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Development of blast furnace slag mixtures against frost salt attack

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ABSTRACT

Carbonation is considered to be one of the most detrimental processes contributing to the frost salt attack deterioration of blast furnace slag (bfs) concrete. In this paper, the application of sodium monofluorophosphate (Na-MFP) as a curing solution or surface pre-treatment compound to improve frost salt scaling resistance of carbonated bfs mortar was studied. It was found that the treated specimens were more durable against frost salt attack than a conventional mortar with air-entrainment. The optimum mixture design can be achieved by using a suitable dosage of air-entraining agent, along with the Na-MFP application. The experimental results show that the optimized mixtures have an acceptable frost salt scaling durability that is comparable to the performance of ordinary Portland cement mixtures. The results obtained from a natural exposure confirm this healing phenomenon.

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1. Introduction

The use of blast furnace slag (bfs) in concrete industries is widely accepted, particularly in the northern European countries. From both environmental and economical points of view, bfs is a very attractive mineral admixture to use in concrete manufacturing, as a cement replacement material in concrete mixtures or as a raw material interground with Portland cement clinker to produce blast furnace slag cement. Concrete containing bfs is advisable in various applications, particularly in low heat concrete for massive structures. Apart from the low-heat application, the superior durability of bfs cement (BFSC) against aggressive environments make this cement a suitable binder for concrete exposed to chloride, acid and sulfate attacks.

There are several benefits of using bfs in concrete. However, as generally known, the calcium hydroxide (CH) content in BFSC concrete is drastically lower than that in ordinary Portland cement concrete. In the long-term, BFSC concrete tends to suffer more from carbonation attack due to its low alkalinity. Carbonation makes BFSC concrete more vulnerable to scaling under the combined load of frost attack and de-icing salts, when compared to ordinary Portland cement mixtures [1–7].

Sodium monofluorophosphate (Na_2FPO_3; referred to as *Na-MFP* in this paper) was initially used in the concrete industry as a surface applied corrosion inhibitor [8–11]. The mechanism is to protect the passive layer of the steel rebar against disruption due to carbonation. It is known that Na-MFP hydrolyzes into the pore solution to form PO_4^{3-} and F^-. These anions react with the certain components of the cement matrix to form fluorapatite ($Ca_5(PO_4)_3F$) and fluorite (NaF) which are highly insoluble compounds. It has been reported that the interaction produces amorphous analogues of apatite, and concluded that Na-MFP treatment modifies the transfer properties of the concrete [12]. Moreover, the treatment creates CaF_2 that has a very low solubility [9].

However, it has been recently found that Na-MFP has another benefit: improving the durability of bfs mixtures. Previous studies [13,14] showed that the application of Na-MFP treatment improves the frost salt scaling resistance of carbonated BFSC pastes, where the Na-MFP solution was used as a surface post-treatment compound on already carbonated BFSC mixtures. In general, the results show that the treatment modifies the mineralogical structures, and improves the resistance of carbonated BFSC concrete against frost salt attack. The technique is effective particularly for highly carbonated surfaces since a thick resistant zone can be created by the application.

It has been widely accepted since late 1940s that using an air-entraining agent is a standard practice to improve the resistance of concrete against frost attack. The empty fine air bubbles entrained in the matrix decrease the pressure created by the growth of ice crystal formation. In this study, the influence of Na-MFP application incorporating the utilization of an air-entraining agent (AEA) on the microstructure and frost salt scaling durability of mortars subjected to carbonation was studied. Different from previous works [13,14], the Na-MFP curing or surface pre-treatment was investigated in this study to see whether autogenous healing of carbonated BFSC concrete without requirement of any further

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external application is feasible. In practice, pre-treatment would be more convenient than a post-treatment process that has to be performed during the service life of the structure. Apart from the experiments with an accelerated scheme, the Na-MFP penetration rate and carbonation propagation into mortar under conventional exposure were also performed and compared. Finally, the scaling durability and microstructure of mortars exposed to natural environments was also investigated to confirm the healing mechanism.

2. Experimental investigation

2.1. Materials and preparation

A BFSC with a slag content of 67% by weight (CEM III/B 42,5 N HSR LH) and an ordinary Portland cement (CEM I 42,5 N) from an ENCI cement manufacturer were used. The typical chemical compositions and finenesses of the cements are given in Table 1. An air-entraining agent, *Cugla MMS con 17% LBV* produced by Cugla BV in the Netherlands, was used in this study. De-ionized water was used in the mixing process throughout the experiment, controlling the water-to-cementitious material (*w/cm*) ratio to be on the order of 0.45 by mass. All mixtures were designed based on a sand-to-cement ratio of 2.5 by mass. The mixing sequence was 2 min low speed followed by 2 min high speed mixing with a commercial Hobart mixer. The specimens were cast in plastic containers with 55 mm diameter and a height of about 50 mm. The filled containers were vibrated for 10 s on a vibrating table.

All specimens were cured and treated according to the schedule given in Table 2. It should be remarked that one control mixture made from ordinary Portland cement (CEM I 42,5 N) was also prepared for comparison, designated as mixture *PC*. Other specimens were prepared by using CEM III/B 42,5 N HSR LH . After 24 h, specimens were demolded and subsequently cured in water at a controlled temperature of 25 ± 2 °C for a 3 day period. For *BF00-C, BF03-C, BF07-C* and *BF10-C*, the specimens were cured in a 30% Na-MFP solution, while other mixtures were cured in ordinary tap water. It should be noted that those Na-MFP cured specimens (*BF00-C, BF03-C, BF07-C* and *BF10-C*) were exposed to identical curing and treatment programs. However, the mixture designs contained different air-entraining agent (AEA) dosages, which were 0%, 0.03%, 0.07% and 0.10% by mass of cement, respectively, to investigate the optimum dosage. These values have been chosen based on the advice of the AEA producer (Cugla BV, the Netherlands), where the recommended dosage ranges between 0.03% and 0.10% by mass of cementitious materials. The properties of fresh BFSC mortars with AEA addition are presented in Table 3.

