



Mechanical and durability properties of concrete subjected to early-age freeze–thaw cycles

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Abstract Early-age frost damage to concrete used in winter construction or in cold environments negatively affects the development of the hydration process and the performance of the concrete, thereby reducing the service life of the building structure. Experimental research was carried out to investigate the compressive strength, resistance to chloride penetration and resistance to freeze–thaw of concrete specimens subjected to early-age freeze–thaw cycles (E-FTCs). The effects that different pre-curing times of concrete and mineral admixtures have on the properties of early-age frost-affected concrete were also analyzed. Results show that the earlier the freeze–thaw cycles (FTCs), the poorer the later-age performance. Later-age water-curing cannot

completely restore the damage that E-FTCs do to concrete. In the same conditions used in this study, the effects of E-FTCs on later-age mechanical and durability properties of ordinary Portland cement concrete (OPC) are small. The incorporation of fly ash significantly reduces the resistance to freeze–thaw of concrete during early-age and later-age. The presence of silica fumes has an adverse effect on the later-age resistance to freeze–thaw. In general, the recovery percentage of later-age durability indexes of concrete subjected to E-FTCs is lower than that of compressive strength. For concrete subjected to E-FTCs, it is more important to ensure the recovery of later-age durability.

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Keywords Early-age freeze–thaw cycles · Pre-curing time · Fly ash · Silica fume · Resistance to freeze–thaw

Abbreviations

E-FTC	Early-age freeze–thaw cycle
OPC	Ordinary Portland cement concrete
FA	Fly ash
SF	Silica fume
FAC	Fly ash concrete
SFC	Silica fume concrete
MLR	Mass loss rate
RDM	Relative dynamic modulus of elasticity
DF	Durability factor
FTC	Freeze–thaw cycle
RP	Recovery percentage



1 Introduction

Concrete structures built in winter or cold environments are often subjected to frost or freeze–thaw action at early-age, which not only delays or even stops the hydration of concrete [1], but also causes unrecoverable physical damage to its microstructure [2, 3], thereby affecting the subsequent development of its performance and the service life of the structure.

During freezing, the combined effect of volume expansion caused by ice formation and movement of unfrozen water can generate pressure on the pore walls inside concrete [4–6]. When the pore pressure exceeds the tensile strength of the concrete, cracks and cavities will occur [7–11]. Due to the inadequate hydration and low strength of early-age concrete, the degradation of the microstructure due to frost action is more serious than in older concrete. The pre-curing time before frost damage, and the duration and temperature during freezing, all influence the degree to which the concrete is damaged by frost. Both Yi et al. [12] and Choi et al. [13] highlighted that the damage degree of later-age compressive strength of concrete subjected to frost action during early-age reduces when the pre-curing time of concrete exceeds 6 h. Sang et al. [14] found that the 28 d compressive strength of concrete experiencing temperatures below 0 °C for 3 d during early-age decreases as the freezing temperatures drop from – 5 to – 20 °C. This is attributed to both the amount of frozen water and the expansion stress increasing with the reduction of temperature. Hu et al. [3] studied the effects of frost damage duration on the mechanical properties of early-age frozen concrete and showed that the deterioration in concrete performance worsens as the frost duration increases from 2 to 4 h, while the degree of deterioration does not increase significantly when the frost duration increases from 4 to 8 h. However, some researchers have also suggested that the degree of frost damage to concrete is essentially unchanged after 3 d of freezing [15].

Apart from environments where the temperature does not rise above 0°C, concrete may also suffer short-term freeze–thaw cycles (FTCs) during the first few days after casting. Compared to freezing temperatures, the damage by FTCs to early-age concrete is more serious due to the repetitive freeze–thaw process. Using a slow FTC test on 1 d early-age concrete and 28 d concrete, Maler et al. [16] found that the frost resistance of concrete reduces with increasing cement

content and improves with longer curing times. Gao [17] also proposed that the mechanical performance of early-age frost-affected concrete gradually increases with a reduction in cement dosage and water-cement ratio, but the effect of the former is much smaller than that of the latter. Wei et al. [18] evaluated the effect of later curing on the pore structure of paste subject to early-age freeze–thaw cycles (E-FTCs), and found that the paste with a higher water-cement ratio had greater porosity and pore sizes. In addition, later curing did not completely undo the damage by E-FTCs to the paste pores. To prevent concrete from suffering early-age frost damage, some standards prescribe a minimum antifreeze critical strength, such as 3.5 MPa specified in ACI-306R [19] and 5 MPa specified in the Japanese Concrete Code [20]. Similar requirement is also given in the *fib* Model Code [21]. Nevertheless, Koh et al. [22] indicated that although the 5 MPa antifreeze critical strength can ensure that the later-age compressive strength of concrete subjected to E-FTCs meets the requirements, it does not make its durability indexes, such as resistance to freeze–thaw and chloride penetration, reach the expected results. Therefore, it is particularly important to evaluate durability performance of concrete subjected to E-FTCs.

Mineral admixtures, such as fly ash (FA), silica fume (SF) and slag, are usually used to replace part of the cement to reduce carbon dioxide emissions and protect the environment [23]. Yalçinkaya et al. [24] indicated that adding high-volume FA and ground granulated blast furnace slag decreases the resistance to freeze–thaw of concrete aged 14 d due to the low reaction activities of these additives and insufficient curing. Both Toutanji et al. [25] and Radlinski et al. [26] also obtained similar results. Badr [27] also suggested that air entrainment is more important for concrete incorporating FA if it is expected to experience FTCs during early-age. From these results it seems clear that incorporating some mineral admixtures in concrete significantly affect the freeze–thaw resistance of concrete. However, the above literature does not consider the effects of pre-curing time and later-age curing on the mechanics and durability of concrete subjected to E-FTCs. In cold environment, the concrete can suffer the FTCs action within a few days after casting. During the period, the influence of mineral admixtures on the hydration of concrete is obvious [28], and it can be predicted that concrete with mineral admixtures may show different early frost



resistance from ordinary concrete. Therefore, it is worth paying attention to the freeze–thaw resistance of concrete with mineral admixtures after different pre-curing ages. In addition, concrete subjected to E-FTCs will be cured in temperatures above 0°C again afterwards so its performance will also further develop. Therefore, it is necessary to investigate whether the later curing can recover the performance of damaged concrete and the difference in recovery effect of performance among the different concretes. Only by understanding the damage of E-FTCs to concrete from the micro- and macro-indices, can we effectively provide some guarantees for the construction of concrete in cold environments.

Therefore, in this study, the pre-curing time and mineral admixtures are taken as the main factors to study the effect of E-FTCs on the mechanical and durability properties of concrete. Three types of concrete with water-to-binder ratios by mass of 0.4 were investigated experimentally, including ordinary Portland cement concrete (OPC), fly ash concrete (FAC) with 30% FA and silica fume concrete (SFC) with 5% SF. The specimens were subjected to short-term FTCs at 24 h and 72 h and subsequently re-cured to 28 d in water and in temperatures above 0°C. Finally, the compressive strength test, rapid FTC test and chloride ion electric flux test were carried out. The pore structure of some samples was also measured via the mercury intrusion porosimetry (MIP) test.

