Copyright © 2018 Elsevier Ltd. All rights reserved. This is the accepted manuscript version of an article which has been published in final form at https://doi.org/10.1016/j.conbuildmat.2018.03.038, made available on this repository under a Creative Commons CC BY-NC-ND attribution licence (https://creativecommons.org/licenses/by-nc-nd/4.0/).

1	Chloride ion penetration resistance of concrete containing fly ash
2	and silica fume against combined freezing-thawing and chloride
3	attack
4	Dezhi Wang ^{a,b,c,d*} , Xiangming Zhou ^a , Bo Fu ^e and Lirong Zhang ^f
5	^a Department of Civil & Environmental Engineering, Brunel University London,
6	Uxbridge, Middlesex UB8 3PH, United Kingdom
7	^b College of Civil & Water Conservancy Engineering, Ningxia University, Yinchuan
8	750021, China
9	^c Ningxia Water-efficient Irrigation Engineering Research Center, Yinchuan 750021,
10	Ningxia, China
11	^d Water Resources Engineering Research Center in Modern Agriculture in Arid
12	Regions, Yinchuan 750021, China
13	^e School of Civil Engineering, North Minzu University, Yinchuan 750021, China
14	^f Henan Communication Vocational and Technical College, Zhengzhou 450015, China
15	
16	Abstract:
17	Chloride ion penetration resistance (CPR) of concrete containing fly ash (FA)/silica
18	fume (SF) against combined freezing-thawing and chloride attack was studied. The
19	total charge passed, immersed in tap water and sodium chloride solution, subjected to
20	50 freezing-thawing cycles was evaluated. It was found that immersed in tap water,
21	SF had more evident improvement on concrete's resistance to combined effects than

^{*}Corresponding author at: Department of Civil & Environmental Engineering, Brunel University London, Uxbridge, Middlesex UB8 3PH, United Kingdom. E-mail address: dezhi.wang@brunel.ac.uk (Dezhi Wang).

27	Keywords: concrete durability; chloride penetration resistance; total charge passed;
26	
25	attack accelerated concrete deterioration.
24	while that with SF decreased. Interaction between freezing-thawing and chloride
23	than tap water. After 50 freezing-thawing cycles, CPR of concrete with FA increased,
22	FA. Sodium chloride solution immersion for 41d prior to test was more aggressive

fly ash; silica fume; freezing-thawing; chloride attack; sodium chloride concentration;
interaction between freezing-thawing and chloride attack

30

31 **1. Introduction**

Concrete is versatile and the most widely used construction material in the world. But 32 33 owning to aggressive marine exposure environment and the extensive use of de-icing salts in many countries, chloride induced corrosion becomes one of the most common 34 causes of degradation of reinforced concrete structures [1-4]. The first effect of 35 36 chloride ions is physical salt attack leading to surface cracking and scaling which is similar in appearance to freezing-and-thawing damage and total disintegration of 37 low-quality concrete [5]. Another effect is that chloride ions are the most important 38 cause of corrosion of embedded rebar. When chloride ions penetrate concrete cover 39 and arrive at reinforcement bars, as their amount accumulates, the passive film may 40 break down (i.e. de-passivation) and corrosion of embedded rebar can then initiate [6, 41 42 7]. The accumulation of corrosion products can build up the swelling pressure around the rebar resulting in cracking or spalling of concrete[8], which in turn facilitates the 43

ingress of moisture, oxygen, and chlorides to the rebar and accelerates rebar corrosion
[9]. Pitting corrosion is another threat to RC structures in a chloride environment [10]
and is a type of more serious corrosion on structural safety than general corrosion[11,
12], since it has resulted in quite high loss of cross-sectional area of reinforcement
bars [13] and structural damages[14], or in extreme situations, the final collapse of the
structure.

50 Chloride penetration in concrete can be characterized by the chloride diffusion 51 coefficient and the binding ability of matrix-forming solids [15]. In concrete, 52 chlorides can be chemically bound with cement's C3A or C4AF phases (e.g., Friedel's 53 salt) [16], or physically hold to the surface of hydration products (e.g., adsorption on 54 C-S-H) [3, 17]. Chloride diffusion depends on pure diffusion for water-saturated 55 concrete and capillary absorption of salty water for non-saturated concrete [18].

Recently, there are several studies reported in literature on the transport of chloride 56 ions in concrete and numerical models developed to simulate the process [7, 19-22]. 57 58 Meanwhile, chloride penetration into concrete is governed by many factors. Due to the chemical and physical bond between chloride ion and hydrated product of cement 59 changing the micro-structure, the chloride diffusion coefficient changes during the 60 exposure period and decreases with an increased period of exposure [23-26]. Nobuaki 61 [27] and Page [28] both studied chloride ions diffusion in concrete at different 62 temperatures and the results reveal that the rates of diffusion of Cl⁻ in concrete rises 63 64 with increases in temperature. In real environments, concrete structures are subjected to various environmental factors acting in a combined and possibly synergistically 65

