complete experimental set up is shown in Fig.1.

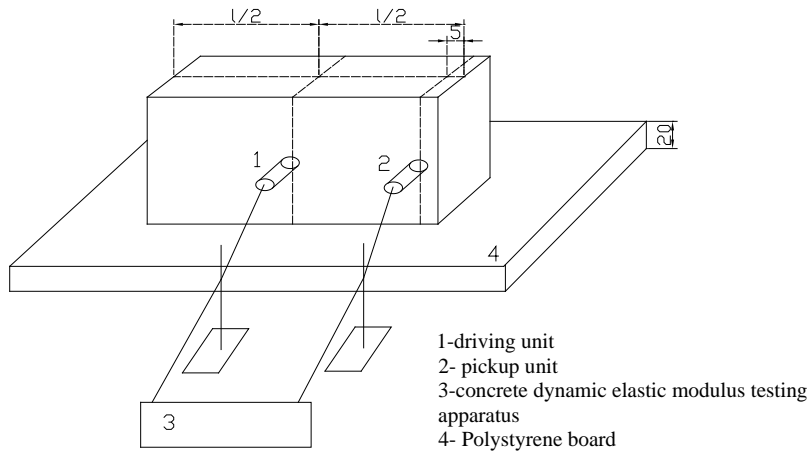
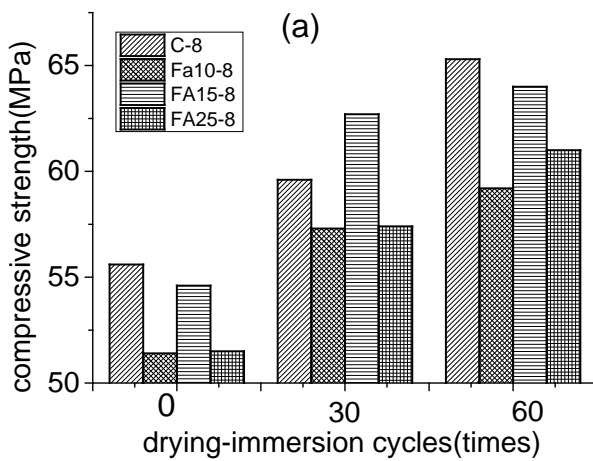
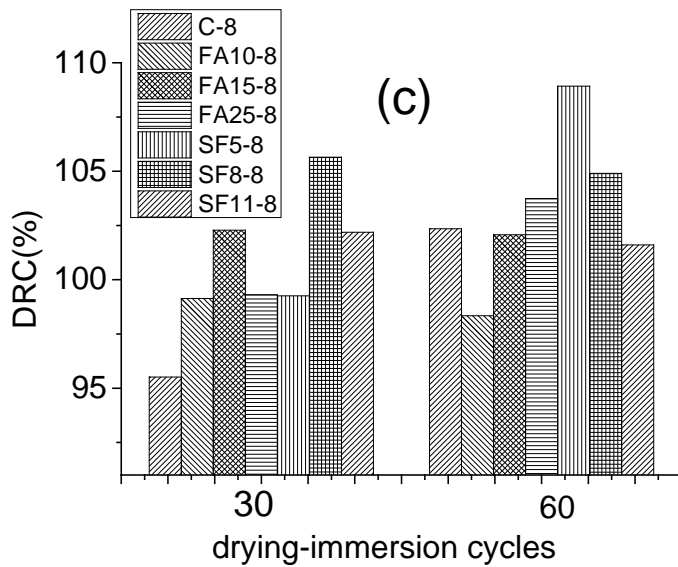
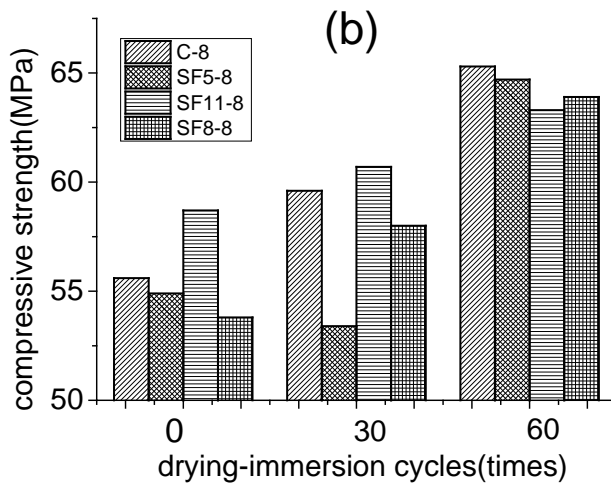


Fig.1 Equipment set up for the determination of the transverse frequency of a concrete specimen

### 3. Results and discussion

#### 3.1. Deterioration resistant coefficient of compressive strength (DRCCS)





Figs.2 Compressive strength changes of concrete with FA and SF

results were consistent with Bakharev's findings[30] on compressive strength variation subjected to sulfate attack and strength of specimens exposed to sulfate solution increased in the first month of the test, and then had a steady decline. Dulaijan [31] indicated that 20% FA and 7% SF by weight replacement level of OPC could improve the resistance of OPC concrete to sulfate attack.