2 Materials and experiments

2.1 Materials and mixture compositions

Portland cement (P.O 42.5), FA and SF were used in the experiments as cementitious materials; their chemical compositions are shown in Table 1. P.O 42.5 cement was produced by the China Cement Plant Co., Ltd; its physical and mechanical properties are shown in Table 2. Natural river sand classified as

medium sand (fineness modulus is 2.90) was used as the fine aggregate; the average particle size of the sand was 0.35–0.5 mm, the mud concentration was less than 1.5% and the bulk density was 1410 kg/m³. A secondary mixed gravel with average particle sizes of 5–10 mm and 10–20 mm and a mixing ratio of 4:6 was used as the coarse aggregate; its mud concentration was less than 0.5%, and its apparent density was 2680 kg/m³. Polycarboxylate superplasticizer SBT-801 produced by Sobute New Materials Co., Ltd. was used in this experiment to ensure the good workability of fresh concrete. The water used for mixing the concrete was tap water containing no deleterious materials.

Three types of concrete with the ratio of water to binder in mass of 0.4 were used for this study: OPC, FAC and SFC. The percentages of FA and SF used in place of Portland cement for the FAC and SFC mixtures were 30% and 5%, respectively following the recommendation from JGJ 55–2011 [29]. The proportions used for the concrete mixtures are shown in Table 3.

2.2 Experiment design

In order to evaluate mechanical and durability properties of concrete subjected to E-FTCs, the experimental process in this study was divided into four sections as shown in Fig. 1. First, the concrete samples were pre-cured. The three types of cement were cast into plastic molds following standard GB/T 50080–2016 [30], then compacted using a vibrating table and finally cured in an indoor environment (storage at about 30 °C and above 50% RH (i.e., relative humidity) for the planned pre-curing times, 24 h and 72 h. All specimens were removed from their molds after 24 h. Second, the E-FTCs were carried out. After 24 or 72 h of pre-curing, specimens were subjected to rapid FTCs with the temperature ranging from – 17 °C to 5 °C and the finished time of each FTC within 4 h, to simulate freeze–thaw damage to

Table 1 Chemical compositions of cementitious materials

Cementitious materials	Chemical composition (wt.%)							
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	K ₂ O	LOI*
Portland cement	60.82	20.40	5.20	3.06	1.71	3.01	0.50	2.59
FA	1.17	50.61	23.43	14.61	0.72	0.91	1.10	3.56
SF	0.93	92.31	1.02	2.21	1.68	0.40	1.30	0.10

*Loss on ignition

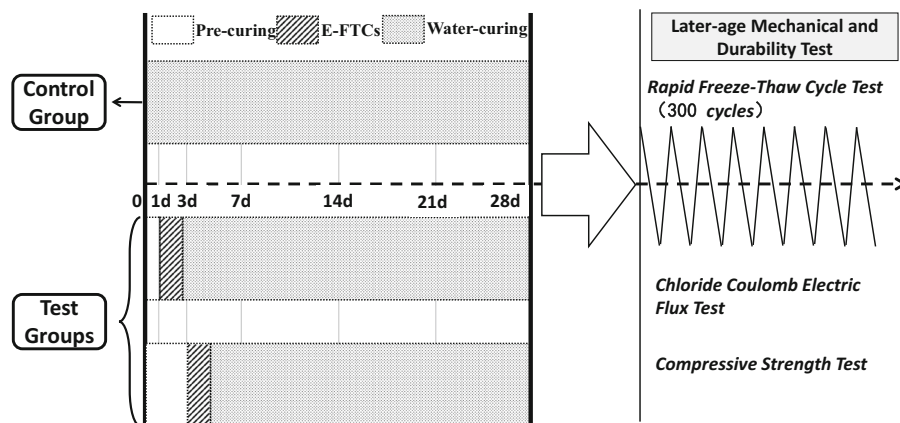


Table 2 Physical and mechanical properties of Portland cement

Specific surface area (m ² /kg)	Setting time (min)		Flexural strength (MPa)		Compressive strength (MPa)	
	Initial setting	Final setting	3 d	28 d	3 d	28 d
379	209	247	6.6	9.1	36.5	52.5

Table 3 Mix proportions of the three types of concrete

Types of concrete	Mix proportions (kg/m ³)							Slump (mm)
	Cement	FA	SF	Water	Sand	Gravel	Superplasticizer	
OPC	513	0	0	205	588	1094	0.300	154
FAC	360	153	0	205	588	1094	0.000	150
SFC	488	0	25	205	588	1094	0.375	141

**Fig. 1** Technology roadmap of this study

concrete in winter conditions. To ensure the integrity of specimens and allow subsequent testing, the number of E-FTCs was limited. Therefore, in this study, 10 FTCs were carried out, capable of properly damaging early-age concrete. Third, the specimens were water-cured again to repair the damage. After finishing the E-FTCs, samples were cured in water (storage at $\sim 30\text{--}35\text{ }^{\circ}\text{C}$ and 100% RH) until the age of 28 d. The temperature and RH of the curing environment can be measured by the thermometer and hygrometer placed in indoor laboratory. Last, the later-age mechanical and durability tests were carried out. A compressive strength test, a rapid FTC test and a

chloride ion electric flux test were carried out. Detailed test procedures are described in Sect. 2.3.

Nine groups of concrete specimens were set up in this study, including three control groups and six experimental groups, as shown in Table 4. OPC-control, FAC-Control and SFC-Control denote the OPC, FAC and SFC with no E-FTCs but with water-curing for 28 d. OPC-24-FT, FAC-24-FT and SFC-24-FT denote the OPC, FAC and SFC that underwent E-FTCs after 24 h of pre-curing. OPC-72-FT, FAC-72-FT and SFC-72-FT denote the OPC, FAC and SFC that underwent E-FTCs after 72 h of pre-curing.

Table 4 Grouping of specimens

Designation	Concrete types	Pre-curing time (h)	Designation	Concrete types	Pre-curing time (h)	Designation	Concrete types	Pre-curing time (h)
FAC-Control	FAC	Without E-FTCs	OPC-Control	OPC	Without E-FTCs	SFC-Control	SFC	Without E-FTCs
FAC-24-FT		24	OPC-24-FT		24	SFC-24-FT		24
FAC-72-FT		72	OPC-72-FT		72	SFC-72-FT		72

2.3 Experimental methods

2.3.1 Cubic compressive strength test

The compressive strength of 100 mm cubes of the concrete was measured. A 2000 kN universal compression machine (WAW-2000) was used in this test in accordance with GB/T 50081–2019 [31]. The average value for three specimens was used as the final value of cubic compressive strength of each group. To evaluate the influence of E-FTCs on the performance development of early-age concrete, the compressive strengths of each experimental group before and after the E-FTCs were measured too. Due to the strength of early-age concrete being lower than that of mature concrete, the loading rate for the compression test was set to 0.4 MPa/s. At the age of 28 d, the compressive strengths of the experimental and control groups were measured, with the loading rate set to 0.5 ~ 0.8 MPa/s.

2.3.2 Chloride ion electric flux test

According to GB/T 50082–2009 [32], a chloride ion electric flux test is used to evaluate the resistance to chloride penetration of concrete using NEL-PEU concrete chloride ion electric flux apparatus. Cylindrical samples with ϕ 100 mm \times 50 mm, obtained by cutting the central cores of ϕ 100 mm \times 200 mm concrete cylinders, were used in this test to measure the total charge passed over 6 h, using the method described in GB/T 50082-2009. According to ASTM C1202-19 [33], the five grades of chloride penetrability of concrete based on charge passed are high penetrability (Charge Passed: $Q > 4000$ C), moderate penetrability (Charge Passed: $2000 < Q \leq 4000$ C), low penetrability (Charge Passed: $1000 < Q \leq 2000$ C), very low penetrability (Charge Passed: 100

$C < Q \leq 1000$ C) and negligible (Charge Passed: $Q < 100$ C).