physical and chemical manner to accelerate the destruction process. Therefore, it is 66 significant to study chloride resistance of concrete under combined deteriorating 67 68 factors to obtain sufficient information on concrete durability. Chloride penetration and carbonation of concrete are often considered to be the most significant coupled 69 deterioration factors and numerous studies have taken both factors into account in 70 assessing concrete durability [29-35]. As reported by Chindaprasirt [29], Tumidajski 71 [31] and Houst [36], carbonation decreases chloride penetration and diffusivity in 72 ordinary Portland cement (OPC) mortar and concrete. While other test results [30, 34, 73 74 35] indicate that chloride penetration is accelerated when the carbonation process is combined with the chloride ingress due to liberate bound chloride. The carbonation 75 effect on chloride penetration is controversial and considered to depend on the types 76 77 and mix proportions of concretes [29, 33, 35]. Initial cracks in concrete significantly influence chloride penetration and the influence of crack width and depth has been 78 experimentally and numerically studied. It is clear that chloride transport is very rapid 79 80 along and across crack boundaries [37]. Concrete specimens are made with artificial 81 cracks by means of the positioning and removal after approximately 4 h of thin copper 82 sheets inside the specimen[38]. These copper sheets have a thickness of 0.2 mm, 0.3 mm or 0.5 mm. The copper sheets are placed at a depth in the concrete specimen of 5 83 84 mm, 10 mm, 15 mm or 20 mm. The test results also indicate that the penetration depth increases with an increasing notch depth and that the influence of notch depth is more 85 pronounced for longer test duration while the influence of notch width is not clear [38, 86 39]. The chloride permeability of a concrete is influenced significantly by loading 87

style and critical stress [40-43]. The application of static loading up to 90% of the
ultimate strength had little effect on chloride permeability while load repetitions at the
maximum stress levels of 60% or more caused chloride permeability to increase
significantly [41].

In addition, drying and wetting cycles are always identified as the most unfavorable
environment condition for reinforced concrete structure subjected to chloride-induced
deterioration processes and it accelerates the ingress of chloride ions and affects
concrete durability [44, 45].

96 Investigations on chloride penetration resistance of concrete have also been conducted in concrete science and engineering community, but studies on the effects of chloride 97 ion on deterioration of concrete with FA and SF under combined freezing-thawing and 98 99 chloride attack is very limited in literature. Rapid chloride permeability test (RCPT) is the most widely specified durability test method and is standardized by ASTM. 100 The total charge passed (in Coulombs), the result of RCPT, provides a rapid 101 indication of its resistance to the penetration of chloride ions and is calculated via 102 Equation (1). In this research, concrete's total charge passed, immersed in tap water 103 and sodium chloride solutions, subjected to 50 freezing-thawing cycles was evaluated. 104 The influence of FA and SF replacement level of OPC and sodium chloride 105 concentration on durability of concrete under the combined freezing-thawing and 106 chloride attack was also investigated. 107

108

109 **2. Experimental program**

110 **2.1 Materials**

42.5 R Portland cement, manufactured by Saima Cement Manufacturing Company of 111 Ningxia, China conforming to EN197-1:2009, was used for preparing concrete in this 112 research and its physical and mechanical properties are listed in Table 1. Table 2 113 presents the chemical composition of the cement, FA and SF used in this study as 114 partial replacement of OPC. Crushed limestone aggregates were used as coarse 115 aggregates and washed mountain sand as fine aggregates, and the sieving curves are 116 presented in Fig.1. The fineness modulus of fine aggregates was evaluated 117 118 conforming to ASTM C136-01 and the results are presented in Table 3. Tap water was used for mixing concrete. A commercially available naphthalene-based water reducer 119 120 (i.e. FDN, produced by MUHU Concrete Admixture Ltd.) was used to keep concrete 121 slump between 80 and 100 mm and its chemical characteristics are listed in Table 4. Sodium chloride anhydrous with 99.5% purity and sodium hydroxide anhydrous with 122 99.0% purity were used for making chlorate solutions as the chloride attack source. 123

124 Table 1

125 Physical and mechanical properties of OPC used for this research

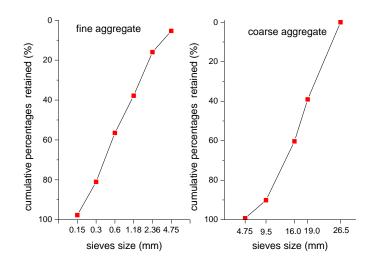
	80µm sieving residue (%)	requirement of sieving normal	setting setting time time	Final setting	Compressive strength (MPa)		Flexural strength (MPa)		soundness
		consistency (%)		(min)	3 days	28 days	3 days	28 days	
Experimental result	1.60	27.3	90	135	26.0	45.9	6.0	8.3	qualified

126

127 Table 2

128 Chemical compositions of Portland cement, fly ash (FA) and silica fume (SF)

Chemical composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na2O+11220
Cement weight percent (%)	22.04	5.77	3.36	66.43	0.45	0.00	0.51 130
FA weight percent (%)	31.93	8.98	5.2	43.87	2.14	0.2	1.95
SF weight percent (%)	97.2	0.26	0.45	0.17			131