Fig.2(c) shows the results of DRCCS. The DRCCS of concretes without any admixture (C-8) were 95.5% and 102.4% after 30 and 60 drying-immersion cycles, respectively. The results suggested that FA and SF were effective to increase DRCCS and the resistance to sulfate attack in 5%  $\text{Na}_2\text{SO}_4$  solution and by comparison SF performed better than FA.

## **3.2 Relative dynamic elastic modulus (RDEM)**

### **3.2.1 RDEM and sodium sulfate content**

Fig.3 presents the RDEM of the series C concrete up to 175 freezing-thawing cycles in sodium sulfate solutions in which the C-3-0, C-3-5 and C-3-10 series represents concrete specimens subjected to freezing-thawing cycles in sodium sulfate solutions of the concentration of 0%, 5% and 10% by weight respectively.

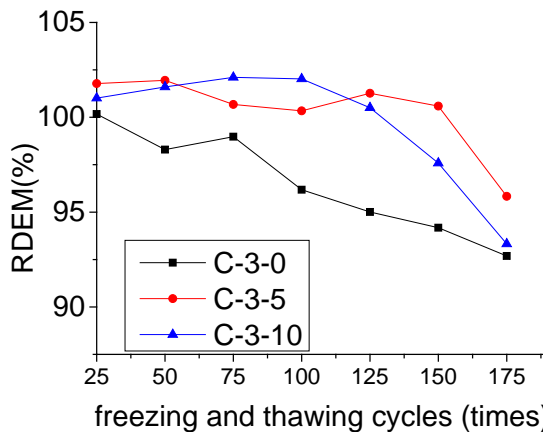
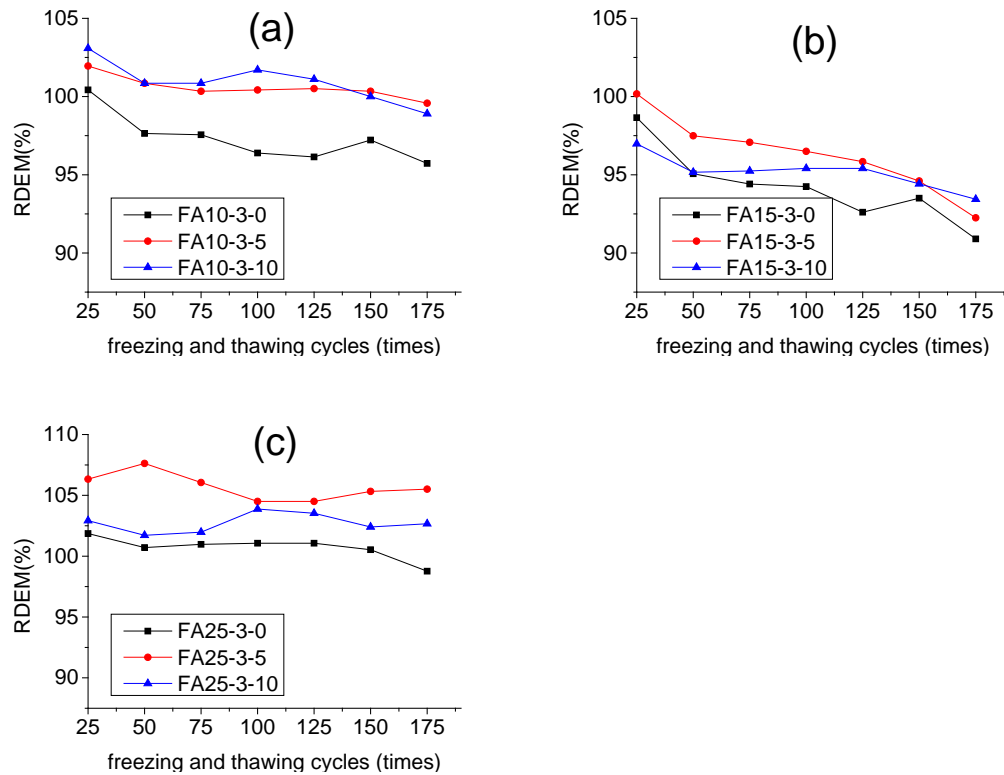


Fig.3 RDEM of series C concrete in clean water and sodium sulfate solution under freezing-thawing cycles