After curing, all specimens were conditioned in a CO_2 free dessicator at 50–55% relative humidity. After 10 days of the conditioning process, the treatment was performed on the surface of *BF07-ST* by submerging into a 30% Na-MFP solution for 3 days. During the same period, other specimens were cured in de-ionized water instead of the Na-MFP solution. This process was essential to ensure identical pore saturation between surface treated and untreated specimens. *NB: BF07, BF07-C* and *BF07-ST* specimens were prepared from the identical mixture proportions, but exposed to different conditioning programs as demonstrated in Table 2. The notations "*-C*" and "*-ST*" indicate that the mortars were subjected to Na-MFP curing and Na-MFP surface treatment, respectively. Eventually, all specimens were exposed to laboratory air for a 14-day period. Before that, the circumference surface and the bottom area of specimens were coated with epoxy. The top trowel surface was only the area which was subsequently exposed to the environment.

Table 1
Properties of cements used in the experiment.

Properties	CEM I 42,5 N	CEM III/B 42,5 N
Chemical (%wt.)		
CaO (%)	63.9	45.0
SiO_2 (%)	20.9	27.6
Al_2O_3 (%)	5.5	12.2
Fe_2O_3 (%)	2.8	1.3
SO_3 (%)	3.3	3.3
Fineness (blaine) (m^2/kg)	315	376

Table 2
Mixture design and conditioning program.

Designation	Mix design		Curing	Treatment
	Type of cement	AEA dosage (%wt. cement)		
PC	CEM I	0	Water	Water
BF		0		
BF07		0.07%		
BF00-C		0	30% Na-MFP sol	
BF03-C	CEM III/B	0.03%		
BF07-C		0.07%		
BF10-C		0.10%		
BF07-ST		0.07%	Water	30% Na-MFP sol

Table 3
Properties of fresh mortars with AEA addition.

Mix	Unit weight (kg/m^3)	Air content (%vol.)
Fresh *BF03*	2156	9.4
Fresh *BF07*	2111	12.5
Fresh *BF10*	2040	18.5

Specimens were subjected to an accelerated carbonation environment with a carbon dioxide concentration of 3% by volume and a relative humidity of 65% for a period of 28 days. After the carbonation period, all specimens were sprayed with de-ionized water six times a day for 3 days. The purpose of this process is to imitate a real condition where the outdoor concrete has to be exposed to rain from time to time. The chemical reaction between Na-MFP and the products of carbonation would be increased with the presence of moisture within the pores of the specimens [14]. Eventually, specimens were bench-dried in laboratory conditions (∼45% R.H., 20–25 °C) for 28 days.

Apart from accelerated tests, carbonation propagation up to 1 year under natural atmospheric conditions was investigated on BFSC mortars in two different exposure conditions, namely indoor and outdoor (no shelter). Additionally, the rate of Na-MFP penetration into BFSC mortar (*BF07-C*) exposed to an outdoor environment (no shelter) for 10 months was evaluated.

2.2. Analysis and testing methods

2.2.1. Microstructure

The microstructure of mortars was studied by using an environmental scanning electron microscope (ESEM): *Philips XL30*, equipped with an EDS. The integrity of the samples was maintained by impregnation with a low viscosity epoxy under vacuum. The specimens were vertically sliced to a thickness of about 10 mm by a machine saw and dried in the oven at 35 °C until no further significant mass change. A DBT Diamond Roller and Grinder/86 thin sectioning unit were used for initial preparation of polished sections for the ESEM study. Finally, specimens were polished with 6 μm, 3 μm, 1 μm and 0.25 μm diamond pastes, respectively. Apart from microstructure, the profile of Na-MFP penetration was evaluated by determining the phosphorous content in the specimens. The EDS analysis was employed on the polished sections at a resolution of 0.317 μm/pixel (500× magnification). The results for phosphorous content were obtained from the average values of two measurements.

2.2.2. Frost salt scaling

A custom frost salt scaling test with 17 h in −20 °C freezing and then 7 h at 25 °C thawing cycles was used. The un-coated surface of mortars was facing downward submerged 5 ± 1 mm into the 3% NaCl solution (brine) during the test. The specimens were placed on plastic racks to allow free circulation of the salt solution. The scaled material was collected by using a dense filter paper after 2, 4, 7, 10, 12 and 15 cycles. Eventually, the filter paper with scaling material was oven-dried at 105 °C and weighted after 24 h drying. The scaling mass per unit area of exposed surface was calculated from the average value of two specimens.

2.2.3. Capillary water uptake

Mortar samples were placed in a similar fashion as in the frost salt scaling test. The specimens were placed on glass rods to allow free access to water. The specimens had to be weighed and returned to the water pond within 30 s in each investigation. Before weighing, the excess water on the surface was wiped off with a clean damp tissue paper. As the water penetration is mainly due to capillary suction, the clock has not been paused during the measurement. The weight change of specimens was monitored with respect to immersion time to determine the rate of water uptake per unit area of exposed surface.