2.3.3 Rapid FTC test

A rapid FTC test using a 400 mm \times 100 mm \times 100 mm prism evaluated the resistance to freeze–thaw of concrete. A NELD-FC810 concrete rapid freeze–thaw test apparatus was used, where the temperature at the center of the control specimens ranged from -17 to 5 °C and each cycle lasted about 3.5 h. The test was carried out following the specifications described in GB/T 50082–2009 [32]. After every 25 FTCs, the mass loss rate (MLR) and relative dynamic modulus of elasticity (RDM) of samples were measured and, at the end of the test, the frost resistance durability factor (DF) of concrete was calculated. The FTCs continued until the specimen had undergone 300 cycles or until its RDM was less than 60% or until its MLR was more than 5%. The equations of MLR, RDM and DF are shown in Eqs. (1), (2) and (3). The dynamic modulus of elasticity was obtained by measuring the longitudinal pulse velocity of the specimen using a ZBL-U520 non-metal pulse velocity test apparatus (Fig. 2) as described by ASTM C597-16 [34].

$$\Delta W_n = \frac{W_0 - W_n}{W_0} \times 100\% \quad (1)$$

where ΔW_n is the MLR after n FTCs (%), W_0 is the mass at 0 FTC (kg), and W_n is the mass after n FTCs (kg).

$$E = \frac{\rho V^2(1 + \mu)(1 - 2\mu)}{(1 - \mu)} \quad (2 - 1)$$

$$RDM = \frac{E_n}{E_0} \times 100\% \quad (2 - 2)$$

where E is the dynamic modulus of elasticity (MPa), ρ is the density of concrete (kg/m^3), μ is the dynamic

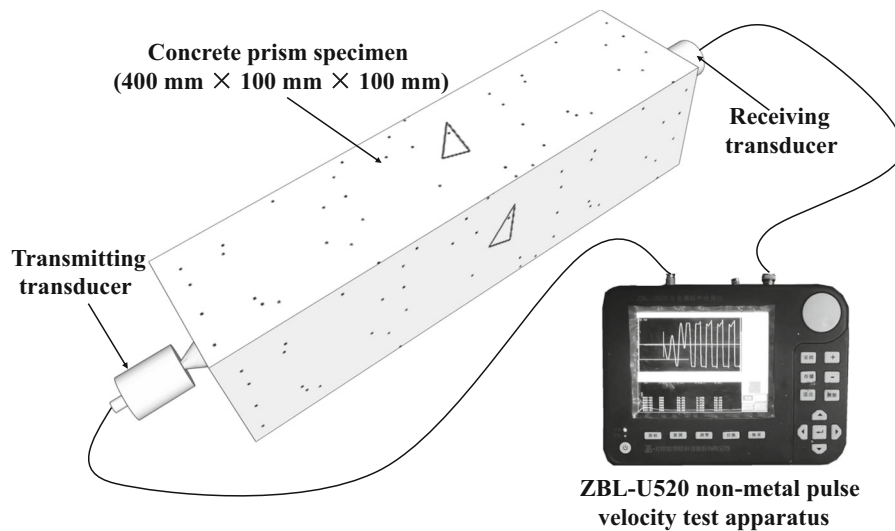


Fig. 2 Schematic of concrete pulse velocity measurement

Poisson's ratio, $\mu = 0.2$, V is the pulse velocity of the specimen (m/s), E_n is the dynamic modulus of elasticity after n FTCs (MPa), and E_0 is the dynamic modulus of elasticity at 0 FTC (MPa).

$$DF = \frac{E_{300}}{E_0} \times 100\% \quad (3-1)$$

$$DF = \frac{0.6N}{300} \times 100\% \quad (3-2)$$

where E_{300} is the dynamic modulus of elasticity after 300 FTCs (MPa). If the RDM has been less than 60% or the MLR has been more than 5% after N FTCs, note N is less than 300, the DF is calculated with the N , as shown in Eq. (3-2) [35].

2.3.4 Mercury intrusion porosimetry (MIP)

MIP measurement was performed by using AutoPore IV 9500 to obtain the pore structure information of concrete sample. The pressure range is from 0.52 psi to 32,842.41 psi, and the contact angle were assumed to be 130°. The samples with the size of about 5 mm were collected from broken specimens after the compressive strength test. Before measuring, samples were dried for 3 d in a vacuum drying oven with the temperature of 60 °C to remove the free water inside the sample.

3 Results and discussion

3.1 Cubic compressive strength

Figure 3 shows the compressive strength of the three types of concrete before and after being subjected to 10 E-FTCs. The results show that the compressive strength of concrete showed different development trends for different types of concrete before and after E-FTCs. When the pre-curing time was 24 h, after 10 E-FTCs, the compressive strength of OPC and SFC increased by 59.9% and 59.1% respectively, while that of FAC decreased by 31.6%. When the pre-curing time was 72 h, after 10 E-FTCs, the compressive strength of OPC, FAC and SFC increased by 11.6%, 0.66% and 26.7%, respectively. During early-age, the hydration process of concrete is rapid and continuous. During the E-FTCs, the moisture released by the thawing process can aid hydration and increase the concrete's strength [27], while repeated FTCs, as with fatigue loading, can damage the internal microstructure and reduce its strength. These two opposite effects jointly determine the strength development of concrete. The above results indicate that for the FAC, when the pre-curing time is 24 h, the adverse effect of FTCs on strength is greater than the beneficial effect of the thawing process on strength, while the advantageous effect of the thawing process is offset by the adverse effect of FTCs on concrete when the pre-curing time increased to 72 h. However, for OPC and

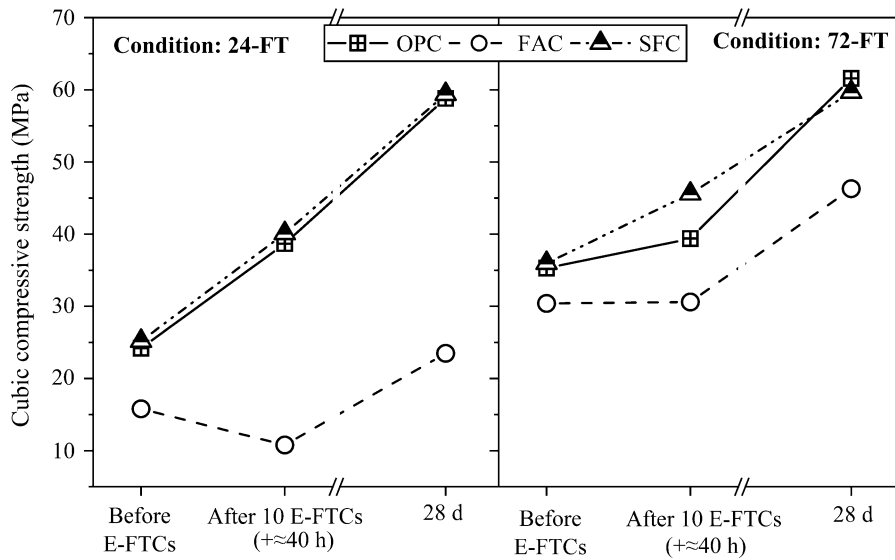


Fig. 3 Development of compressive strength of the three types of concrete subjected to E-FTCs

SFC, the advantageous effect of E-FTCs on strength is always greater than its adverse effect regardless of whether the pre-curing time is 24 h or 72 h.