The average initial frequencies of C-3 series concrete prior to immersion in sodium sulfate solution were 2335, 2373 and 2385 Hz, respectively and RDEM up to 175 freezing-thawing cycles is presented in Fig.3. According to the figure, RDEM of concrete decreased after freezing-thawing cycles in clean water (C-3-0) and the concrete had the minimum RDEM value of 92.7% up to 175 freezing-thawing cycles in clean water. There were 2 different stages during deterioration process immersed in 10% (93.3%) and 5% (95.8%) sodium sulfate solution. Up to 125 freezing-thawing cycles, the RDEM increased slightly compared to that of the corresponding concrete prior to immersion and decreased after that. The RDEM decreased more in 10% sodium sulfate solution (i.e. down to 93.3% of original value) than in 5% solution which (i.e. only down to 95.8% of original value). The results also indicated that concrete was more vulnerable to clean water than to sodium sulfate solution under freezing-thawing cycles. Besides, 5% and 10% sodium sulfate solution had the similar

improvement effects on REDM.



Figs.4 REDM of FA series concrete in sodium sulfate solution subjected to freezing-thawing cycles

Fig.4 (a), (b) and (c) presents the evolution of the REDM of concrete containing FA (i.e. FA series concrete) exposed to sodium sulfate solutions with various concentrations up to 175 freezing-thawing cycles. Similar trend was observed in concrete with different FA contents. It is clear that clean water was more aggressive and caused larger fall of REDM under freezing-thawing cycles while the concrete immersed in 5% and 10% sodium sulfate solutions had the similar overall performance over the time of experiment indicating less deterioration.

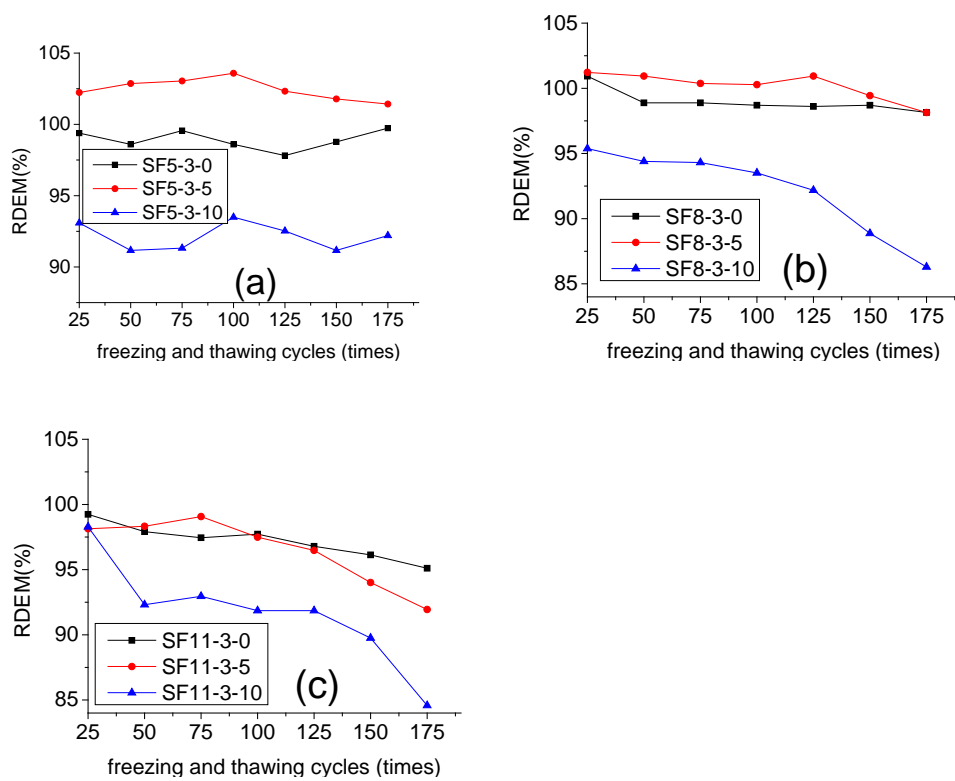
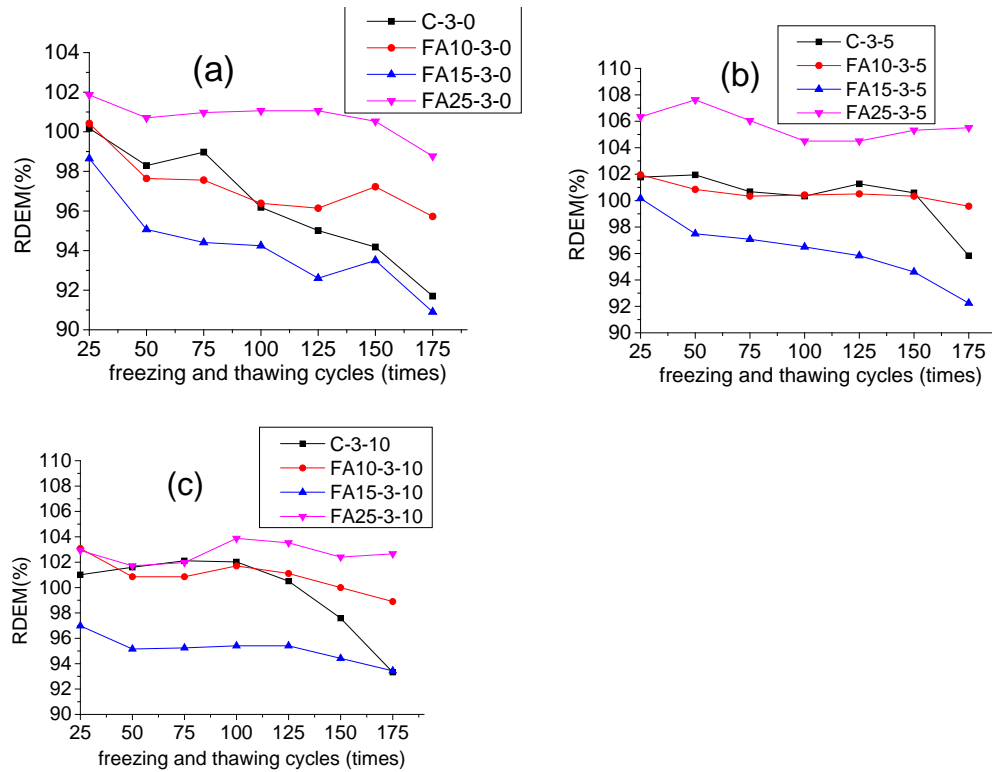