2.2.4. Carbonation depth

As mentioned earlier, a set of BFSC mortar specimens was exposed to the environment in two different exposure conditions; namely indoor and outdoor (no shelter) for up to a period of 1 year to investigate the carbonation propagation under natural exposure. At 1, 6 and 12 months age, the samples were half-broken, and then the broken fresh surfaces were applied with phenolphthalein indicator (0.1 g phenolphthalein in 100 ml 95% ethanol). The color of the indicator turns pink when the pH is higher than nine, but will remain colorless at a lower pH, indicating a carbonated area. The carbonation depth was measured to the nearest millimeter.

2.2.5. Compressive strength

The compressive strength test was measured on *BF* and *BF00-C* mortars to investigate the influence of Na-MFP curing on the mechanical properties of bfs mixtures, particularly at early ages. It should be noted that the size of cube specimens used for compressive strength tests were rather small (20 × 20 × 20 mm). The reaction between hydration/carbonation products and Na-MFP takes place at the near surface area where the penetration of the compound and carbon dioxide would occur. Therefore, if there is any negative influence of Na-MFP submerged curing on the compressive strength, it would be pronounced on these small specimens. After following the program in Table 2, the mortar cubes were crushed to investigate the compressive strength at 4 and 28 days. The compressive strength results were obtained from the average of three specimens. It is known that carbonation attack alters microstructure, and decreases the matrix strength of mixtures rich in bfs. In this study, the compressive strength was also investigated on the mortars after carbon dioxide attack. The specimens were crushed after the accelerated carbonation periods of 14 and 28 days. Before testing, all carbonated specimens were submerged in water for 3 days. The mortar cubes were crushed in wet condition. It is true that frost salt performance can be influenced by many parameters. However, from a micromechanical view, the frost salt scaling resistance should be strongly related to the tensile strain capacity of the matrix. The results of compressive strength would indirectly reflect the tensile strength of these matrices.

3. Results and discussion

The photomicrographs of BFSC mortars exposed to the accelerated carbonation corresponding to the distance from the exposed surface are presented in Fig. 1. Generally, dark areas show the lowest total atomic value (epoxy) which indicates the porosity of the specimen, while the unreacted slag particles could be seen as light grey areas. Unhydrated clinker particles are even brighter. The dark circular areas in *BF07-C* represent the entrained air voids. It can be seen that carbonation induces severe shrinkage which leads to a coarsening of pores in the matrix, particularly on the control specimen (*BF*). This could be the result of the decomposition of C–S–H phases and formation of a porous silica gel according to the equation:

$$(\mathrm{CaO})_x \cdot (\mathrm{SiO_2})_y \cdot (\mathrm{H_2O})_z + x\mathrm{CO_2} \rightarrow x\mathrm{CaCO_3} + (\mathrm{SiO_2})_y \cdot (\mathrm{H_2O})_{z-w} + w\mathrm{H_2O} \quad (1)$$

The chemical reaction yields a reduction in volume of the matrix, due to carbonation shrinkage. In OPC paste systems, the carbonation of calcium hydroxide (CH) forms a more voluminous calcite that compensates for the pore volume increase due to porous silicate-hydrate formation (Eqs. (2) and (3)). With regard to OPC containing a low CH in CEM III/B paste (∼1–2% by weight [15]), the carbonation process produces a coarser and even weaker microstructure [16].

$$\mathrm{CO_2} + \mathrm{H_2O} \rightarrow \mathrm{H_2CO_3} \quad (2)$$

$$\mathrm{H_2CO_3} + \mathrm{Ca(OH)_2} \rightarrow \mathrm{CaCO_3} + 2\mathrm{H_2O} \quad (3)$$

The phenolphthalein test indicates carbonation depths of about 9 mm and 7 mm in *BF* and *BF07-C* specimens, respectively. The carbonation measurement results show that the treatment slightly decelerates the rate of carbonation. As seen in Fig. 1, in the deeper area where carbonation could not reach, the matrices show much denser structures. In comparison, the photomicrographs clearly reveal that the BFSC matrix was significantly damaged by the carbonation attack. However, it was also found that the Na-MFP curing obviously reduces the total porosity of the carbonated matrix, particularly at the area near to the surface. The pore size was significantly reduced. The difference in porosity between BF and BF07-C specimens becomes less as the distance from the exposed surface increases. It is assumed to be related to the penetration depth of the Na-MFP solution applied. At the depth of 7 mm, there is no obvious difference in the microstructure between *BF* and *BF07-C* specimens.

In Fig. 2a, intense coarsening of the pores can be observed at the interfacial transition zone (ITZ) between aggregate and matrix, when subjected to carbonation. It is seen that the damage was more serious than that within the bulk matrix zone. However, the ITZ has been improved due to Na-MFP curing as obviously seen in Fig. 2b. Under a high magnification (Fig. 3), sponge-like products can be observed around unreacted slag particles in the treated specimens. This formation would improve bonding between the particle and hydration products. This could be realized with the reactions of $\mathrm{PO_3F^{2-}}$, $\mathrm{PO_4^{3-}}$ and $\mathrm{F^-}$ with $\mathrm{Ca(OH)_2}$, $\mathrm{CaCO_3}$ or porous silica which possibly forms fluorapatite ($Ca_5(PO_4)_3F$) or carbonate fluorapatite ($Ca_5(PO_4,\mathrm{CO_3})_3F$) as well as some other unidentified amorphous formations [13]. Apart from the transformation of cement phases, the improvement of bonding between the unreacted particles and hydration products due to apatite formation would

