

Properties of carbonated blast furnace slag mortars after Na_2FPO_3 treatment

Kritsada Sisomphon*, O. Çopuroğlu, A.L.A. Fraaij

Faculty of Civil Engineering and Geosciences, Delft University of Technology, Delft, The Netherlands

*Corresponding author, e-mail: k.sisomphon@tudelft.nl, sisomphon@hotmail.com

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ABSTRACT: This project studies the application of sodium monofluorophosphate (Na-MFP) solution as a surface applied compound for carbonated blast furnace slag mortar treatment against frost salt scaling. A 10% Na-MFP solution was applied on the surface of specimens, and microstructure and frost salt scaling performance were investigated. The results from electron microscopy and nano-indentation showed that the Na-MFP treatment improves the quality of the microstructure and reduces the pore coarsening of the matrix phase. A denser interfacial transition zone can be observed after the treatment. Frost scaling durability of carbonated blast furnace slag mortar has been significantly improved. This method of pre-treatment, which can be applied to the concrete surface during the construction period, would result in the concrete being able to self-heal without the need of a further application later.

KEYWORDS: carbonation, frost salt scaling, ground granulated blast furnace slag, Na-MFP

INTRODUCTION

Blast furnace slag cement (BFSC) concrete is used extensively, particularly in northern European countries. In the Netherlands, BFSC has a market share of more than 50%. From both environmental and economical points of view, blast furnace slag (BFS) is a very attractive mineral admixture to use in concrete, particularly in low-heat concrete for massive structures or in high performance concrete. Apart from the low-heat application, the superior durability of BFSC against aggressive environments makes this cement a suitable binder for concrete exposed to chloride, acid, and sulphate attacks. However, one of the disadvantages of BFS concrete is its poor resistance against carbonation. After carbonation attack, BFS concrete is vulnerable to scaling under the combined load of freezing-thawing and de-icing salt. Owing to surface disintegration, other attacks on the structure are more likely which can result in a dramatic decrease in durability.

The application of sodium monofluorophosphate (Na_2FPO_3 ; referred to as Na-MFP from this point on) as a surface-applied corrosion inhibitor has been widely studied¹⁻⁵. The mechanism is to protect the passive layer of steel rebar against disruption due to chloride and carbonation. It is known that Na-MFP hydrolyses into pore solution to form P_4^{3-} and F^- . These anions react with certain components of the cement matrix to form fluoroapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) and

fluorite (NaF) which are highly insoluble compounds.

Complex interactions take place between Na-MFP and hardened Portland cement (OPC) paste components, especially $\text{Ca}(\text{OH})_2$, producing an amorphous gel and modifying the transport properties of the concrete⁵. However, Na-MFP applied treatment as a surface agent on both chloride-induced and carbonation-induced corrosion leads to a gradual decrease in the corrosion rate³.

It has been recently found that Na-MFP has another benefit, namely, it improves the frost salt scaling resistance of carbonated BFSC pastes⁶. A 10% Na-MFP solution was used as a surface post-treatment compound on carbonated BFSC paste in the study in Ref. 6. The results showed that the treatment modifies the mineralogical structure and improves the resistance of carbonated BFSC paste against frost salt attack. The technique is effective particularly for a highly carbonated surface since a thick resistant zone can be created by the application.

In this study, the effect of carbonation on the properties of BFSC mortars was investigated. The influence of Na-MFP application on microstructure and frost salt scaling durability of carbonated specimens was evaluated. The Na-MFP pre-treatment, which is an application on the surface of specimens before carbonation attack, was also analysed in this study.

MATERIALS AND METHODS

Materials and preparation

A BFSC with a slag content of 67% (CEM III/B 42,5 N HSR LH) from ENCI cement manufacturer was used. Two types of specimens, cement paste and mortar, were prepared in this study. De-ionized water was used in mixtures throughout the experiment. Pastes and mortars with a water-to-cement ratio of 0.45 were used for the analysis. For mortar, the mixture was designed with the sand-to-cement ratio of 2.5 by weight. Most experiments were performed on mortars, except the nano-indentation which was analysed on paste specimens. In the mixing process, the 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 to a height of about 50 mm. The containers were vibrated for 15 s on a vibrating table. In the case of cement paste, the containers were then rotated at a speed of 5 rpm for 24 h to prevent segregation. This rotating process is not necessary for mortar specimens. After 24 h, the specimens were cured in tap water at $25 \pm 2^\circ\text{C}$ for 3 days. The specimens were then pre-conditioned in a CO_2 free desiccator at 50–55% relative humidity for 28 days. After that, the circumference surface and the bottom area were coated with epoxy. The top trowel surface was exposed to the environment.