Fig.5 RDEM of SF series concrete in sodium sulfate solution subjected to freezing-thawing cycles

Fig.5 (a), (b) and (c) illustrates the evolution of RDEM of concrete containing SF (i.e. SF series concrete) exposed to sodium sulfate solutions with different concentrations up to 175 freezing-thawing cycles. For concretes with different SF contents, it was observed that 10% sodium sulfate solution had the most aggressive influence on the RDEM under freezing-thawing cycles (i.e. down to 91.2%, 86.3% and 84.6% of original value in Fig.5 (a), (b) and (c) after 175 freezing-thawing cycles), while 5% sodium sulfate solution had the minimal impact on RDEM. In fact, 5% sodium sulfate solution even led to an increase in dynamic elastic modulus when the SF replacement level was 5%.



### 3.2.2 RDEM and FA content



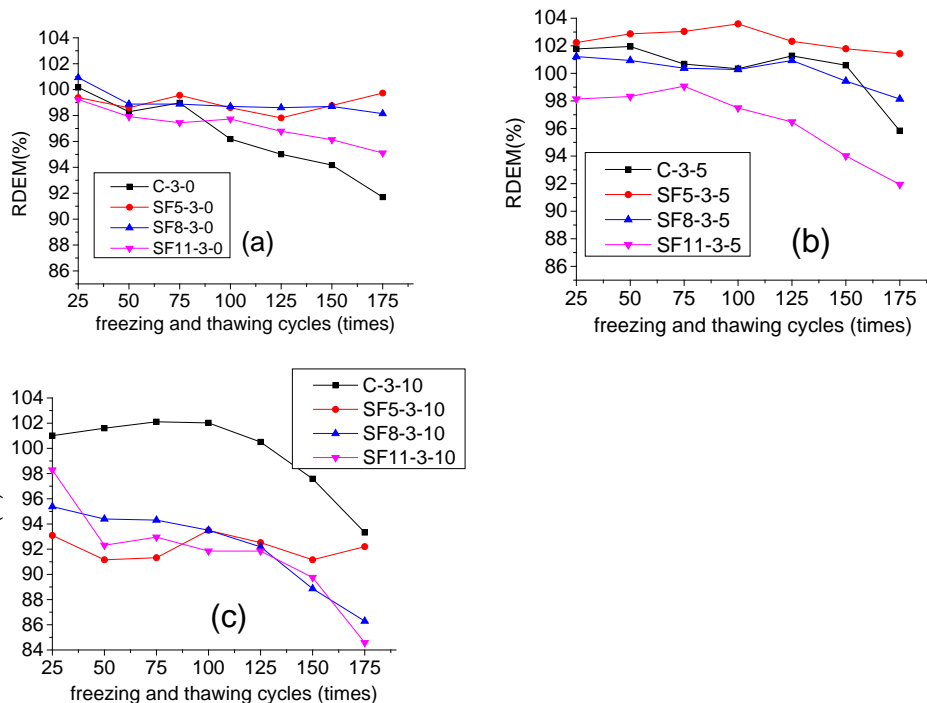
Figs.6 RDEM of concrete with FA exposed to clean water and sodium sulfate solutions under freezing-thawing cycles