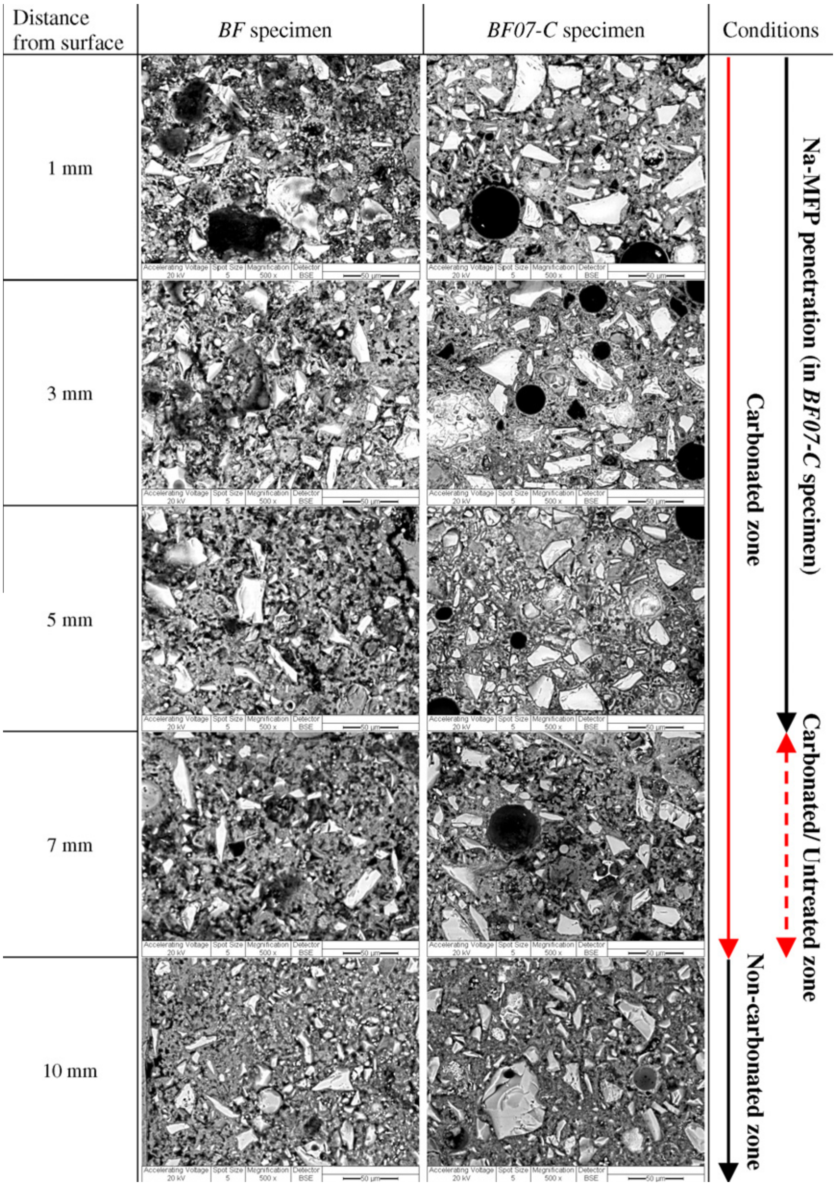
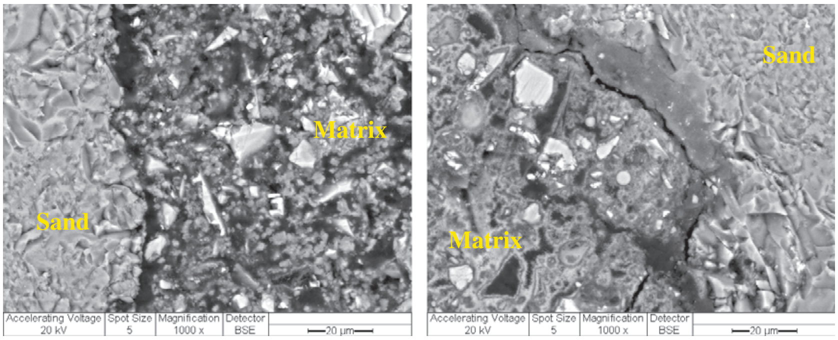


Fig. 1. Photomicrograph profiles of BFSC mortars subjected to accelerated carbonation.



(a) *BF* mortar (b) *BF07-C* mortar

Fig. 2. Interfacial transition zone of carbonated BFSC mortars.

be also another important factor which promotes the micromechanical properties of the carbonated BFSC matrix. No sponge-like products can be observed within the untreated specimens.

The EDS analysis on *BF00-C*, *BF07-C* and *BF07-ST* mortars consist of phosphorous and fluorine elements along with the existing Ca, Si, Al, Fe and S elements which are commonly found in cement-based

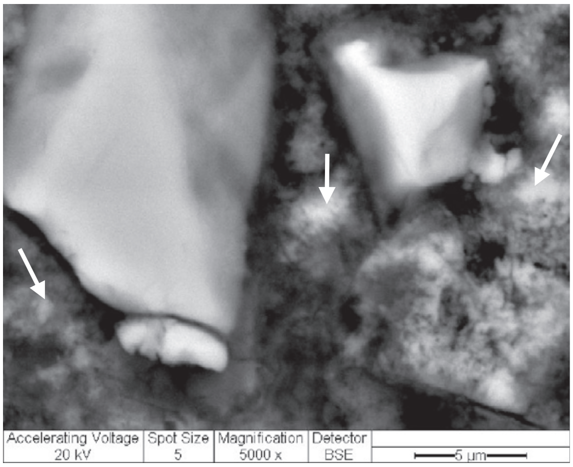


Fig. 3. Sponge-like products in carbonated *BF07-C*.

materials. The concentration profiles of phosphorous in the mortars were chosen as a criterion to determine the depth of Na-MFP penetration and are presented in Fig. 4. There was no significant difference in the penetration depth of Na-MFP in *BF00-C* and *BF07-C* specimens. Considering the nick point at about 2–4% concentration as a reference, the results show the penetration of the Na-MFP to a depth of about 5–6 mm. In this point of view, the entrained air does not play a role on the penetration of the Na-MFP into the specimens. A significantly shallower depth of penetration (about 3–4 mm) was observed on the *BF07-ST* mortar. In view of penetration, the results indicate that it would be more effective to introduce the Na-MFP solution during the first few days of specimen age, by means of curing. At these early ages, the ongoing chemical shrinkage will produce a significant imbibition of curing solutions, thus increasing the penetration depth.