After pre-conditioning, the specimens were carbonated and treated according to the schedule shown in Table 1. The Na-MFP treatment was applied either before or after carbonation attack which was designated as pre-treatment (Pre) and post-treatment (Pos), respectively. A non-carbonated specimen was also prepared as the control for comparison where the specimens were stored in a CO_2 free desiccator throughout the exposure program. For the Pre-treatment series, the 10% Na-MFP solution was applied on the surface of the specimen 6 times a day by means of a paint brush. De-ionized water was sprayed on the treated surface after each Na-MFP treatment to promote the penetration of solution into the specimen. The treatment period was 4 days (24 treatments in total). The untreated control samples received de-ionized water instead of Na-MFP solution. This process was necessary to ensure identical pore saturation of treated and untreated specimens. The specimens were designated as Pre-M and Pre-W for the pre-treated specimen and untreated control, respectively. Thereafter the specimens were conditioned in laboratory air for 28 days. The specimens were later exposed to accelerated carbonation (carbon dioxide concentration

of 3% by volume, with 65% relative humidity) for 28 days.

For Pos-treatment series, the specimens were exposed to accelerated carbonation immediately after pre-conditioning process for 14 days. After that, the Na-MFP treatment was applied to the surface of the specimen in the same way as for the pre-treatment series. The Pos-M was referred to as the post-treated specimen, while Pos-W is the untreated control. The specimens were then stored in laboratory air for 28 days. Finally, the mortars were exposed to the second period of accelerated carbonation for another 14 days.

Testing methods and analysis

The frost salt scaling test we conducted conformed to the ASTM C672 freezing-thawing cycle. It consisted of 17 h in -20°C and 7 h at 25°C . The uncoated surface of the mortars was placed facing downwards submerged in 3% NaCl solution which was maintained at a level of about 5 mm above the specimen surface during the cycles of freezing and thawing. The specimens were placed on a plastic rack to allow free circulation of the salt solution. The scaled material was collected by using filter paper after 3 and 5 cycles. The scaled material was then dried in an oven at 105°C and weighted after 24 h of drying.

The microstructure of the mortars was studied by using an environmental scanning electron microscope (ESEM, Philips XL30) equipped with EDX detector. The specimens were vertically cut to a thickness of about 10 mm by a machine saw and dried in the oven at 35°C until no further significant weight change was observed. Low viscosity epoxy was used to maintain the integrity of the samples. A DBT diamond roller and a thin sectioning unit were used to prepare perfectly smooth ESEM specimens. The specimens were then polished with 6 μm , 3 μm , 1 μm , and 0.25 μm diamond pastes.

The porosity of mortars was determined from the backscatter electron (BSE) image by means of image analysis. To identify the carbonated zone, the carbonation front can be visualized by spraying phenolphthalein indicator on fresh broken surface. It is generally known that the dark areas in BSE photomicrographs represent pores. Other solid products show lighter shades. The threshold grey-level between porosity and solid cement phases was identified by a technique based on the shape of the histogram of the BSE image. The threshold grey-level for pores was manually determined from the inflection point of the brightness histogram. According to the principle of stereology, the fractional area of BSE in 2D cross-

Table 1 Treatment and exposure program after 28-day pre-conditioning.

Series	Notation	Treatment and Exposure Description			
Non-carbonated Control	NC	CO ₂ -free storage (60 days)			
Pre-treatment	Pre-M	Na-MFP treatment (4 days)	CO ₂ -free storage (28 days)	Acc. carbonation (28 days)	
	Pre-W	Water treatment (4 days)	CO ₂ -free storage (28 days)	Acc. carbonation (28 days)	
Post-treatment	Pos-M	Acc. carbonation (14 days)	Na-MFP treatment (4 days)	CO ₂ -free storage (28 days)	Acc. carbonation (14 days)
	Pos-W	Acc. carbonation (14 days)	Water treatment (4 days)	CO ₂ -free storage (28 days)	Acc. carbonation (14 days)