The deterioration in RDEM of plain and blended cement concrete (i.e. with FA) exposed to clean water under freezing-thawing cycles is depicted in Fig.6 (a). There was a relatively larger decrease in RDEM associated with FA15-3, and the RDEM decreased gradually and had a reduction ranged from 1.4% to 9.1% over the test period. Then C-3 and FA-10 followed. Their RDEM was comparable up to 125 freezing-thawing cycles. It can be seen that C-3 decreased at a faster rate and had the total 6.7% RDEM reduction at the end of test. As is evident in Fig6.(a), RDEM of FA25-3 was greater than 100% up to 150 cycles and then reduced to 98.8% at the end

of the test (i.e. at 175 cycles). Therefore it can be concluded that 25% by weight FA replacement level was effective to enhance the resistance of concrete to freezing-thawing attack in sodium sulfate solutions.

Fig.6 (b) and (c) presented the deterioration in RDEM when concrete was exposed to 5% and 10% sodium sulfate solution, respectively. In the sodium sulfate solution, the RDEM change affected by FA was as approximately in a same manner as in clean water. The RDEM of FA15-3 had the minimum value, followed by FA10-3 and C-3. FA25-3 containing 25% FA by weight of cementitious materials performed the best and had significantly larger RDEM increase over the time of experiment.

### 3.2.3 RDEM and SF content



Figs.7 RDEM of concrete with SF exposed to clean water and sodium sulfate solutions under freezing-thawing cycles

315

316 The RDEM of concrete with SF was higher than that of concrete without SF when  
317 exposed to clean water up to 75 freezing-thawing cycles (i.e. Fig.7 (a)). It was evident  
318 that SF could increase the resistance of concrete to freezing-thawing cycles in clean  
319 water. Exposed to 5% sodium sulfate solution, concrete with 5% SF had a higher  
320 RDEM than concrete without SF and concrete with 8% SF had about the same RDEM  
321 with concrete without SF, but there is a relatively larger decrease in RDEM associated  
322 with SF11-3. Fig.7 (c) showed that in 10% sodium sulfate solution, RDEM of  
323 concrete with SF (i.e. 5%, 8% and 11% by weight of cementitious materials) was  
324 lower than that of concrete without SF, suggesting that concrete with SF is more  
325 vulnerable to freezing-thawing attack. Therefore it can be concluded that 5% and 8%  
326 SF by weight of cementitious materials contributed to enhance the resistance of  
327 concrete to freezing-thawing attack in clean water as well as in 5% sodium sulfate  
328 solutions, while SF seemed not working in 10% sodium sulfate solutions. Namely for  
329 SF concretes up to 175 cycles, it showed that the 5% sodium sulfate solutions had  
330 restrained the damage of concrete, while 10% sodium sulfate solutions had  
331 accelerated the damage.

332

### 333 **3.3 Interaction between freezing-thawing and sulfate attack**

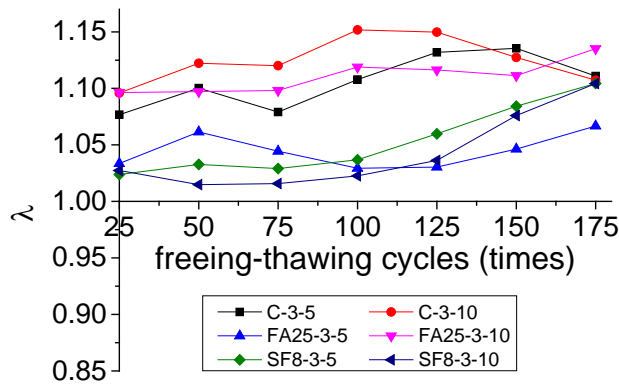
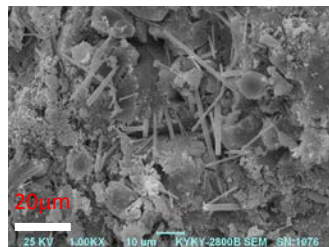


Fig.8  $\lambda$  of concrete with 25% FA, 8% SF and without any admixture exposed to 5% and 10% sodium sulfate solutions up to 175 freezing-thawing cycles