134 Fig. 1 Sieving curves of fine and coarse aggregates

135

133

136 Table 3

137 Physical characteristics of aggregates

	Apparent density (kg/m ³)	Bulk density (kg/m ³)	Crushing value index (%)	Maximum size(mm)	Fineness modulus	Dust content (%)
Fine	2735	1566		5	2.78	0.85
aggregates	2155	1500		5	2.70	0.85
Coarse	2684	1470	7.8	20		0.12
aggregates	2084	1470	7.0	20		0.12

138

139 Table 4

140 Chemical characteristics of naphthalene-based water reducer

РН	Chloride ion content (%)	Na ₂ SO ₄ content (%)	
8.1	0.1	2.5	

142 **2.2 Mix proportion and specimen preparation**

The actual mix proportions in terms of 1 m³ concrete for the mixtures investigated in 143 this study are given in Table 5. In order to investigate the effect of FA and SF on the 144 resistance of concrete to combined freezing-thawing and chloride attack, the total 145 binder content of all mixtures was 500 kg/m³ according to Wu[46] and concrete 146 mixtures were prepared with w/b ratios of 0.38 and 0.33, respectively. In each group, 147 concrete mixtures with three different FA contents (i.e. of 10%, 15% and 25% by 148 weight of cementitious materials (i.e. OPC + FA + SF)), three different silica fume 149 contents (i.e. of 5%, 8% and 11% also by weight of cementitious materials) as partial 150 replacement of OPC were prepared and tested. 151

Cubic specimens with the dimensions of $100 \times 100 \times 100 \text{ mm}^3$ were prepared for 152 measuring compressive strength and cylinder specimens with (100±1) mm in diameter 153 and (50±2) mm in height for assessing Chloride Ion penetration resistance. Concrete 154 mixtures were prepared by a single horizontal-axis forced mixer. After moulded, 155 concrete specimens were placed in a curing room with temperature of (20±5)°C for 24 156 hour. Then they were demoulded and immersed in tap water with temperature of 157 (20±2)°C for another 27 days, which is referred as 28 days standard curing in this 158 paper. Concrete specimens for measuring compressive strength and Chloride Ion 159 penetration resistance were prepared for assessing long-term performance and 160 durability of ordinary concrete. 161

163 Table 5

	w/b	Fly ash	Silica fume	OPC	Coarse aggregates	Fine aggregates	Water
C-8	0.38	0	0	500	1094	616	190
FA10-8	0.38	50	0	450	1094	616	190
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
SF8-8	0.38	0	40	460	1094	616	190
SF11-8	0.38	0	55	445	1094	616	190
C-3	0.33	0	0	500	1145	590	165
FA10-3	0.33	50	0	450	1145	590	165
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
SF8-3	0.33	0	40	460	1145	590	165
SF11-3	0.33	0	55	445	1145	590	165

164 Mix proportions in kg/m³ (except w/b) of concretes investigated in this study

165

166 **2.3 Chloride ion penetration resistance assessment**

For assessing effects of chloride concentration on Chloride Ion penetration resistance 167 of concrete, cylindrical concrete specimens with (100 ± 1) mm in diameter and (50 ± 2) 168 mm in height cured standardly for 28 days were then immersed in tap water and 169 designated solution (i.e. 4% and 10% by wt. sodium chloride solutions), respectively, 170 for another 41 days. Conforming to ASTM C1202-12, the rapid chloride penetration 171 test (RCPT) was proceeded as following. First, cylindrical concrete specimens were 172 placed in a vacuum pump with its pressure decreased to less than 5000 Pa within 5 173 minutes and maintained the pressure for 3 hours; then concrete specimens were 174 175 immersed in distilled water at the vacuum pressure for 1 hour followed by being immersed for (18±2) hours at normal ambient pressure; and finally one side of the 176 cylindrical specimen containing the top surface was filled with 3.0 % NaCl solution 177

and the other side of with 0.3 mol/L NaOH solution. During the 6 hours RCPT test,
temperatures of the specimen and the solutions were targeted to be between 20 and
25°C and they were recorded once every 5 minutes to ensure the target was reached.
The total charge passed during the RCPT test was measured and calculated via
Equation (1).

183
$$Q = 900 (I_0 + 2I_{30} + 2I_{60} + \dots + 2I_t + \dots + 2I_{300} + 2I_{330} + I_{360})$$
(1)

where Q in Coulombs is the total charge passed; I_0 in Amperes current immediately after voltage is applied; I_t in Amperes current at t min after voltage is applied.

186

187 2.4 Freezing-thawing resistance assessment

To assess concrete's resistance to combined freezing-thawing and chloride attack, 188 189 cylindrical concrete specimens with (100±1) mm in diameter and (50±2) mm in height were cured standardly for 56 days, then they were subjected to rapid 190 freezing-thawing cycle test in tap water and designated solution (i.e. 4% and 10% by 191 wt. sodium chloride solutions), respectively. Conforming to ASTM C666/C666M-03, 192 a standard rapid freezing-thawing cycle lasted for 6 hours and was proceeded as 193 following: a cylindrical concrete specimen was frozen in the tap water or designated 194 sodium sulfate solution for 3 hours at $-18(\pm 2)^{\circ}$ C, and subsequently it was that for 195 3 hours in water at $5(\pm 2)^{\circ}$ C. All concrete specimens were subjected to 50 such 196 freezing-thawing cycles. After that the RCPT was conducted. The deterioration 197 coefficient of total charge passed during the RCPT test was calculated via Equation 198 (2). 199

$$\lambda = \frac{Q_c}{Q_s}$$
(2)

where λ in % the deterioration coefficient of total charge passed; Q_c and Q_s in

Coulombs the total charge passed of a concrete specimen after subjected to combined

freezing-thawing and chloride attack and to solely freezing-thawing attack in tap

204

water, respectively.