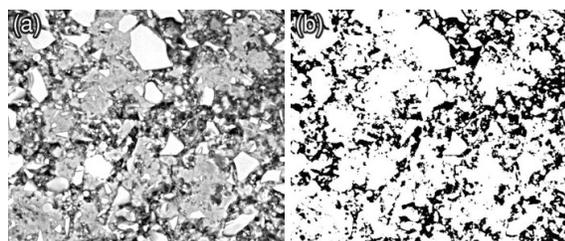


Fig. 1 Determination of porosity from BSE by image analysis: (a) original BSE image; (b) pore segmentation in which black areas represent porosity.

sectional views can be assumed to represent 3D volumetric fractions in a porous specimen. As presented in Fig. 1, the porosity was evaluated by the percentage of dark domain to the total area in the photomicrograph following a well-known image analysis technique^{7,8}. To investigate the penetration depth of the Na-MFP into specimens, EDX analysis was employed on the polished sections at a resolution of 0.317 μm/pixel (500 × magnification).

Nano-indentation was used in this study for measuring the modulus of elasticity of microscopical phases of the materials. With the technique developed in Ref. 9, this facilitates the measurement of properties at the micro- and nano-scale. The mechanical properties at the nano-scale can be determined from indentation load and displacement measurement. To prepare specimens, the carbonated paste specimens were horizontally cut to a thickness of about 5 mm. Thereafter, grinding and polishing were done in the same way as for mortars for ESEM but with no epoxy impregnation. The investigation was performed on the top trowel surface of the specimen. The modulus of elasticity can be calculated from

$$E_s = \frac{1 - \nu_s^2}{1/E_r - (1 - \nu_i^2)/E_i}$$

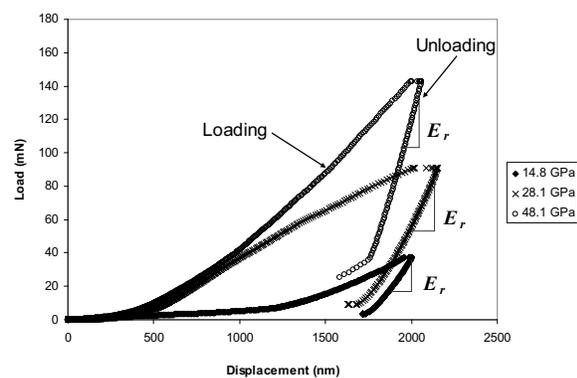


Fig. 2 Typical load-displacement curve showing the determination of E_r .

where E_r is the reduced elasticity modulus which can be obtained from the slope of unloading curve (Fig. 2), ν_s is the Poisson's ratio of the sample, ν_i is the Poisson's ratio of the indenter (~ 0.07), E_s is the modulus of elasticity of the sample, and E_i is the modulus of elasticity of the indenter (~ 1141 Gpa)⁹.

RESULTS AND DISCUSSION

The photomicrographs of carbonated BFSC mortars corresponding to the distance from carbonated/treated surface are presented in Fig. 3. The results from conventional phenolphthalein test indicated carbonation depths of 4 mm, 4 mm, and 7 mm for Pre-W, Pre-M, and Pos-M, respectively. Generally, dark areas show the porosity while the unreacted slag particle can be seen as light grey areas. Unreacted clinker particles are even lighter. It is clearly seen that carbonation induces severe shrinkage which leads to coarsening of pores in the matrix. This is the result of the decomposition of C-S-H phases and the formation of porous silica gel. The chemical reaction reduces the volume of the matrix and so results in substantial carbonation

shrinkage. In the OPC paste system, the carbonation of $\text{Ca}(\text{OH})_2$ forms calcite which compensates for the pore volume increase due to porous silica formation. However, due to a low $\text{Ca}(\text{OH})_2$ content in CEM III/B paste ($\sim 1\text{--}2\%$ by weight¹⁰), carbonation attack induces a coarser and weaker microstructure than the OPC matrix¹¹.