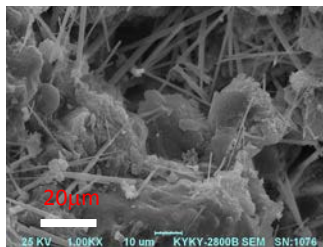
Concrete deterioration was associated with the interaction between freezing-thawing and sulfate attack. Via Equation (3), if  $\lambda > 1$ , it means the sulfate solution has a positive effect on concrete's resistance to freezing-thawing attack. If  $\lambda < 1$ , the sulfate solution has a negative effect on concrete's resistance to freezing-thawing. When the  $\lambda$  value is larger or smaller, the positive or negative effect becomes more obvious. In Fig.8 as for concrete without any admixture (i.e. C-3) exposed to 5% and 10% sodium sulfate solutions,  $\lambda$  increased (i.e.  $\lambda > 1$ ) and positive effect was the determining factor up to 125 freezing-thawing cycles and 10% sodium sulfate solutions demonstrated less deterioration effect than 5% solution, while the  $\lambda$  decreased and negative effect was dominant after 125 freezing-thawing cycles and in this case 10% sodium sulfate solutions demonstrated similar deterioration effect with 5% solution. As for concretes with 25% FA replacing OPC, positive effect was the determining factor up to 175 freezing-thawing cycles. 10% sodium sulfate solution

had a highly positive effect and caused a higher degree of  $\lambda$  increment up to 175 freezing-thawing cycles. As for concretes with 8% SF, it demonstrated similar performance trends in 5% and in 10% sodium sulfate solution. 5% and 10% sodium sulfate solution increased the resistance to freezing-thawing up to 175 freezing-thawing cycles and retarded the concrete deterioration.

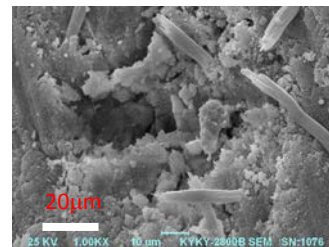
### 3.4. SEM



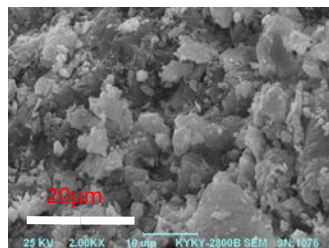
(a) C-3



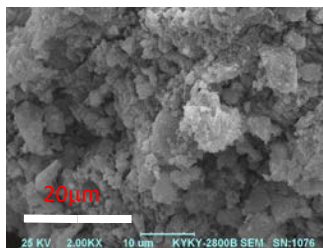
(b) FA25-3



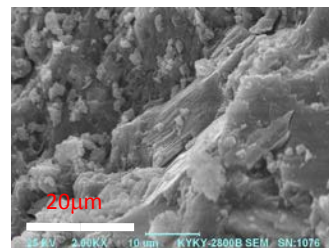
(c) SF8-3



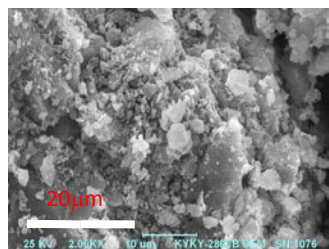
(d) C-3-0



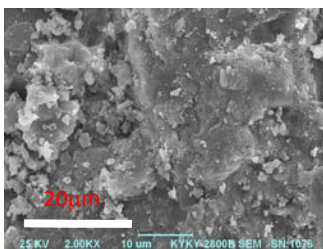
(e) FA25-3-0



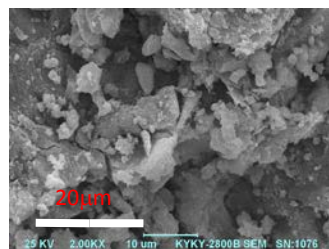
(f) SF8-3-0



(g) C3-3-10



(h) FA25-3-10



(i) SF8-3-10

Figs.9 SEM images of concrete with 25% FA, 8% SF and without any admixture exposed to 5% sodium sulfate solutions up to 60 drying-immersion cycles ((b),(c) and (a) x1K), to clean water ((e),(f) and (d) x2K) and to 10% sodium sulfate solutions ((h),

(i) and (j) x2K) after 175 freezing-thawing cycles

Figs.9 present SEM images of concrete specimens at a depth of 5mm exposed to 5% sodium sulfate solutions up to 60 drying-immersion cycles, to clean water and to 10% sodium sulfate solutions at 175 freezing-thawing cycles respectively.

Gypsum and ettringite are the main hydration products generated during sulfate attack. Up to 60 drying-immersion cycles in 5% sodium sulfate solutions (i.e. Fig.9(a), (b) and (c)), it was obvious that there were a number of needle crystals (ettringite) formed. Among the three types of specimens, the one with 25% by weight FA replacing OPC generated the most ettringite (i.e. Fig.9(b)), while the second was the concrete without any admixture (i.e. Fig.9(a)) and the least the concrete with 8% by weight SF replacing OPC (i.e. Fig.9(c)). Up to 60 drying-immersion cycles, sodium sulfate diffused into concrete along micropores and microcracks, where some ettringite crystals produced and filled the micropores and microcracks. Consequently, the reaction products increased the density and the strength.