201

202

203

205

206 2.5 Observation under the Scanning Electron Microscopy (SEM)

The morphology and microstructure observation under SEM (KYKY2800B) from Ningxia University were carried out on the specimens in order to understand the influence of freezing-thawing and chloride attack. SEM specimens were dried in drying oven for 48 hours at (80 ± 5) °C, and subsequently specimens' surfaces were coated using a gold sputter coater to eliminate effects of charging during micrograph collection.

213

214 **3. Results and discussion**

3.1 FA or SF dosage and chloride ion penetration resistance

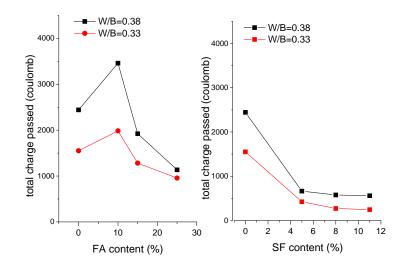
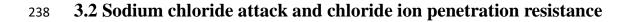


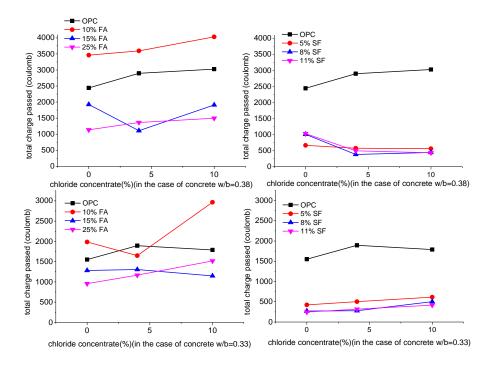
Fig.2 Total charge passed of concretes with various FA and SF contents

216

Measured total charge passed of the concrete specimens with various FA and SF 219 contents after immersed in tap water for 69 days (i.e. 28 days + 41 days) is presented 220 221 in Fig.2. The test results demonstrated that in general concrete's total charge passed actually decreased, as the FA or SF dosage increased and it was obvious that SF had 222 more evident improvement on concrete chloride penetration resistance (i.e. on 223 reducing total charge passed) than FA. Cured in tap water, concrete specimens with 224 10% FA had the highest total charge passed (i.e. 3460.1C in case of the 225 water-to-binder ratio of 0.38 and 1985.2 C in case of the water-to-binder of 0.33) than 226 concrete specimens with other FA dosages, while concrete with 25% FA had the 227 lowest value (i.e. 1135.1C with a water-to-binder ratio of 0.38 and 955.8C with a 228 water-to-binder ratio of 0.33). In case of concretes with SF, the total charges passed 229 were all less than 1000C and the higher chloride penetration resistance can be found 230 from concretes with higher FA and SF dosage which exhibited lower total charge 231

```
passed. According to ASTM C1202, C-8 and C-3 mixtures were classified as
moderate (2000-4000 coulombs) and low (1000-2000 coulombs), respectively, level
of chloride ion penetrability, FA25-8 as low (1000-2000 coulombs) level of chloride
ion penetrability, while FA25-3 and all concretes with SF as very low (100-1000
coulombs) level of chloride ion penetrability.
```

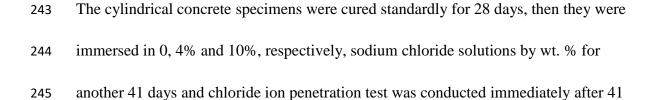




239

Fig.3 Total charge passed of concretes immersed in sodium chloride solutions with