The comparison of 28 d compressive strength of the three types of concrete subjected to E-FTCs is shown in Fig. 4. After conducting later-age water-curing, the compressive strength of all specimens that underwent E-FTCs increased to different degrees. Compared with FAC, OPC and SFC had higher later-age compressive strengths under the test conditions used in this study, and even the 28-d compressive strength of SFC-72-FT was slightly higher than that of SFC-Control.

However, for FAC, although the 28-d compressive strength of FAC-Control reached 52.3 MPa, which is slightly lower than that of the other two types of concrete, that of FAC-24-FT was only 23.5 MPa. It means that the E-FTCs caused significant damage to FAC, and this damage could not be repaired even when later-age positive temperature curing was carried out. When the pre-curing time increased to 72 h, the 28 d compressive strengths of FAC-72-FT increased to 46.3 MPa. This indicates that increasing pre-curing time can reduce the adverse effects of E-FTCs on FAC to some extent.

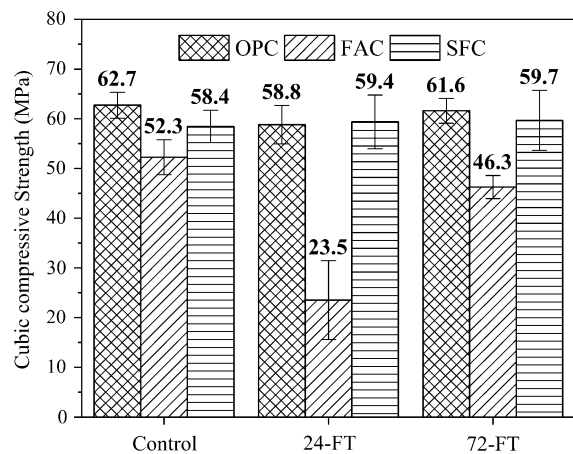


Fig. 4 28 d compressive strength of three types of concrete subjected to E-FTCs

3.2 Resistance to chloride penetration

In this study, chloride ion electric flux of concrete was used to evaluate its resistance to chloride penetration. Figure 5 shows the later-age chloride ion charge passed for the three types of concrete subjected to E-FTCs. Unlike the results for compressive strength shown in Fig. 4, FAC-Control and SFC-Control had lower chloride penetrability compared with OPC-Control. However, regardless of the pre-curing time, later-age chloride penetrability of the three types of concrete increased by different degrees when being subjected to E-FTCs. Compared with OPC-Control, the percentage increases in chloride ion electric flux for OPC-24-FT and OPC-72-FT were 31.7% and 13.1%, respectively. Compared with FAC-Control,

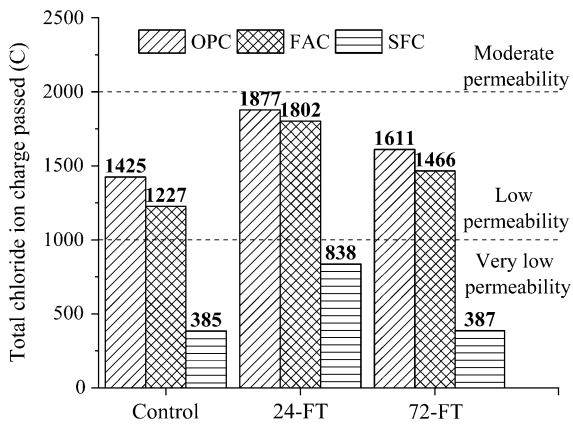


Fig. 5 Chloride ion charge passed by three types of concrete subjected to E-FTCs

the percentage increases in chloride ion electric flux for FAC-24-FT and FAC-72-FT were 46.9% and 19.5%, respectively. This indicated that the extension of pre-curing time is beneficial for improving the later-age resistance to chloride penetration. However, after being subjected to the same E-FTC environment, the degree of increase in chloride ion electric flux for FAC was greater than that for OPC. For concrete mixed with SF, the chloride ion penetrability of SFC-24-FT and SFC-72-FT remained very low.

3.3 Resistance to freeze–thaw

3.3.1 MLR and RDM

The changes in MLR and RDM of the three types of concrete subjected to E-FTCs during the later-age freeze–thaw test are shown in Figs. 6 and 7. By comparing the test results of OPC-Control, FAC-Control and SFC-Control, it can be seen that, for the same FTCs, FAC-control had the largest MLR and the lowest RDM. After only 175 FTCs, the RDM of FAC-Control had been reduced to below 60%, which means that this specimen reached the performance failure state. However, the RDM of OPC-Control and SFC-Control were 98.1% and 77.4% respectively at 300 FTCs.

In addition, resistance to freeze–thaw of all the three types of concrete at later-age was affected by the E-FTCs, but to varying degrees. For OPC, the MLR of OPC-24-FT was slightly higher than that of OPC-Control, and its RDM clearly decreased after 200 FTCs while RDM variation of OPC-Control was

small. However, when the pre-curing time was 72 h, i.e., for OPC-72-FT, the effect of E-FTCs on its RDM was negligible, and even its MLR was slightly lower than that of OPC-Control. For FAC, the E-FTCs had a significant adverse effect on its later-age resistance to freeze–thaw. The RDM of FAC-24-FT decreased to 58.0% after only 25 FTCs, and the specimen was deemed to have failed. When the pre-curing time increased to 72 h, the later-age resistance to freeze–thaw of specimens slightly improved, with the MLR and RDM of FAC-72-FT clearly lower and higher respectively than that of FAC-24-FT at the beginning of the freeze–thaw test. However, after 50 FTCs, the RDM of FAC-72-FT decreased rapidly and was only 38.1% at 100 FTCs; the MLR grew quickly after 50 FTCs. For SFC, the E-FTCs had some negative effect on its later-age resistance to freeze–thaw, especially for SFC-24-FT. The RDM of SFC-24-FT dropped sharply after 125 FTCs until the specimen was considered destroyed after 200 FTCs. For SFC-72-FT, its MLR was always lower than that of SFC-Control during the later-age freeze–thaw test. This is because the physical damage caused by FTCs might have increased the porosity of concrete, which increases water absorption and the mass of concrete. Up to 175 FTCs, the RDM of SFC-72-FT was above 90% and subsequently began to decrease rapidly. After 300 FTCs, the RDM of SFC-72-FT was 48.6%, which means this type of concrete can survive 275 FTCs during the later-age freeze–thaw test.

3.3.2 Frost resistance-DF

Figure 8 shows the comparison of DF of the three types of concrete subjected to E-FTCs. The DFs of OPC-Control, FAC-Control and SFC-Control were 98.1%, 35.0% and 77.4% respectively. Clearly, the DF of FAC-Control was markedly lower than those of the other types of concrete.