Comparing the Na-MFP penetration profile of *BF07-C* to the microstructures in Fig. 1, it can be observed that the carbonation depth progressed beyond the penetration depth of the applied Na-MFP. Hence, the photomicrograph of *BF07-C* shows a significant pore coarsening which is not different than that of the untreated control (*BF*) at this particular depth (7 mm). In the accelerated carbonation scheme, the diffusion of gaseous CO_2 into mortars can be accelerated; however, the penetration rate of Na-MFP was not. Therefore, it is necessary to clarify a potential of healing ability by comparing the carbonation rate and also the Na-MFP penetration rate under the conditions of a natural exposure.

The penetration depth profiles of Na-MFP into the *BF07-C* specimen exposed to a natural environment (outdoor – no shelter exposure) represented by the concentration of phosphorous are demonstrated in Fig. 5. The concentration was obtained from the average value of two measurements. The absolute error of measurement is within ±0.8%. It is seen that the Na-MFP compound increasingly penetrated corresponding to the exposure time. Assuming the nick point at about 2–4% concentration as a reference, the penetration depths were estimated to be about 5.5, 7, 8.5 and 10 mm for 1, 2, 5 and 10 month exposures, respectively. Compared to the results of carbonation depth in Fig. 6, it is likely that the carbonation depth always lags behind the penetration front of Na-MFP applied. Hence, the carbonated/untreated zone could not appear under the natural exposure condition. Particularly for the outdoor exposure specimens, the margin between Na-MFP penetration front and carbonation depth was considerable. It should be remarked that the results of carbonation depth propagation in Fig. 6 were investigated on the untreated mortars. From the accelerated carbonation test, it was found that the carbonation depth of treated mortar was lower than the control which could be due to the formation of apatite-like products and the reduction of porosity in the matrix. In practice, it might be possible that Na-MFP treatment may decelerate the rate of carbonation.

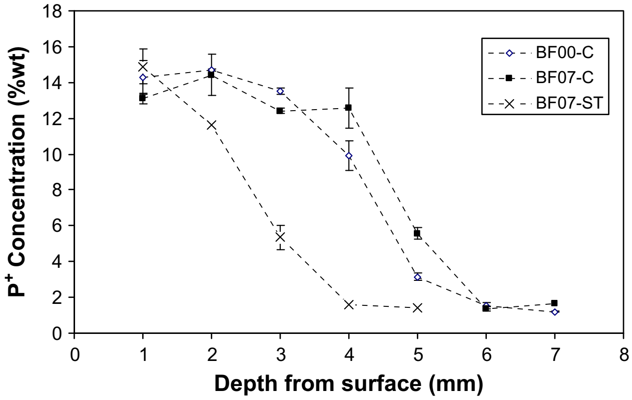


Fig. 4. Penetration depth of Na-MFP solution determined by EDS.

Fig. 7 shows the frost salt scaling performance of Na-MFP cured mortars with different amounts of AEA dosages. Initially, the objective of this set of mixtures was to investigate the optimum dosage of the AEA used in this study. The results indicate that *BF07-C* showed the best frost durability performance. Hence, for the air-entrained specimen with normal water curing (*BF07*) and also

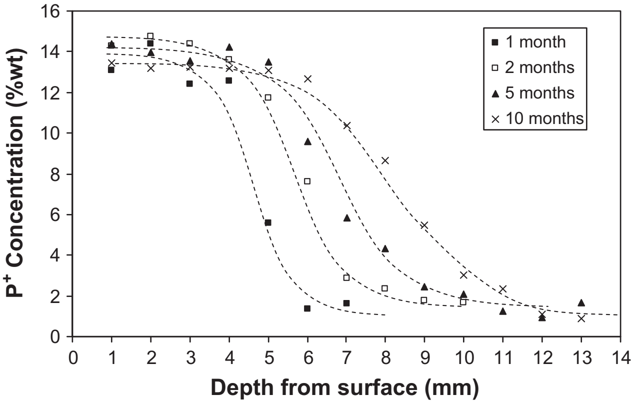


Fig. 5. Penetration depth of Na-MFP solution under long-term outdoor exposure.

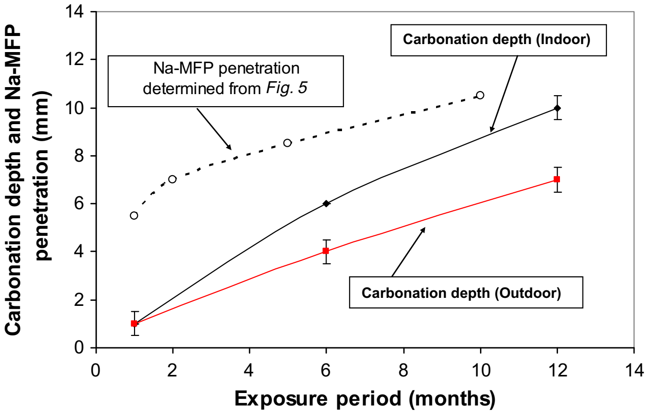


Fig. 6. Carbonation depth of *BF* specimen under indoor and outdoor natural exposure.