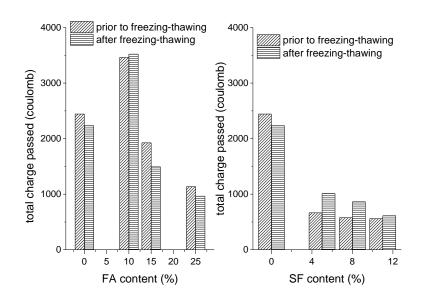
241 various concentrations



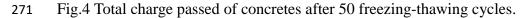
246	days immersion. Fig.3 presents the evolution of the total charge passed of concretes
247	exposed to sodium chloride solutions with various concentrations. Similar trend was
248	observed in concretes with different FA or SF contents. The results indicated that
249	under the two water-to-binder ratios (i.e. $w/b = 0.38$ and 0.33), sodium chloride
250	solution immersion for 41 days prior to the test was more aggressive than tap water
251	and 10% sodium chloride solution caused the largest rise in total charge passed. In the
252	case of w/b of 0.38, total charge passed of concretes with 0, 10%, 15% and 25% by
253	weight FA immersed in 10% sodium chloride solution had raised to 124.0%, 116.5%,
254	99.2% and 131.9%, respectively, of their corresponding original value, and in the
255	case of w/b =0.33, the counterpart value was 115.4%, 149.4%, 89.6% and 158.8%,
256	respectively. As for w/b =0.38 concretes with 5%, 8% and 11% SF by weight, total
257	charge passed had raised to 155.2%, 85.8% and 77.4 %, respectively, of their
258	corresponding original value; and for $w/b = 0.33$ concretes, the counterpart value was
259	144.8%, 185.9% and 170.3%, respectively.
260	In addition, 10% FA decreased chloride penetration resistance and had higher total
261	charge passed than OPC concrete not only in tap water but also in sodium chloride
262	solution while 15-25% FA can significantly improve chloride penetration resistance in
263	the same condition. All of the three SF dosages played more actively important role
264	than FA in raising the chloride penetration resistance and all concrete mixtures with
265	SF were at very low (100-1000 coulombs) level of total charge passed, indicating very
266	low level of chloride ion penetrability.

3.3 50 freezing-thawing cycles and chloride ion penetration resistance

269







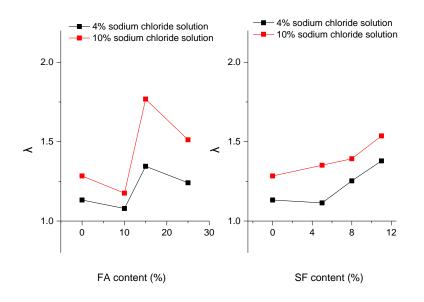
272

273 The cylindrical concrete specimens were cured under standard curing condition for 56 days and then subjected to freezing-thawing cycles in tap water, 4% and 10% sodium 274 chloride solutions up to 50 cycles, which lasted around 13 days, and subsequently 275 chloride ion penetration test were conducted. The total charge passed of various 276 concretes exposed to tap water under freezing-thawing cycles are depicted in Fig.4 277 (for concretes with w/b=0.38). There was a significant decrease in total charge passed 278 ranged from 8.6% to 22.6% over the test period for the concrete with 15% and 25% 279 FA by weight, respectively, while a slight increase by 1.7% for concrete with 10% FA 280 by weight. In the case of concrete with SF, the total charge passed increased by 52.2%, 281 49.7% and 9.0% at the SF content of 5%, 8% and 11% by weight, respectively. It can 282 be concluded that under 50 freezing-thawing cycles, chloride ion penetration 283

- -

resistance of concrete with FA increased while that of concrete with SF decreased.

3.4 Chloride ion penetration resistance against combined freezing-thawing and chloride attack



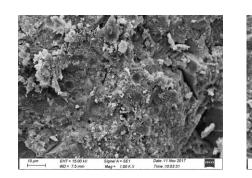
288

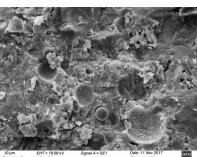
Fig.5 Deterioration coefficient of total charge passed of concretes exposed to tapwater and sodium chloride solution after 50 freezing-thawing cycles.

291

292 Concrete deterioration was associated with the interaction between freezing-thawing and chloride attack. Via Equation (2), if $\lambda > 1$, it means the interaction accelerates 293 concrete deterioration. If $\lambda < 1$, the interaction retards concrete deterioration. When λ 294 becomes larger or smaller, the accelerating or retarding effect on concrete 295 deterioration becomes more significant. In Fig.5 the interaction between 296 freezing-thawing and chloride attack accelerated the deterioration of all concrete 297 298 specimens, 10% sodium chloride solution demonstrated higher deterioration effect 299 than 4% solution. In the case of concretes with 15-25% FA, their λ values were 300 obviously higher than those of OPC concretes, while in the case of concretes with SF, 301 λ increased as the SF dosage increased. It can be concluded that when the FA dosage 302 was more than 15% or SF dosage more than 8%, both by weight, the acceleration 303 effect of the interaction between freezing-thawing and chloride attack on concrete 304 deterioration was more significant, and these concretes were more vulnerable to the 305 interaction and had the lower chloride ion penetration resistance against combined 306 freezing-thawing and chloride attack.