As seen in Fig. 3, in the deeper area where carbonation could penetrate, 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 Na-MFP treatment obviously reduces the total porosity of the carbonated matrix, particularly near the surface. The pore size was significantly changed with both pre- and post-treatment. The differences in porosity between treated and untreated specimens decreased with increasing distance from the exposed surface. This would be related to the penetration depth of the Na-MFP solution applied. The mortar with Na-MFP pre-treatment (Pre-M) had obvious dense structure on the very top surface (≤ 1 mm). The experimental results support previous findings¹² where Na-MFP treatment significantly improved the quality of mortars in terms of their transport properties. The lowering of capillary water absorption and further carbonation rate results from a reduction of the capillary porosity in treated specimens.

As pore structure varies with the distance from exposed surface, the quantitative determination of the fraction of porosity has to be individually performed on each particular depth. The porosity determined from the specimens as a bulk would not be thoroughly informative. Hence mercury intrusion porosimetry, which is a commonly used method to determine the porosity of porous materials, would not be a suitable technique in this application. The image analysis on the BSE images was used as a method to evaluate the porosity of matrix in mortar in this study. The value was determined from the average of 20 different randomly selected paste areas through the prepared section at a depth of 3–4 mm from the exposure surface under $500\times$ magnification. The reduction of porosity due to Na-MFP treatment is clearly seen from the results of the image analysis on the ESEM photomicrographs. The analysis results indicate that the porosities were about 32%, 26%, and 27% for Pre-W, Pre-M, and Pos-M, respectively. Consistent results have been obtained with acceptable low values of standard deviation (~ 2.8 to 2.9).

In Fig. 4, the coarsening of pores can be observed at the interfacial transition zone (ITZ) between aggregate and matrix subjected to carbonation. A dense

structure of ITZ can be found on the mortar that has not been carbonated (Fig. 4a). After carbonation attack, a significant coarsening can be seen in the first 100 μm from the aggregate surface (Fig. 4b). However, the ITZ has been improved due to Na-MFP treatment as clearly seen in Fig. 4c,d.

In view of concrete durability, it is generally known that the microstructure of the ITZ is different from that of the bulk paste area. The ITZ contains more and larger pores and less anhydrous cement and calcium silicate hydrate gel¹³. Hence the ITZ would be rather susceptible to stronger chemical ingress and attack than that of the bulk paste. For this reason, the ITZ would be one of the most critical areas subjected to pore coarsening due to carbonation shrinkage. In comparison to the photomicrographs in Fig. 3, it is clearly seen that the carbonation shrinkage causes more serious pore coarsening on the ITZ rather than on the bulk matrix. However, with Na-MFP treatment, the structure of ITZ in carbonated mortars has been improved accordingly.

The EDX analysis on Na-MFP treated mortar reveals phosphorous and fluorine along with Ca, Si, Al, Fe, and S which are commonly found in cement-based mixtures. The concentration profiles of phosphorous and fluorine in treated pastes were chosen as a criterion to determine the depth of Na-MFP penetration (Fig. 5). There was no significant difference in the penetration depth of Na-MFP in Pre-M and Pos-M specimens. Taking the nick points of P profiles at about 1–3% concentration as a reference, the results show the penetration of Na-MFP to a depth of about 4–5 mm. The capability of the healing process would be strongly related to the concentration of Na-MFP in the matrix. It would be worth studying whether an increase in Na-MFP concentration enhances the penetration depth of the compound which would then result in a better healing mechanism. Another possibility is to examine the potential of using Na-MFP as an addition to the cement mixture which would enable the self-healing of carbonated matrix autogenously without any requirement of external application. However, the powder encapsulation on the compound may be required to prevent undesirable interference on the hydration of cement and BFS at an early age.

Fig. 6a,b present the scaling weight due to frost salt attack for the pre-treatment and post-treatment series, respectively. The scaling test on non-carbonated specimen was also performed to show the effect of carbonation on the frost scaling problem. The scaling weights were measured after 3 and 5 freezing-thawing cycles. The results indicated that both pre-treatment