When concretes were exposed to clean water, there were no clear microcracks resulting in a very compact microstructure, and this was the result of the pozzolanic reaction (i.e. Fig.9(d), (e) and (f)). With further freezing-thawing cycles, crack would be generated and the microstructure of the concrete samples would be very loose.

When concrete specimens were exposed to 10% sodium sulfate solutions up to 175 freezing-thawing cycles (i.e. Fig.9 (h), (h) and (i)), ettringite and gypsum crystals could scarcely be seen in all concrete specimens and these specimens possessed fine

pore structures. During freezing, low temperature slows down the diffusion of sulfate ions. Therefore, no gypsum is found in concrete. So low temperature somehow reduced the severity of sulfate attack at certain initial stage. Similar findings[32] have been reported that a small amount of ettringite crystals can be seen in concrete after subjected to 100 freezing-thawing cycles and the amount of ettringite crystals and gypsum crystals continuously increased with freezing-thawing period, especially after 300 cycles.

#### **4. Conclusions**

Durability of concretes with w/b of 0.38 and 0.33 containing FA and/or SF against combined freezing-thawing and sulfate attack was investigated in this study. The following conclusions can be drawn based on the experimental results.

(1) Exposed to 5% sodium sulfate solutions, concrete containing FA and SF both gained compressive strength and DRCCS during the period of 60 drying-immersion cycles. Both FA and SF can improve the resistance of concrete to sulfate attack with SF performing better than FA.

(2) Sulfate solution has a combined positive and negative effect on concrete subjected to freezing-thawing cycle. As for concrete without any admixture, 5% and 10% sodium sulfate solutions could enhance concrete's resistance to freezing-thawing cycle up to 125 while decrease after 125 cycles. 10% sodium sulfate solutions more obviously restricted the deterioration of concrete with 25% by weight FA replacing OPC than 5% sodium sulfate solutions up to 175

freezing-thawing cycles. As for concretes with 8% by weight SF replacing OPC, 5% and 10% sodium sulfate solution retarded concrete deterioration and the effect was similar.

(3) In general, FA and SF as the concrete admixture improved concrete's resistance against the combined freezing-thawing and sulfate attack with 25% FA and 5-8% SF by weight replacement level of cementitious materials leading to significant improvement in concrete durability.

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## References

- [1] P.K. Mehta, Durability of concrete in marine environment--a review, Journal of the American Concrete Institute 77(5) (1980) 378-378.
- [2] M.L. Conjeaud, Mechanism of sea-water attack on cement mortar, Journal of the American Concrete Institute 77(5) (1980) 378-379.
- [3] V. Zivica, V. Szabo, The behavior of cement composite under compression load at sulfate attack,



433 Cem. Concr. Res. 24(8) (1994) 1475-1484.

434 [4] Y.X. Zhou, M.D. Cohen, W.L. Dolch, Effect of external loads on the frost-resistant properties of  
 435 mortar with and without silica fume, ACI Mater. J. 91(6) (1994) 595-601.

436 [5] U. Schneider, E. Nagele, F. Dumat, Stress-corrosion initiated cracking of concrete, Cem. Concr. Res.  
 437 16(4) (1986) 535-544.

438 [6] A. Cwirzen, P. Sztermen, K. Habermehl-Cwirzen, Effect of Baltic seawater and binder type on frost  
 439 durability of concrete, J. Mater. Civ. Eng. 26(2) (2014) 283-287.

440 [7] W. Kunther, B. Lothenbach, J. Skibsted, Influence of the Ca/Si ratio of the C-S-H phase on the  
 441 interaction with sulfate ions and its impact on the ettringite crystallization pressure, Cem. Concr. Res.  
 442 69 (2015) 37-49.

443 [8] W. Kunther, B. Lothenbach, K. Scrivener, Influence of bicarbonate ions on the deterioration of  
 444 mortar bars in sulfate solutions, Cem. Concr. Res. 44 (2013) 77-86.

445 [9] R.S. Gollop, H.F.W. Taylor, Microstructural and microanalytical studies of sulfate attack III.  
 446 Sulfate-resisting portland cement: Reactions with sodium and magnesium sulfate solutions, Cem.  
 447 Concr. Res. 25(7) (1995) 1581-1590.

448 [10] G.A. Novak, A.A. Colville, Efflorescent mineral assemblages associated with cracked and degraded  
 449 residential concrete foundations in Southern-California, Cem. Concr. Res. 19(1) (1989) 1-6.

450 [11] William G. Hime, Ross A. Martinek, Lisa A. Backus, L.M. Stella, Salt hydration distress, Concrete  
 451 International 23(10) (2001) 43-50.