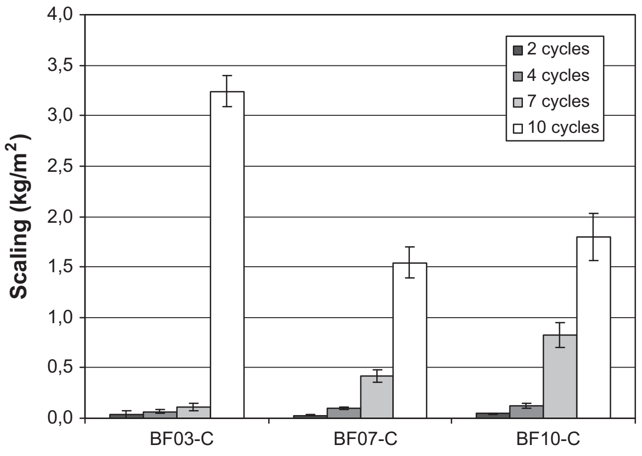


Fig. 7. Influence of AEA dosage on frost salt scaling performance.

the air-entrained specimen with Na-MFP surface treatment (*BF07-ST*), the mixtures were designed based on this dosage value (0.07% by mass of cement) for comparison. It has to be noted that the initial scaling of *BF03-C* was rather low. There is no clear explanation for this phenomenon. A possible hypothesis is that the mortar with a low AEA dosage (*BF03-C*) would have a higher compressive (and also tensile) strength than the higher AEA dosage mixtures. The tensile strength of the matrix may play a role on frost salt scaling resistance during the first few cycles. After seven cycles, however, the scaling mass of *BF03-C* was substantially increased. In the long term, the effect on the scaling durability would be dominated by the entrained air pore system.

Fig. 8 presents the frost salt scaling of Na-MFP cured/surface treated mortars compared to the reference *PC* and *BF* mixtures. It is seen that *BF* mortar without any treatment was severely damaged by frost attack. The scaling results of *BF07* show the benefit of entrained air on frost salt scaling durability. The scaling mass of *BF07* was significantly decreased compared to the control *BF*. However, the Na-MFP cured mortar (*BF00-C*) performed even better than did *BF07*. For the air-entrained mortars which were cured or treated by Na-MFP solution (*BF07-C and BF07-ST*), the specimens showed the best performance against frost salt scaling, comparable to the *PC* specimen.

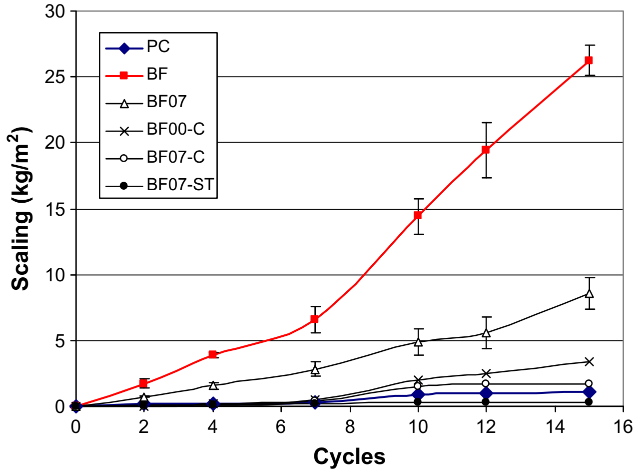


Fig. 8. Frost salt scaling performance.

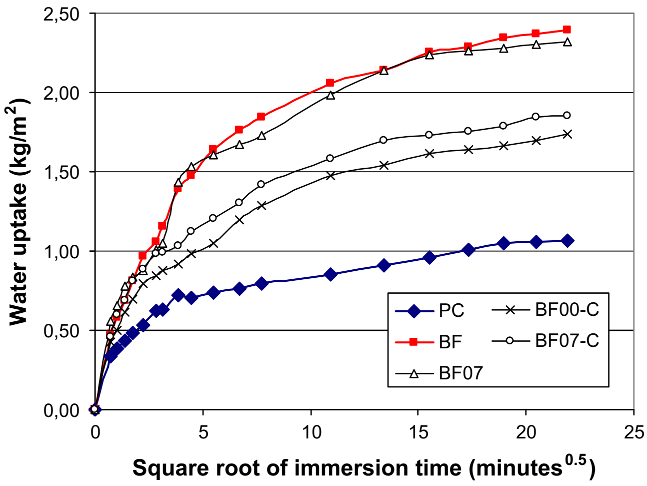


Fig. 9. Capillary water uptake of carbonated mortars.

Fig. 9 compares the amount of capillary absorbed water penetrating into carbonated *PC* and *BF* mortars as well as carbonated BFSC specimens with Na-MFP curing. The result was obtained from an average of two specimens. The absolute error of measurement is within ±0.1 kg/m^2. The results indicate that the *BF* mortar yielded the highest water uptake, while *PC* was the lowest. This could be due to the fact that carbonation attack on bfs specimens induces a significant coarsening of the pore structure. On the other hand, the plentiful amount of CH in OPC would create calcite as a carbonation product. After the carbonation product has formed, it would be possible that the OPC mixture will become even denser compared to the original non-carbonated condition. It could then be expected that the mortars cured in Na-MFP (*BF00-C and BF07-C*) would have lower capillary absorption than the control *BF*. As obviously seen in the micrographs presented earlier, the Na-MFP curing plays an important role in the reduction of pore coarsening due to carbonation attack. Consequently, the quality of Na-MFP cured mortars in terms of transport properties would be also improved. However, it would be remarked that the outcome of this experiment was particularly relevant to the change of solid volume upon Na-MFP application, which was an alternative way of assessing the surface mechanical quality. However, it should be emphasized that since the water uptake and internal ice formation are not likely to have an influence on the amount of surface scaling [17], an increase in water uptake was of interest only as an indication of a smaller solid phase portion and a lower surface strength.