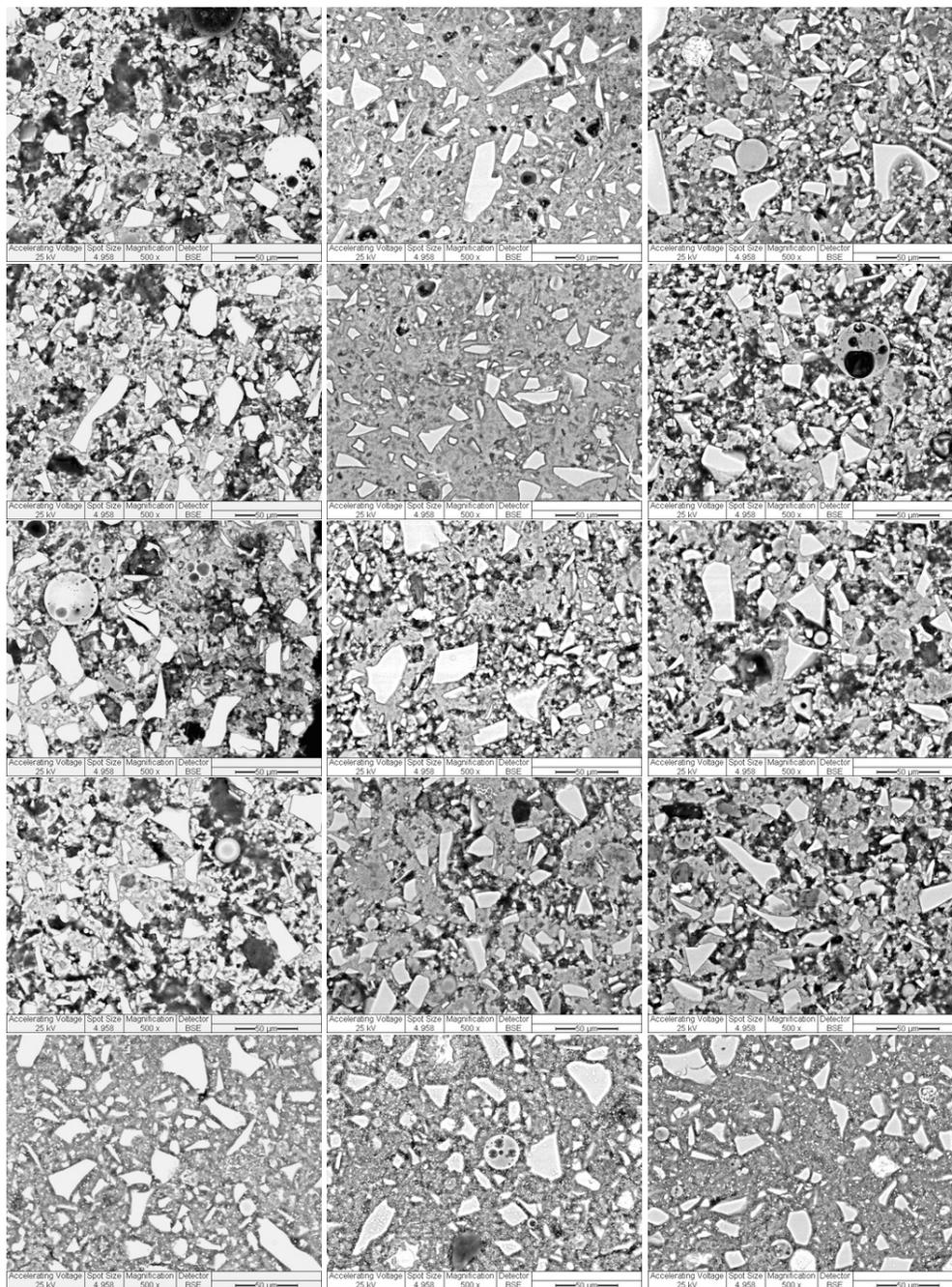


Fig. 3 Photomicrograph profiles of carbonated BFSC mortars. From left to right: Pre-W, Pre-M, and Pos-M. From top to bottom: 0.5 mm, 1.0 mm, 2.0 mm, 4.0 mm from surface, and non-carbonated zone.

and post-treatment reduced the scaling significantly. Before testing, two reference lines were drawn on each specimen. The first line was on the edge of the sample. The other was drawn 5 mm from the exposed surface. The area between the two lines is the part of the specimen which was immersed in salt solution during testing. It is clearly seen in Fig. 7 that

the mortars without treatment were severely attacked. The part of specimens submerged in salt solution was almost completely disintegrated. There is almost no scaling after 3 cycles for the treated specimens; only a few locations of local pop-out can be observed on the surface. Both pre-treated and post-treated specimens can be considered resistant to frost salt attack.