452 [12] N. Yoshida, Y. Matsunami, M. Nagayama, E. Sakai, Salt weathering in residential concrete  
 453 foundations exposed to sulfate-bearing ground, J. Adv. Concr. Technol. 8(2) (2010) 121-134.

454 [13] O.S.B. Al-Amoudi, Attack on plain and blended cements exposed to aggressive sulfate

455 environments, Cem. Concr. Compos. 24(3-4) (2002) 305-316.

456 [14] L.X. Liu, Brief introduction on the study of erosion and prevention of concrete in salt lake and  
 457 saline soil area of Chaerhan, Chadamu, Journal of Building Materials 04(04) (2001) 395-400.

458 [15] A.C. 201, Guide to durable concrete (ACI 201.2R-08), American concrete institute, MI, 2008.

459 [16] M.A. Gonzalez, E.F. Irassar, Ettringite formation in low C(3)A Portland cement exposed to sodium  
 460 sulfate solution, Cem. Concr. Res. 27(7) (1997) 1061-1071.

461 [17] J. Monteny, N. De Belie, E. Vincke, W. Verstraete, L. Taerwe, Chemical and microbiological tests to  
 462 simulate sulfuric acid corrosion of polymer-modified concrete, Cem. Concr. Res. 31(9) (2001)  
 463 1359-1365.

464 [18] A. Soive, E. Roziere, A. Loukili, Parametrical study of the cementitious materials degradation  
 465 under external sulfate attack through numerical modeling, Constr. Build. Mater. 112 (2016) 267-275.

466 [19] P.W. Brown, S. Badger, The distributions of bound sulfates and chlorides in concrete subjected to  
 467 mixed NaCl, MgSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub> attack, Cem. Concr. Res. 30(10) (2000) 1535-1542.

468 [20] H. Haynes, R. O'Neill, P.K. Mehta, Concrete deterioration from physical attack by salts, Concrete  
 469 International 18(1) (1996) 63-68.

470 [21] H. Haynes, R. O'Neill, M. Neff, P.K. Mehta, Salt weathering distress on concrete exposed to sodium  
 471 sulfate environment, ACI Mater. J. 105(1) (2008) 35-43.

472 [22] J.F. Young, Sulfate attack (letter to the Editor), Concrete International 20(8) (1998) 7.

473 [23] P.K. Mehta, Sulfate attack on concrete separating myths from reality, Concrete International 22(8)  
 474 (2000) 57-61.

475 [24] J. Skalny, I. Odler, F. Young, Discussion of the paper "Sulfate attack," or is it? by W.G. Hime and S.  
 476 Mather, Cem. Concr. Res. 30(1) (2000) 161-162.

477 [25] H.F. Yu, W. Sun, Y.S. Zhang, L.P. Guo, M. Li, Durability of concrete subjected to the combined  
478 actions of flexural stress, freeze-thaw cycles and bittern solutions, J. Wuhan Univ. Technol.-Mat. Sci.  
479 Edit. 23(6) (2008) 893-900.

480 [26] E. Ganjian, H.S. Pouya, Effect of magnesium and sulfate ions on durability of silica fume blended  
481 mixes exposed to the seawater tidal zone, Cem. Concr. Res. 35(7) (2005) 1332-1343.

482 [27] M. Maes, N. De Belie, Resistance of concrete and mortar against combined attack of chloride and  
483 sodium sulphate, Cem. Concr. Compos. 53(-) (2014) 59-72.

484 [28] L. Jiang, D.T. Niu, L.D. Yuan, Q.N. Fei, Durability of concrete under sulfate attack exposed to  
485 freeze-thaw cycles, Cold Reg. Sci. Tech. 112 (2015) 112-117.

486 [29] J.B. Wang, D.T. Niu, Influence of freeze-thaw cycles and sulfate corrosion resistance on shotcrete  
487 with and without steel fiber, Constr. Build. Mater. 122 (2016) 628-636.

488 [30] T. Bakharev, Durability of geopolymer materials in sodium and magnesium sulfate solutions, Cem.  
489 Concr. Res. 35(6) (2005) 1233-1246.

490 [31] S.U. Al-Dulaijan, M. Maslehuddin, M.M. Al-Zahrani, A.M. Sharif, M. Shameem, M. Ibrahim, Sulfate  
491 resistance of plain and blended cements exposed to varying concentrations of sodium sulfate, Cem.  
492 Concr. Compos. 25(4-5) (2003) 429-437.

493 [32] D.T. Niu, L. Jiang, Q.N. Fei, Deterioration mechanism of sulfate attack on concrete under  
494 freeze-thaw cycles, Journal of Wuhan University of Technology Materials Science Edition 28(6) (2013)  
495 1172-1176.

496