307 **3.5. SEM**





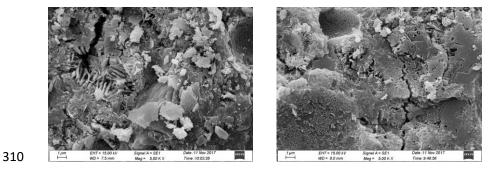
308

309

(a) FA25-3

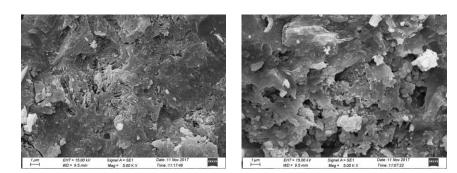
(c) FA25-3

(b) FA25-3



311

(d) FA25-3

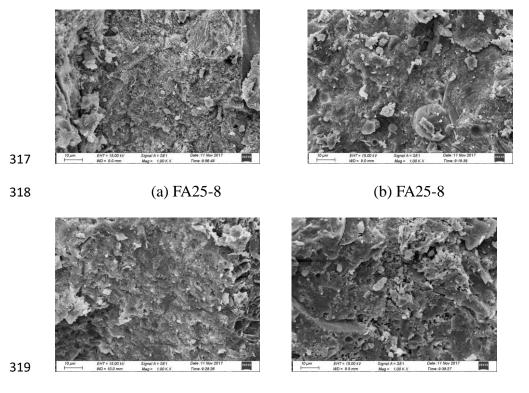




Figs.6 SEM images of concrete with 25% FA, 8% SF by weight exposed to tap water

315 ((a), (c) and (e) and 10% sodium chloride solution ((b), (d) and (f))

316



320

(c) SF8-8

(d) SF8-8

Figs.7 SEM images of concrete with 25% FA, 8% SF by weight exposed to tap water ((a) and (c)) and to 10% sodium chloride solution ((b) and (d)) after 50 freezing-thawing cycles

Figs.6 and Figs.7 present SEM images of concrete specimens at a depth of 5mm. When concretes were exposed to tap water, there were no clear microcracks resulting in a very compact microstructure, and this was the result of the pozzolanic reaction (i.e. Figs. 6(a) and (e). The use of pozzolanic materials (i.e. FA and SF) increases the

CSH, reduce the CH and the porosity in the cementitious matrix [47, 48]. The decrease of total charge passed of concrete with pozzolanic materials was attributed to the decrease of the porous system which is directly related to the electrical resistivity [49] and the low water to binder ratio.

When concretes were exposed to sodium chloride solution up to 41 days, it can be observed that there were not obvious differences in microstructures up to 1000 times magnification (i.e. Figs.6 (a) and (b)), while at 5000 times magnification the concrete specimen with 25% FA and 8% SF exposed to tap water had smaller pore and denser

structure than those to 10% sodium chloride solution (i.e. Figs.6 (c), (d), (e) and (f)).

When concrete specimens were exposed to 10% sodium chloride solution solutions up to 50 freezing-thawing cycles (i.e. Figs.7), there were two different trends. Concrete specimens with 25% by weight FA replacing OPC possessed compacter microstructure than those in tap water, while the microstructure of the one with 8% by weight SF replacing OPC would be looser after 50 freezing-thawing cycles.

343

344 **4. Conclusions**

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

(1) Immersed in tap water, concrete's total charge passed actually decreased as the
 FA or SF dosage increased and, in comparison, SF had more evident
 improvement on concrete chloride penetration resistance than FA. It was

clearly indicated that 15% and 25% by weight FA and all SF dosages were
more effective to reduce concrete total charge passed and to enhance chloride
penetration resistance. All concretes with SF were classified as at very low
(100-1000 coulombs) level of chloride ion penetrability.

(2) Sodium chloride solution immersion was more aggressive to concrete than tap 355 water and 10% sodium chloride solution caused the lowest chloride 356 penetration resistance. In addition, 15-25% by weight FA can significantly 357 improve chloride penetration resistance not only in tap water but also in 358 359 sodium chloride solution. All of the three SF dosages played more actively important role than FA in raising the chloride penetration resistance and all 360 concretes with SF were at very low (100-1000 coulombs) level of chloride ion 361 362 penetrability when immersed in sodium chloride solution.

363 (3) After 50 freezing-thawing cycles in tap water, chloride ion penetration 364 resistance of concrete with FA increased, while that of concrete with SF 365 decreased.

(4) The interaction between freezing-thawing and chloride attack accelerated the
deterioration of all concrete specimens and 10% sodium chloride solution
demonstrated higher deterioration effect than 4% solution. Concretes with
more than 15% FA or 8% SF by weight replacing OPC had lower chloride ion
penetration resistance against combined freezing-thawing and chloride attack

371

372 Acknowledgement

373	The authors would like to acknowledge the National Natural Science Foundation of
374	China (through the grant 51368049 and 51668001), Ningxia First Class Discipline
375	Project (through the grant NXYLXK2017A03) and Ningxia University Subject
376	Development Project for sponsoring this research. The first author would also like to
377	acknowledge the China Scholarship Council for sponsoring his one-year visit to
378	Brunel University London where this paper was completed.
379	
380	References
381	[1] U. Angst, B. Elsener, C.K. Larsen, O. Vennesland, Critical chloride content in
382	reinforced concrete - A review, Cem. Concr. Res. 39(12) (2009) 1122-1138.
383	[2] L. Basheer, J. Kropp, D.J. Cleland, Assessment of the durability of concrete from its
384	permeation properties: A review, Constr. Build. Mater. 15(2-3) (2001) 93-103.
385	[3] X. Shi, N. Xie, K. Fortune, J. Gong, Durability of steel reinforced concrete in
386	chloride environments: An overview, Constr. Build. Mater. 30 (2012) 125-138.
387	[4] M.G. Stewart, D.V. Rosowsky, Time-dependent reliability of deteriorating
388	reinforced concrete bridge decks, Struct. Saf. 20(1) (1998) 91-109.
389	[5] A.C. 201, Guide to durable concrete (ACI 201.2R-08), American concrete institute,
390	MI, 2008.
391	[6] D.W.S. Ho, R.K. Lewis, Carbonation of concrete and its prediction, Cem. Concr. Res.
392	17(3) (1987) 489-504.
393	[7] Z.P. Bazant, Physical model for steel corrosion in concrete sea structures-theory,
394	ASCE J Struct Div 105(6) (1979) 1137-1153.