It has been reported in a previous study [14] that the Na-MFP treatment does not reduce the pore coarsening significantly, particularly when the Na-MFP solution has been applied prior to carbonation attack. However, this finding would be due to the reason that the specimens were conditioned and stored in laboratory air which has a low relative humidity. The lack of moisture would cause an inefficiency of the apatite and fluorapatite formations, since they are both through-solution reactions. In the absence of a water supply, i.e. indoor concrete, the Na-MFP may not efficiently react with carbonation products. Hence, the marginal reduction of porosity should not be expected. Nevertheless, this may not be a common situation in practice that the indoor concrete which is exposed to an arid environment would be concerned with water penetration and frost salt scaling problems. In a recent study, experiments took into account the fact that outdoor concrete has to be exposed to rain from time to time. Therefore, the specimens in this study were sprayed with water after accelerated carbonation exposure to simulate this condition. As seen in Fig. 1, the pore structure of treated specimens was reduced drastically. It would be possible to claim that in the real situation where the outdoor concrete has to be exposed to rain from time to time, the Na-MFP curing/pre-treatment would reduce pore coarsening as observed in the accelerated test.

Fig. 10 demonstrates the compressive strength of bfs mortars before and after carbonation attack. No difference in the early-age strength (4 days) was observed. At 28 days, however, the results indicate that the mortar cured in Na-MFP solution (*BF00-C*) shows slightly lower compressive strength than the control (*BF*). The results indicate that Na-MFP slightly retards the hydration reactions. A possible hypothesis would be due to the decreased dissolution rates of various ions into the alkaline pore solution. After Na-MFP has hydrolyzed into the pore water, the formation of PO_4^{3-} and F^- would delay the dissolution rate of Ca^{++} from clinker and retard the formation of C–S–H. Nevertheless, the benefit of Na-MFP curing on the compressive strength can be observed after carbonation attack. Carbonation reduced the strength of the control mortar significantly. With Na-MFP curing, however, *BF00-C* mortar revealed a further development of compressive strength after carbonation. Eventually, after 28-day carbonation, *BF00-C* shows a higher compressive strength than the untreated control by more than 10 MPa. The improvement of mechanical properties could explain the excellent frost salt scaling durability of Na-MFP cured/surface treated specimens since surface scaling durability is directly related to these parameters. Moreover, the compressive strength result at early-age indicates that there is no negative effect of Na-MFP curing on the hydration of BFSC.

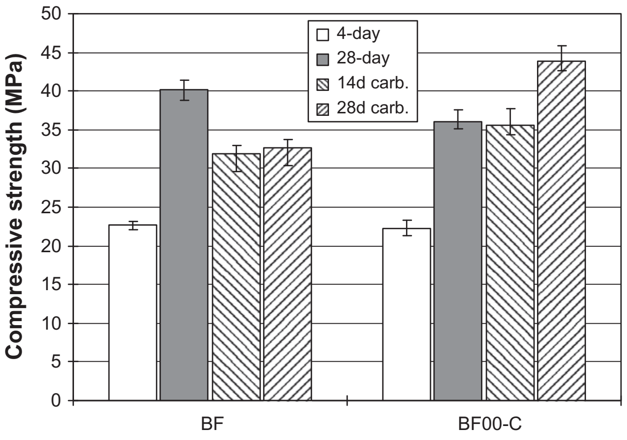
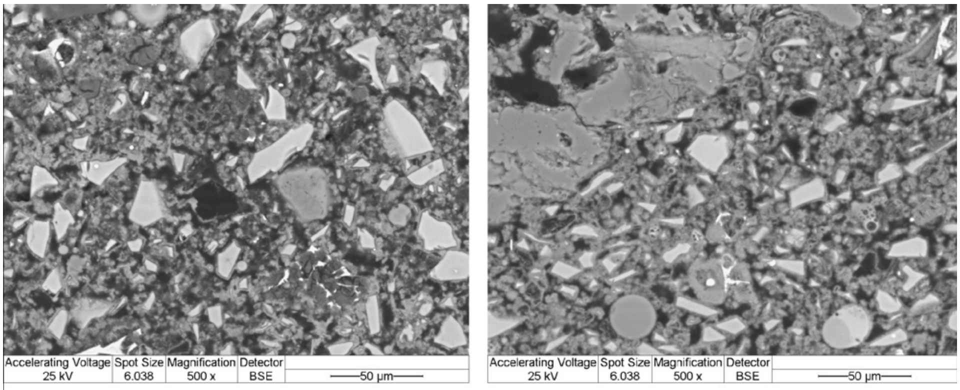


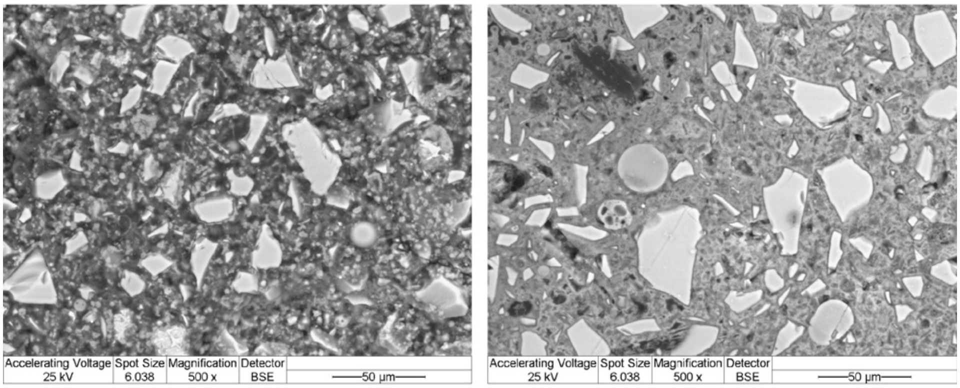
Fig. 10. Compressive strength of carbonated mortars.