If specimens underwent E-FTCs, the DF would still reduce even if the restorative water-curing was carried out. It can be seen from Fig. 8 that the DFs of OPC specimens subjected to E-FTCs, so OPC-24-FT and OPC-72-FT, were both above 85%, and even that of OPC-72-FT was slightly higher than that of OPC-Control. However, the DFs of FAC-24-FT and FAC-72-FT were only 5.0% and 20%, respectively, which are significantly lower than those of OPC under the same conditions. From Fig. 8, it can be seen that the



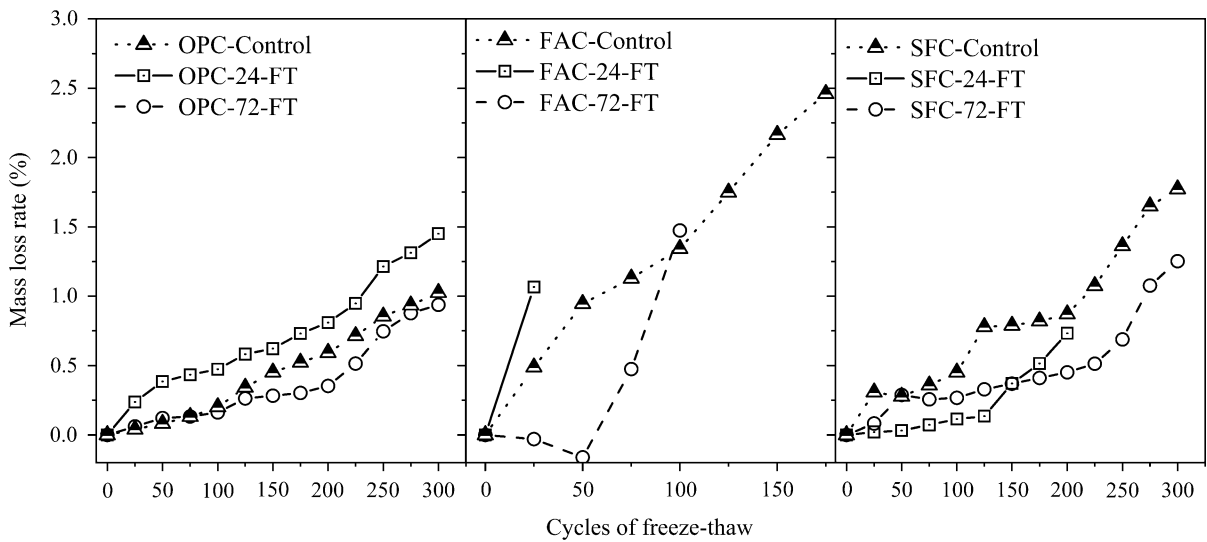


Fig. 6 Variations in MLR of three types of concrete subjected to E-FTCs

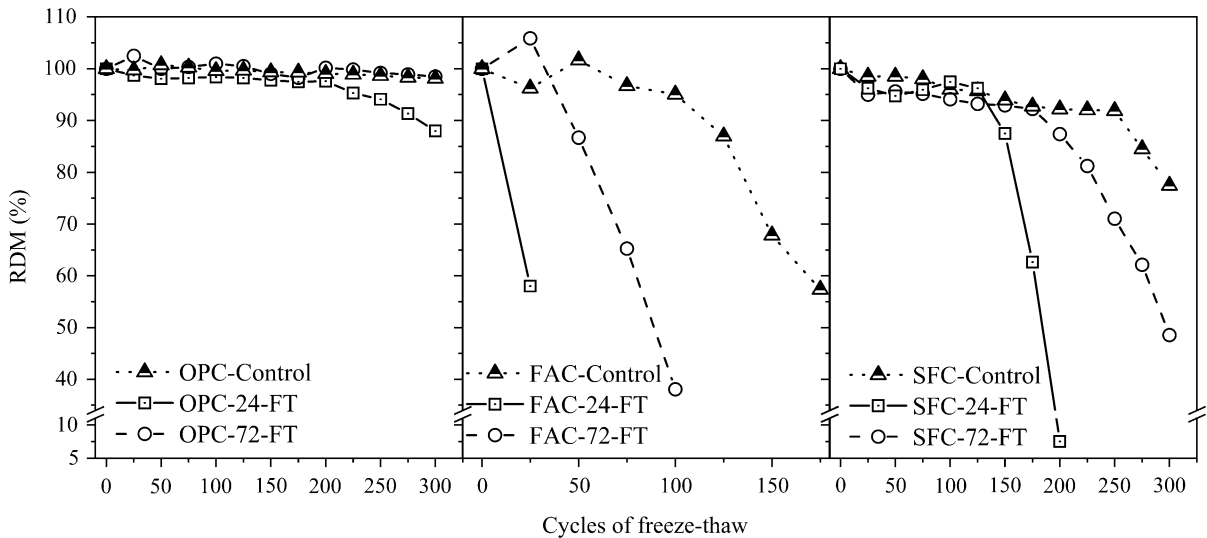


Fig. 7 Variations in RDM of three types of concrete subjected to E-FTCs

DF of SFC was also clearly lower than that of OPC, and was greatly influenced by the pre-curing time. When the pre-curing time was 24 h, the DF of SFC-24-FT was only 40%. However, for SFC-72-FT with a pre-curing time of 72 h, its DF increased to 60%, which means SFC-72-FT can withstand about 300 FTCs during the later-age freeze–thaw test. On the whole, the OPC with pre-curing times of 24 h and 72 h had better resistance to freeze–thaw than FAC and SFC, and better later-age DFs.

3.4 Discussion

3.4.1 Effect of mineral admixtures

Combined with the test results above, we can conclude that different types of concrete subjected to E-FTCs have markedly different mechanical and durability properties. In terms of early strength development of concrete, the cubic compressive strength of OPC and SFC increased to different degrees after being subjected to 10 E-FTCs regardless of the pre-curing time,

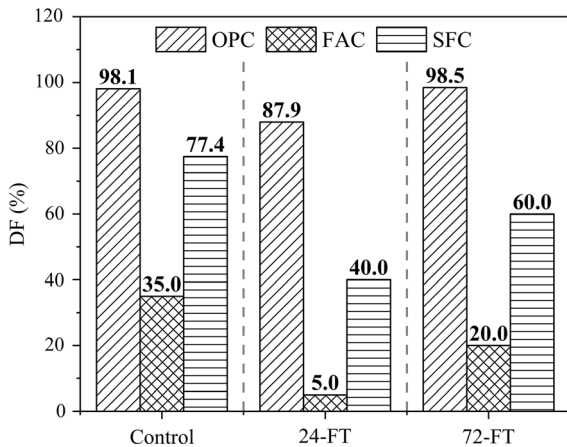


Fig. 8 DFs of the three types of concrete subjected to E-FTCs

while the compressive strength of FAC decreased when the pre-curing time was 24 h. For the later-age performance, generally, the incorporation of FA significantly reduces compressive strength and resistance to freeze–thaw of concrete, while the presence of SF has an adverse effect on the later-age resistance to freeze–thaw. Incorporation of FA and SF can reduce the chloride penetrability of concrete, but E-FTCs action can significantly increase the later-age chloride penetrability of FAC while has less effect for SFC.

The above experiment results are related to the frost resistance of the three types of concrete before being subjected to E-FTCs. Some studies pointed out the development of frost resistance in concrete at early-age is linked to the hydration progress [12] [36]. The difference in early hydration process of OPC, FAC and SFC, with the same materials and mix proportion as this study, was investigated in reference [37]. The change of the resistivity of concrete with curing age is similar to the heat of hydration, which means that early hydration process can be analyzed by the development of resistivity [38, 39]. Figure 9 shows the resistivity and its change rate of three types of fresh concrete from casting to the age of 72 h, and change rate of resistivity can reflect the hydration rate. The results clearly indicate that adding the FA significantly decreased the hydration rate before age of 36 h, and delayed the second hydration acceleration. However, addition of 5% of SF only slightly reduced the peak of hydration rate, and OPC and SFC had similar the development of hydration process. Although both FA and SF have pozzolanic material properties, the pozzolanic reaction of SF is higher than that of FA