- [8] C. Cao, M.M.S. Cheung, Non-uniform rust expansion for chloride-induced pitting
 corrosion in RC structures, Constr. Build. Mater. 51 (2014) 75-81.
- [9] L. Bertolini, B. Elsener, P. Pedeferri, E. Redaelli, R.B. Polder, Corrosion of steel in
 concrete: prevention, diagnosis, repair, John Wiley & Sons.2013.
- [10] M.S. Darmawan, Pitting corrosion model for reinforced concrete structures in a
 chloride environment, Mag. Concr. Res. 62(2) (2010) 91-101.
- 401 [11] G.C. Marano, G. Quaranta, M. Mezzina, Fuzzy Time-Dependent Reliability
- 402 Analysis of RC Beams Subject to Pitting Corrosion, J. Mater. Civ. Eng. 20(9) (2008) 403 578-587.
- 404 [12] J. Wu, W. Wu, Study on wireless sensing for monitoring the corrosion of
 405 reinforcement in concrete structures, Measurement 43(3) (2010) 375-380.
- 406 [13] M.G. Stewart, Spatial variability of pitting corrosion and its influence on 407 structural fragility and reliability of RC beams in flexure, Struct. Saf. 26(4) (2004) 408 453-470.
- [14] E. Mazario, R. Venegas, P. Herrasti, M.C. Alonso, F.J. Recio, Pitting corrosion and
 stress corrosion cracking study in high strength steels in alkaline media, Journal of
 Solid State Electrochemistry 20(4) (2016) 1223-1227.

[15] C. Andrade, R. Buják, Effects of some mineral additions to Portland cement on
reinforcement corrosion, Cem. Concr. Res. 53 (2013) 59-67.

[16] U.A. Birnin-Yauri, F.P. Glasser, Friedel's salt, Ca2Al(OH)6(Cl,OH)·2H2O: Its solid
solutions and their role in chloride binding, Cem. Concr. Res. 28(12) (1998)
1713-1723.

- [17] A. Delagrave, J. Marchand, J.-P. Ollivier, S. Julien, K. Hazrati, Chloride binding
 capacity of various hydrated cement paste systems, Adv. Cem. Based Mater. 6(1)
 (1997) 28-35.
- 420 [18] E.P. Nielsen, M.R. Geiker, Chloride diffusion in partially saturated cementitious

421 material, Cem. Concr. Res. 33(1) (2003) 133-138.

- 422 [19] M.D.A. Thomas, P.B. Bamforth, Modelling chloride diffusion in concrete: Effect of
- 423 fly ash and slag, Cem. Concr. Res. 29(4) (1999) 487-495.
- 424 [20] G.K. Glass, N.R. Buenfeld, The influence of chloride binding on the chloride
- induced corrosion risk in reinforced concrete, Corrosion Sci. 42(2) (2000) 329-344.
- 426 [21] C.A. Apostolopoulos, V.G. Papadakis, Consequences of steel corrosion on the
- 427 ductility properties of reinforcement bar, Constr. Build. Mater. 22(12) (2008) 428 2316-2324.
- [22] C. Cao, 3D simulation of localized steel corrosion in chloride contaminated
 reinforced concrete, Constr. Build. Mater. 72 (2014) 434-443.
- 431 [23] P.S. Mangat, M.C. Limbachiya, Effect of initial curing on chloride diffusion in
 432 concrete repair materials, Cem. Concr. Res. 29(9) (1999) 1475-1485.
- 433 [24] M.D.A. Thomas, J.D. Matthews, Performance of pfa concrete in a marine
 434 environment 10-year results, Cem Concr Compos 26(1) (2004) 5-20.
- [25] S.-W. Pack, M.-S. Jung, H.-W. Song, S.-H. Kim, K.Y. Ann, Prediction of time
 dependent chloride transport in concrete structures exposed to a marine
 environment, Cem. Concr. Res. 40(2) (2010) 302-312.
- 438 [26] K. Audenaert, Q. Yuan, G. De Schutter, On the time dependency of the chloride