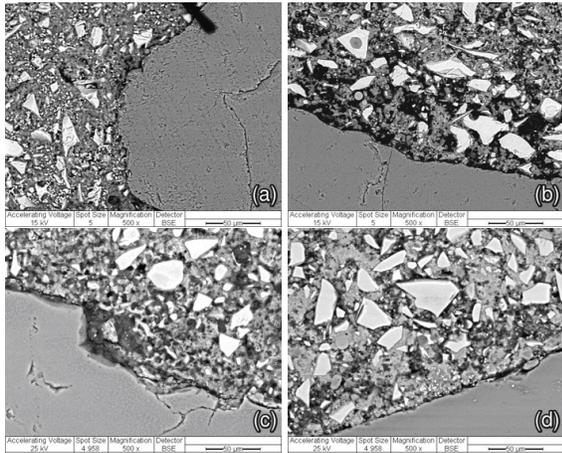


Fig. 4 Photomicrographs of interfacial transition zone in mortars (a) Pre-W: non-carbonated, (b) Pre-W: carbonated, (c) Pre-M: carbonated, (d) Pos-M: carbonated.

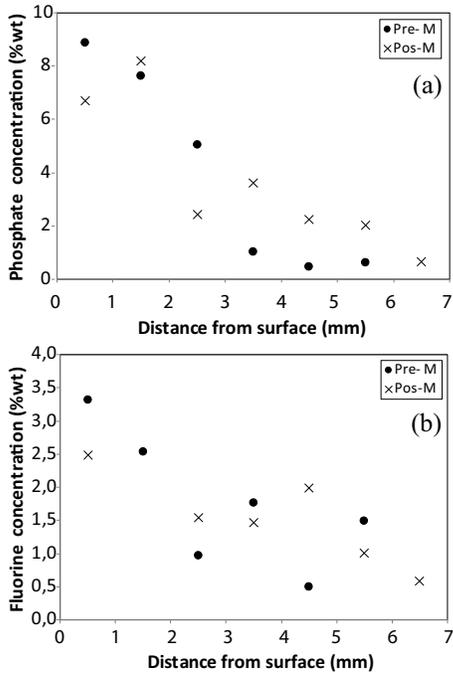


Fig. 5 Element concentration determined by EDX versus the distance from treated surface of mortars. (a) Concentrations of (a) phosphorous (b) fluorine.

Nano-indentation tests were carried out on polished paste specimens at about 100 different randomly selected locations to observe the modulus of elasticity of microscopic phases (Fig. 8). The histograms of the nano-indentation results reveal that the carbonated paste without any treatment mostly have a modulus of 10–30 GPa. With pre-treatment (Fig. 8a), the phase of

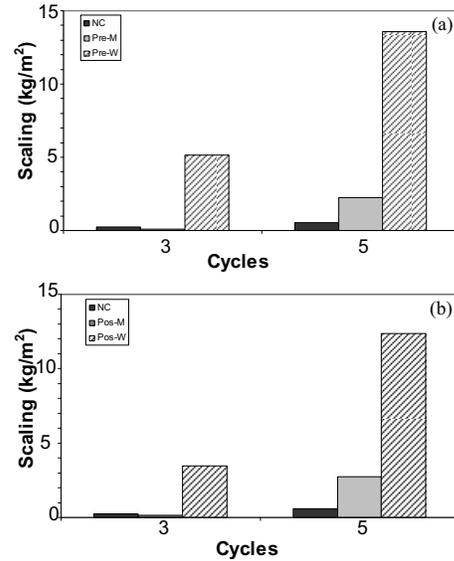


Fig. 6 Frost salt scaling performance of mortars: (a) pre-treatment series, (b) post-treatment series.