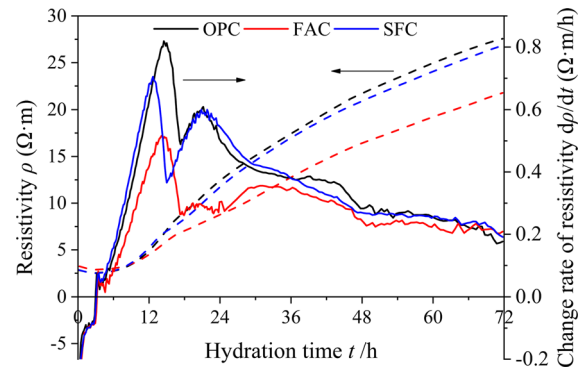


Fig. 9 Resistivity and its change rate of three types of concrete before E-FTCs [37]

due to its finer particles [40]. The main component of SF, silica, can react with calcium hydroxide, the hydration product of cement, to form C–S–H gel, thereby enhancing the bond between cement-based materials and aggregate and increasing the resistivity of matrix [25, 41]. The lower hydration rate of FAC cause the lower strength and resistivity compared with SFC and OPC [42, 43]. Especially when pre-curing time was 24 h, the compressive strength of OPC and SFC were both above 20 MPa, while that of FAC was only 15.8 MPa. Due to the lower strength, FAC is more likely to be damaged by the frost heaving stress and hydrostatic pressure during the E-FTCs. What's more, the electrical resistivity of concrete, as a comprehensive index of the resistivity of pore phase and solid phase, can reflect the changes of concrete microstructure and compactness [38]. The lower resistivity of FAC means the higher porosity and lower compactness, which makes the concrete pores more susceptible to saturation and more freeze–thaw damage occurs. Therefore, the serious damage occurs on the FAC, which suppresses the development of its compressive strength during the E-FTCs. On the contrary, due to the higher degree of hydration and better compactness of OPC and SFC at early-age compared to FAC, the damage suffered during E-FTCs is less.

After experiencing the E-FTCs, the strength and microstructure of concrete are further developed during the subsequent water-curing. This is because that E-FTCs with low temperature condition can reduce the hydration degree of the concrete, so that there are still some un-hydrated cement or mineral admixture particles in the hardened concrete [44].

E-FTCs action can not only damage the hydration products deposited on the surface of the un-hydrated clinkers, but also generate the micro-cracks inside concrete, which can make it easier for the water in the subsequent water-curing to reach the surface of the un-hydrated clinkers, thereby improving the hydration degree of the concrete [45, 46]. However, according to the macroscale performance data of concrete after 28 d mentioned above, it can be seen that on the whole, regardless of the types of concrete, the later-age performance of concrete subjected to E-FTCs was inferior to that of control specimens, especially the durability. The pore structure parameters measured by MIP test for three groups of SFC specimens at age of 28 d are listed in Table 5, and Fig. 10 shows their pore distributions in the pore size range of 5–10,000 nm. It can be seen that there was small difference in the total porosity between control concrete SFC-Control and the concretes subjected to E-FTCs, and the porosity of control sample was the lowest. However, the pores in the range of 5–200 nm were coarsened by the E-FTCs. The pores inside the cement-based materials can be classified according to pore diameter as harmless pores ($D < 20$ nm), less-harmful pores ($20 \text{ nm} < D < 50$ nm), harmful pores ($50 \text{ nm} < D < 200$ nm), and more-harmful pores ($200 \text{ nm} < D$) [47]. Compared with the SFC-Control sample, the pore volume of internal harmless pores of SFC-24-FT sample was significantly reduced and that of harmful pores was obviously increased; for SFC-72-FT sample, although the pore volume of internal harmful pores was similar to that of control sample, the pore volume of less-harmful pores was significantly higher while that of harmless pores was less than that of control sample. In addition, experiencing the E-FTCs increased the most probable pore diameter of concrete, which corresponds to the pore diameter at the peak point on pore distribution curve. It is indicated that E-FTCs can damage the microstructure of concrete sample, and this damage cannot be completely restored by subsequent water-curing after E-FTCs.

Among the three types of concrete, as mentioned earlier, the early frost ability of FAC was the worst, the damage of E-FTCs to sample was the most serious, so the most of damage cannot be restored by later-age water-curing, resulting in the significant difference in later-age compressive strength, resistance to chloride penetration and freeze–thaw between FAC-24-FT/ FAC-72-FT and FAC-Control. Due to the higher early

Table 5 Pore parameters measured by MIP for SFC samples at the age of 28 d

Group	Porosity (%)	Total pore volume (mL/g)	Pore volumes (proportions) of different pores (mL/g)						Most probable pore (nm)
			Harmless pore		Less-harmful pore		Harmful pore		
			5–20 nm	20–50 nm	200–10 ³ nm	10 ³ –10 ⁴ nm	10 ⁴ –10 ⁵ nm	More-harmful pore	
SFC-Control	11.90	0.06075	0.0183 (30.10%)	0.0208 (34.22%)	0.0121 (19.86%)	0.0025 (4.13%)	0.0021 (3.42%)	0.0050 (8.27%)	40.2
SFC-24-FT	12.35	0.06093	0.0109 (17.85%)	0.0140 (22.99%)	0.0232 (38.00%)	0.0036 (5.97%)	0.0044 (7.18%)	0.0049 (8.02%)	62.5
SFC-72-FT	12.39	0.06185	0.0113 (18.25%)	0.0233 (37.69%)	0.0157 (25.38%)	0.0029 (4.74%)	0.0023 (3.79%)	0.0063 (10.15%)	50.3



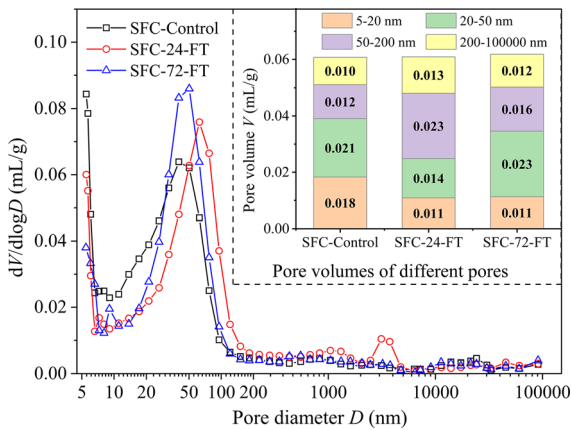


Fig. 10 Pore distributions for SFC samples at the age of 28 d by MIP

frost ability of OPC and SFC than FAC, the damage of E-FTCs to concrete was less, so more damage can be repaired with subsequent water-curing. Therefore, the OPC and SFC specimens subjected to E-FTCs have the more satisfactory later-age performance than FAC. However, it is remarkable that later-age resistance to freeze–thaw of SFC is not quite satisfactory, especially for SFC-24-FT. Other studies have shown that compared with OPC specimen, the addition of SF produced the higher compressive strength but the lower resistance to freeze–thaw exposure [25, 48]. This is because the incorporation of SF clearly reduces the workability of concrete due to its larger specific surface area of SF [49, 50]. Although a superplasticizer was used in this study, the workability of SFC was still significantly lower than that of OPC, making it easy to generate local pores with large sizes in the concrete. The presence of local pores does not greatly affect the compressive strength and resistance to chloride penetration, but it does have a significant adverse effect on resistance to freeze–thaw. Figure 11 shows the surface appearances of OPC-24-FT, OPC-72-FT, SFC-24-FT and SFC-72-FT after 300 FTCs. Note, as mentioned earlier, SFC-24-FT was deemed to have failed after 200 FTCs, so the surface appearances of SFC-24-FT at 200 FTCs was shown in Fig. 11. We can see that the peeling in OPC-24-FT and OPC-72-FT was uniformly distributed over the entire surface, while the severe surface peeling, cracking or aggregate detaching mainly were concentrated in a certain local area for SFC-24-FT and SFC-72-FT. Especially for SFC-24-FT, three visible and wide cracks extend