- 439 migration coefficient in concrete, Constr. Build. Mater. 24(3) (2010) 396-402.
- 440 [27] N. Otsuki, M.S. Madlangbayan, T. Nishida, T. Saito, M.A. Baccay, Temperature
- 441 Dependency of Chloride Induced Corrosion in Concrete, Journal of Advanced
- 442 Concrete Technology 7(1) (2009) 41-50.
- [28] C.L. Page, N.R. Short, A. El Tarras, Diffusion of chloride ions in hardened cement
 pastes, Cem. Concr. Res. 11(3) (1981) 395-406.
- [29] P. Chindaprasirt, S. Rukzon, V. Sirivivatnanon, Effect of carbon dioxide on chloride
- 446 penetration and chloride ion diffusion coefficient of blended Portland cement mortar,
- 447 Constr. Build. Mater. 22(8) (2008) 1701-1707.
- [30] X.-m. Wan, F.H. Wittmann, T.-j. Zhao, H. Fan, Chloride content and pH value in
- the pore solution of concrete under carbonation, Journal of Zhejiang University
 SCIENCE A 14(1) (2013) 71-78.
- [31] P.J. Tumidajski, G.W. Chan, Effect of sulfate and carbon dioxide on chloride
 diffusivity, Cem. Concr. Res. 26(4) (1996) 551-556.
- 453 [32] I.S. Yoon, Simple approach to calculate chloride diffusivity of concrete
 454 considering carbonation, Comput. Concr. 6(1) (2009) 1-18.
- 455 [33] V.T. Ngala, C.L. Page, Effects of carbonation on pore structure and diffusional
- 456 properties of hydrated cement pastes, Cem. Concr. Res. 27(7) (1997) 995-1007.
- 457 [34] M.K. Lee, S.H. Jung, B.H. Oh, Effects of Carbonation on Chloride Penetration in
- 458 Concrete, ACI Mater. J. 110(5) (2013) 559-566.
- [35] C.F. Yuan, D.T. Niu, D.M. Luo, Effect of carbonation on chloride diffusion in fly ash
- 460 concrete, Disaster Adv. 5(4) (2012) 433-436.

- 461 [36] Y.F. Houst, F.H. Wittmann, Depth profiles of carbonates fonned during natural
 462 carbonation, Cem. Concr. Res. 32(12) (2002) 1923-1930.
- 463 [37] T. Ishida, P.O.N. Iqbal, H.T.L. Anh, Modeling of chloride diffusivity coupled with
- 464 non-linear binding capacity in sound and cracked concrete, Cem. Concr. Res. 39(10)
- 465 (2009) 913-923.
- 466 [38] L. Marsavina, K. Audenaert, G. Schutter, N. Faur, D. Marsavina, Experimental and
- 467 numerical determination of the chloride penetration in cracked concrete, Constr.
- 468 Build. Mater. 23(1) (2009) 264-274.
- 469 [39] B. Šavija, J. Pacheco, E. Schlangen, Lattice modeling of chloride diffusion in
 470 sound and cracked concrete, Cem Concr Compos 42 (2013) 30-40.
- [40] C.C. Lim, N. Gowripalan, V. Sirivivatnanon, Microcracking and chloride
 permeability of concrete under uniaxial compression, Cem Concr Compos 22(5)
 (2000) 353-360.
- 474 [41] M. Saito, H. Ishimori, Chloride Permeability of Concrete under Static and
 475 Repeated Compressive Loading, Cem. Concr. Res. 25(4) (1995) 803-808.
- 476 [42] M.K. Rahman, W.A. Al-Kutti, M.A. Shazali, M.H. Baluch, Simulation of Chloride
- 477 Migration in Compression-Induced Damage in Concrete, J. Mater. Civ. Eng. 24(7)
- 478 (2012) 789-796.
- [43] H.L. Ye, X.Y. Jin, C.Q. Fu, N.G. Jin, Y.B. Xu, T. Huang, Chloride penetration in
 concrete exposed to cyclic drying-wetting and carbonation, Constr. Build. Mater. 112
 (2016) 457-463.
- 482 [44] H. Ye, N. Jin, X. Jin, C. Fu, Model of chloride penetration into cracked concrete

- subject to drying–wetting cycles, Constr. Build. Mater. 36 (2012) 259-269.
- [45] S.J.H. Meijers, J. Bijen, R. de Borst, A.L.A. Fraaij, Computational results of a
 model for chloride ingress in concrete including convection, drying-wetting cycles
 and carbonation, Mater. Struct. 38(276) (2005) 145-154.
- [46] Wu. Zhongwei, L. Huizhen, The high performance concrete, China Railway Press,
 Beijing, China, 1999.
- [47] V. Corinaldesi, G. Moriconi, Influence of mineral additions on the performance of
- 490 100% recycled aggregate concrete, Constr. Build. Mater. 23(8) (2009) 2869-2876.
- 491 [48] W. Sun, Y. Zhang, S. Liu, Y. Zhang, The influence of mineral admixtures on
- 492 resistance to corrosion of steel bars in green high-performance concrete, Cem. Concr.
- 493 Res. 34(10) (2004) 1781-1785.
- 494 [49] R. Corral-Higuera, S.P. Arredondo-Rea, M.A. Neri-Flores, J.M. Gomez-Soberon, J.L.
- Almaral-Sanchez, J.H. Castorena-Gonzalez, A. Martinez-Villafane, F.
 Almeraya-Calderon, Chloride Ion Penetrability and Corrosion Behavior of Steel in
 Concrete with Sustainability Characteristics, Int. J. Electrochem. Sci. 6(4) (2011)
 958-970.