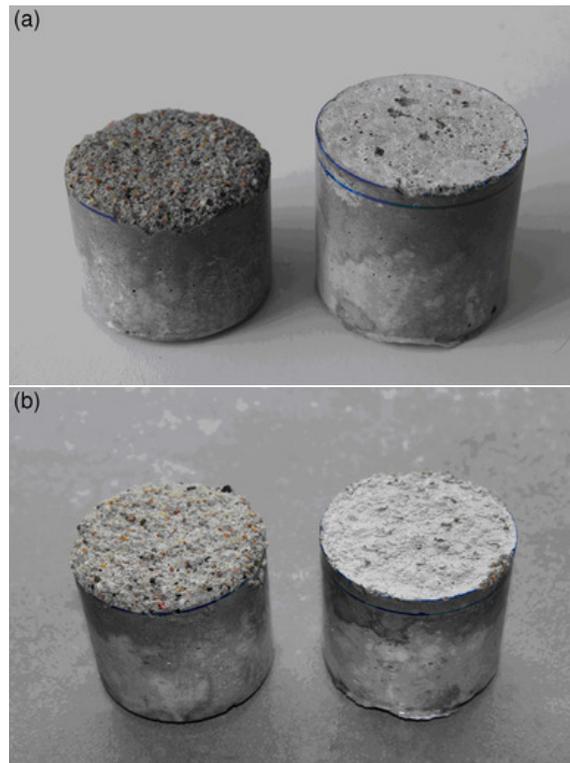


Fig. 7 Conditions of mortars after 3 cycles of frost salt scaling test: (a) pre-treatment series (Left: Pre-W; Right: Pre-M), (b) post-treatment series (Left: Pos-W; Right: Pos-M).

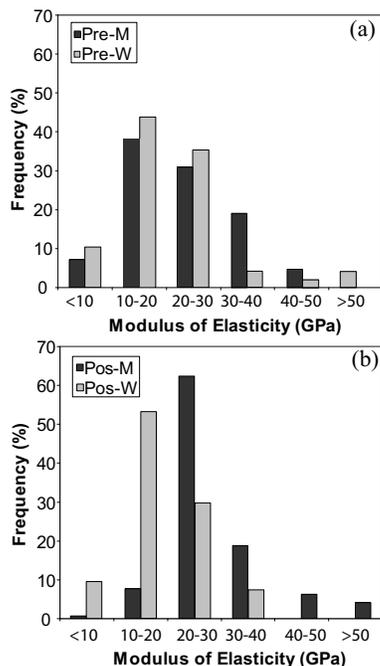


Fig. 8 Nano-indentation results on carbonated pastes: (a) pre-treatment, (b) post-treatment.

30–40 GPa was obviously increased, while the lower modulus phases have been reduced accordingly. It is also clearly seen in Fig. 8b that the histogram was shifted to the higher modulus side when the post-treatment was applied. The increments in modulus of elasticity and also probably the tensile strength of treated pastes would be parameters that lead to a better frost salt scaling durability of the mortar mixtures. The results also support the assumption in an earlier study⁶ that the main role of Na-MFP treatment may probably be the superior contribution to the tensile strength of matrix and interfacial zones. This could be realized with the reaction of PO_3F^{2-} , PO_4^{3-} , and F^- with $\text{Ca}(\text{OH})_2$, CaCO_3 , or porous silica which possibly results in the formation of crystalline fluoroapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) or carbonate fluoroapatite ($\text{Ca}_5(\text{PO}_4)_3\text{CO}_3$) as well as their amorphous formations.

CONCLUSIONS AND RECOMMENDATIONS

The results reveal that the microstructure of the treated mortar has been significantly improved. The EDX result showed the penetration of Na-MFP to about 4–5 mm from the surface. The treatment, reduces the porosity of carbonated matrix, and significantly improves the quality of the ITZ between sand and paste. The nano-indentation result showed the evi-

dence of the beneficial reaction between Na-MFP and carbonated phases which is reflected by the increment of the modulus of elasticity. The improvement of microstructure would lead to a resistant carbonated zone of BFSC mortar against frost salt scaling.

The experimental results showed that both pre- and post-treatment techniques are promising to reduce frost scaling on BFSC specimens. Practically, however, the method of pre-treatment, which can be performed during the construction period, would be more convenient than post-treatment. Future studies should investigate whether the healing ability might be enhanced if the concentration of Na-MFP is increased. The application on the surface of the specimen at an earlier age would also promote the penetration depth of the Na-MFP solution. To maximize the healing process, the penetration depth of Na-MFP would be deeper than the depth of carbonation. Apart from the frost scaling problem, the application of Na-MFP would have a potential to promote other mechanical properties of carbonated BFSC concrete, particularly the surface strength. Improvements in abrasion and erosion resistances of the concrete are possible, and will be studied in future work.

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