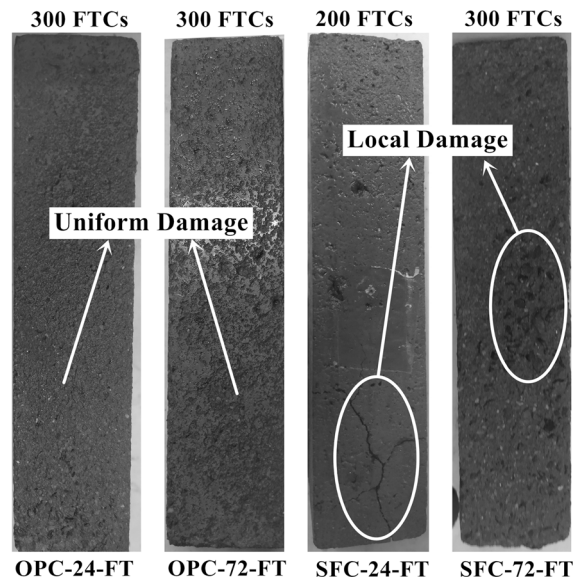


Fig. 11 Surface appearances of concrete subjected to E-FTCs during later-age FTCs test

outward from a certain local point. The occurrence of the local fatal damage may be the result of the local pores of the concrete being vulnerable to FTCs.

Moreover, the test results above show the use of FA and SF had a favorable effect on resistance to chloride penetration of concrete. This can be attributed to the particles of FA and SF being finer than those of cement [51, 52]. FA particles can fill and disperse into the internal pores of the structural matrix, hindering the transmission of chloride ions, so reducing the chloride penetrability [53, 54]. In addition, the presence of FA can increase the chloride binding capacity of concrete. This is because that the higher amount of alumina in FA can increase the amount of tricalcium aluminates which can react with chloride ions to form Friedel's salt, resulting in decreased free chloride ions [55]. Although the SF does not have good chloride binding capacity [56], its finer particles than FA can modify the microstructure and reduce the pore connectivity in concrete, resulting in the decreased chloride diffusion degree [55]. What's more, as mentioned earlier, the higher pozzolanic activity of SF can ensure that the ability to resist E-FTCs of SFC can be comparable to that of OPC, resulting in the less damage during the E-FTCs and then making the resistance to chlorine penetration easier to repair.

3.4.2 Effect of pre-curing time

The aforementioned test results also indicate that as the pre-curing time prolonged, the later-age mechanical and durability properties of the three types of concrete specimens subjected to E-FTCs improved to varying degrees. Especially for FAC, compared with the specimens with the pre-curing time of 24 h (FAC-24-FT), the improvement degree of three later-age performance indexes of the specimens with the pre-curing time of 72 h (FAC-72-FT) is very significant.

Previous studies suggested the critical point of capillary damming of concrete, where the coefficient of water permeability of concrete after the critical point can drop by two to three orders of magnitude, occurs at about the age of 24 h [57, 58]. Therefore, for the concrete with a pre-curing age less than 24 h, the specimen of higher permeability can absorb more water into the freezing pores during the E-FTCs and more serious damage caused by E-FTCs will appear. Prolonged pre-curing time before experiencing E-FTCs can increase strength and improve microstructure of the concrete, resulting in the higher ability to resist E-FTCs and the slighter freeze–thaw damage. From Fig. 10, we can find that when the pre-curing age increased from 24 to 72 h, the pore volume of harmful pores for SFC samples subjected to E-FTCs reduced from 0.023 mL/g to 0.016 mL/g, and the most probable pore diameter also decreased. As a result, the various performances of damaged concrete at later-age gradually improved with the increase of pre-curing age.

In addition, it can be seen from Fig. 9 that the hydration rate of the three types of concretes, OPC, FAC and SFC, enters a deceleration period controlled by ion diffusion after the age of 21.17 h, 31.25 h and 20.83 h, respectively [37]. It means that, for the FAC with a pre-curing of 24 h, the hydration is still dominated by interactions at phase boundaries and the internal microstructure has not been unconsolidated. As a result, if experiencing E-FTCs action at this stage, the concrete will suffer the serious destruction. Toutanji et al. [25] even found by experiment that concrete specimens containing 20% FA that were cured for 14 d have been damaged completely after only 30 FTCs. Therefore, for FAC, only by appropriately prolonging the pre-curing time and avoiding experiencing E-FTCs prematurely, can later-age

mechanical and durability properties meet the requirements.

3.4.3 RPs and correlations of later-age performance indexes for early-age frozen concrete

Based on the test results for the three types of concrete control specimens, the recovery percentages (RPs) for every experimental group of three later-age performance indexes, compressive strength, resistance to chloride penetration and resistance to freeze–thaw, were calculated using Eqs. (4), (5) and (6).

$$RP_{FC} = F/F_{\text{Control}} \times 100\% \quad (4)$$

$$RP_{RCP} = Q_{\text{Control}}/Q \times 100\% \quad (5)$$

$$RP_{RFT} = DF/DF_{\text{Control}} \times 100\% \quad (6)$$

where RP_{FC} , RP_{RCP} and RP_{RFT} are the RPs (%) of compressive strength, resistance to chloride penetration and resistance to freeze–thaw of experimental specimens respectively, F , Q and DF are the compressive strength value (MPa), chloride ion charge passed (C) and DF (%) of experimental specimens respectively, and F_{Control} , Q_{Control} and DF_{Control} are the compressive strength value (MPa), chloride ion charge passed (C) and DF (%) of the three types of concrete control specimens respectively.

When the pre-curing time of concrete was 24 h, from Fig. 12, there was a clear difference in the RPs of later-age performance indexes of the three types of concrete. In general, OPC had higher RPs than FAC and SFC. Although the RP of compressive strength for SFC-24-FT was as high as 101.6%, those RPs for resistance to chloride penetration and resistance to freeze–thaw were only 45.9% and 51.6% respectively. The RPs of later-age performance indexes of FAC-24-FT were lower than those of the other concretes, with resistance to freeze–thaw being only 14.3%. When pre-curing time increased to 72 h, the RP of later-age performance indexes of the three types of concrete improved to different extents, with little difference between OPC-72-FT and SFC-72-FT. This indicated that an increase in pre-curing time can reduce the adverse effects of E-FTCs on later-age performance of concrete. For FAC-72-FT, the RPs of later-age compressive strength and resistance to chloride penetration were both above 80%. Results shown in Fig. 12 also indicate that the RPs of compressive