Though the results from accelerated carbonation tests indicated that the healing ability is promising, it is necessary to confirm the healing phenomena under natural exposures. Another set of non-entrained air BFSC mortars obtained from a previous study [14] was used for this analysis. After surface pre-treatment by 10% Na-MFP solution, the specimens were exposed to the natural exposure for 1 year in two different environments which are indoor and outdoor (*no shelter*). Fig. 11 shows the microstructures of these specimens at the depth of 3 mm from the exposed surface. It is obviously seen that the treated specimen exposed to an outdoor environment (Fig. 11d) has a significantly denser microstructure than the untreated one (Fig. 11c). However, the porosity reduction is not clearly visible on the treated specimen exposed to an indoor environment (Fig. 11b). There is no obvious improvement



(a) Untreated- *Indoor exposure*

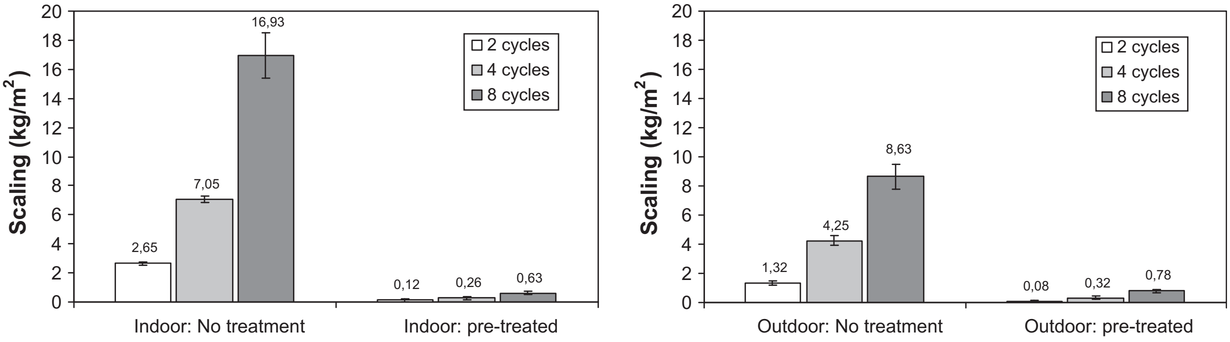
(b) Pre-treated- *Indoor exposure*



(c) Untreated- *Outdoor exposure*

(d) Pre-treated- *Outdoor exposure*

Fig. 11. Microstructure of BFSC mortars after 1 year natural exposure.



(a) Indoor exposure (b) Outdoor exposure

Fig. 12. Frost salt scaling performance of 1 year natural exposure specimens.

compared to the control (Fig. 11a). As mentioned earlier, the lack of moisture for the indoor specimen may cause an inefficiency of the apatite formations.

Fig. 12a and b presents the scaling mass due to frost salt attack of the indoor and outdoor natural exposure specimens, respectively. The results indicate that the treated specimens from both indoor and outdoor natural exposure reduced the frost salt scaling. Unlike the pore coarsening, it should be remarked that it is not only the outdoor specimen but also the indoor exposed mortars that show potential to reduce the frost salt scaling to a comparable extent. A possible hypothesis is that the apatite products can be formed in a very short period of time. When the treated specimen was immersed into the salt solution for the frost salt scaling test, the formation of apatite and fluorapatite can rapidly take place with the concurrent supply of external moisture. Hence, the frost salt scaling durability and microstructure have been improved accordingly.

Within eight cycles of testing, there is no visible different in the performance between indoor treated and outdoor treated mortars. To observe the long-term behavior, a longer period of scaling test is required in future studies. Regarding the results in this work, both Na-MFP pre- and post-treatment methods are promising to prevent frost salt scaling problems for cementitious materials rich in slag. However, in practice, the methods of Na-MFP curing or pre-treatment performed during the construction period would be more convenient than the surface post-treatment which has to be performed during the service life of the structure. Considering curing as a part of concrete manufacturing, the Na-MFP curing methods would enable autonomous healing of BFSC mixtures during the course of carbonation, without the requirement of any further external application.

4. Conclusions

The potential of using Na-MFP as a curing solution or surface treatment compound for BFSC mortars against frost salt scaling was studied. After carbonation attack, it was found that the microstructures of the treated mortars have been significantly improved compared to the untreated control. The EDS measurements showed a progressive penetration of the compound corresponding to the exposure period. With Na-MFP treatment, the pore coarsening of the carbonated matrix was considerably reduced, and the quality of the ITZ between sand and matrix was improved. The capillary water uptakes of treated specimens were decreased. Under outdoor natural exposure, the EDS results indicated that the Na-MFP penetration rate is faster than the rate of carbonation. The mortars with entrained air incorporating the Na-MFP treatment showed significantly better frost salt scaling performance compared to the control. The performances were also better than the mortar with entrained air only. It should be remarked that AEA has a role to decrease the internal stress due to ice crystal formation, while Na-MFP curing improves the micromechanical properties of the matrix. The results from compressive strength tests indicate no significant negative effect of Na-MFP curing on the early hydration of BFSC. Finally, experiments on the natural exposure program have confirmed the healing phenomena of Na-MFP on carbonated BFSC mixtures.

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