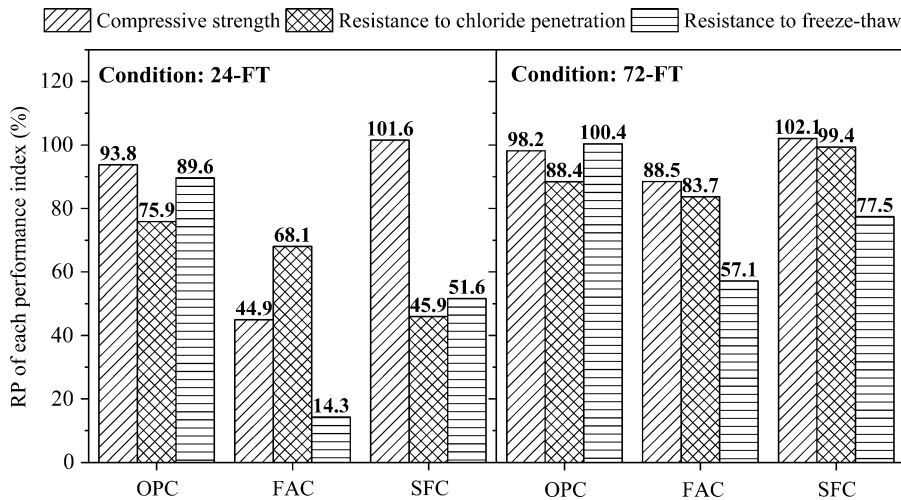


Fig. 12 RPs of each performance index of concrete subjected to E-FTCs

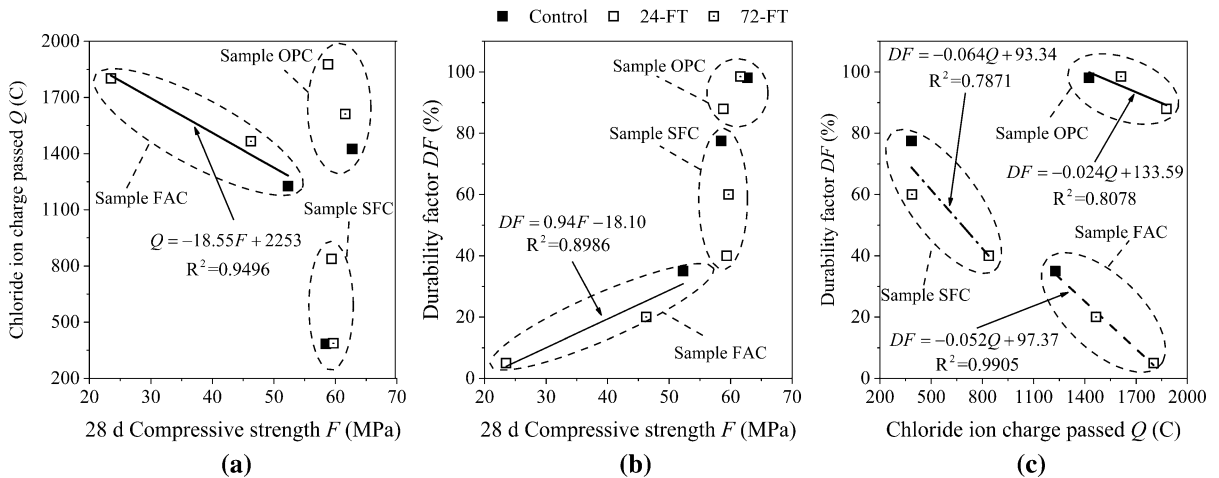


Fig. 13 Relationships between (a) F and Q , (b) F and DF , and (c) Q and DF of three types of concrete

strength of most experimental groups were higher than those of resistance to chloride penetration and resistance to freeze–thaw.

Figure 13 shows the relationships between F and Q , F and DF , and Q and DF of three types of concrete containing control and experimental specimens. It can be observed that for OPC and SFC, the 28-d strength only slightly changed after experiencing E-FTCs, but the durability indexes were significantly deteriorated. On the contrary, as for the FAC, after undergoing E-FTCs, the 28-d strength reduced significantly; correspondingly, its DF reduced and chloride permeability increased. This means that the change of its 28-d compressive strength for FAC can reflect the

change of its durability, but this is not applicable to OPC and SFC. Interestingly, it can be seen from Fig. 13(c) that the changes in the frost resistance factor DF of the three concrete specimens due to E-FTCs can be reflected by the chloride ion charge passed Q at 28 d, i.e., the resistance to chloride penetration. The linear equations between Q and DF for three types of concrete have also been given.

Results above indicate that, for concrete specimens subjected to E-FTCs, even though the later-age compressive strength can be recovered to an ideal level by restorative curing, the durability may not be adequate, especially the resistance to freeze–thaw. Choi et al. also found similar phenomenon [13]. The



pore structure of the concrete determines its strength and durability. Previous studies show that the strength of concrete is related to its total porosity and volume of large capillary pores [59, 60], while the freeze–thaw resistance and other durability depends on the volume of specific capillary pores [61]. In other words, compared with compressive strength, the resistance to freeze–thaw of concrete is more sensitive to the internal small capillary pores [62]. The pore information of three groups of SFC samples have demonstrated the viewpoint. As shown in Table 5 and Fig. 10, there was small difference in the total porosity and volume of more-harmful pores (> 200 nm) between the three samples, and the corresponding 28-d compressive strength was approximately the same. However, due to the E-FTCs, the pore structure in the range of 5–200 nm deteriorated, and the volume of harmful pores increased while that of harmless pores decreased. The DFs of SFC-24-FT and SFC-72-FT are 51.6% and 77.5% of SFC-Control, respectively, and their volumes of harmful pores (50–200 nm) are 1.92 times and 1.30 times that of SFC-Control, respectively. Noted the lower limit temperature of 17°C in later-age FTCs test can freeze the water existing within the pores with size of over 10 nm [63]. Therefore, repeating freeze–thaw action can damage such pores. It is inferred that the difference in later-age freeze–thaw resistance between frozen and unfrozen samples is closely related to the significant change in the volume of harmful pores inside the concrete. Although E-FTCs action does not have a significant adverse effect on the total porosity and volume of large pores of the concrete, it causes a significant increase in volume of harmful pores, which is the main reason for the decline in the late-age freeze–thaw resistance. Therefore, for the concrete expected to experience E-FTCs, it is particularly important to ensure its long-term durability meets requirements.

4 Conclusions

In this study, experimental investigations were carried out to compare the mechanical and durability performance of OPC, FAC and SFC subjected to E-FTCs by using compressive strength, chloride ion electric flux and rapid FTCs tests. The main conclusions are as follows:

- (1) The effect of using 5% SF on the development of compressive strength in concrete subjected to E-FTCs could be negligible. Regardless of the pre-curing time of the concrete, the compressive strength of OPC and SFC increased to different degrees after being subjected to 10 E-FTCs. However, for FAC, due to its weak microstructure and poor mechanical properties, the E-FTCs seriously hindered the increase of its compressive strength at early-age. After 10-E-FTCs, the compressive strength of FAC decreased when the pre-curing time was 24 h.
- (2) Pre-curing time of concrete and mineral admixtures significantly affected the properties of concrete subjected to E-FTCs. The earlier the E-FTCs, the poorer the later-age performance became. E-FTCs had a marginal effect on later-age performance of OPC. The use of FA and SF had a favorable effect on resistance to chloride penetration of concrete subjected to E-FTCs due to their physical filling effect. However, the incorporation of FA significantly reduced later-age compressive strength and resistance to freeze–thaw, and the presence of SF has an adverse effect on the later-age resistance to freeze–thaw. Mineral admixtures, especially FA with low pozzolanic activity, are not suitable for use in concrete structures expected to experience E-FTCs, where long curing times are essential.
- (3) In general, for concrete specimens subjected to E-FTCs, even though the later-age compressive strength can be recovered to an ideal level by restorative curing, the durability may not be adequate, especially the resistance to freeze–thaw. E-FTCs action does not have a significant adverse effect on the total porosity and volume of large pores of the concrete, but it causes a significant increase in volume of harmful pores (50–200 nm), which is the main reason for the decline in the late-age freeze–thaw resistance. Therefore, it is extremely important to ensure the recovery of durability of concrete subjected to E-FTCs.

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Declarations

Conflict of interest The authors declare that they have no conflicts of interest.

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