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Effect of sodium monofluorophosphate treatment on microstructure and frost salt scaling durability of slag cement paste

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Abstract

Sodium-monofluorophosphate (Na-MFP) is currently in use as a surface applied corrosion inhibitor in the concrete industry. Its basic mechanism is to protect the passive layer of the reinforcement steel against disruption due to carbonation. Carbonation is known as the most detrimental environmental effect on blast furnace slag cement (BFSC) concrete with respect to frost salt scaling. In this paper the effect of Na-MFP on the microstructure and frost salt scaling resistance of carbonated BFSC paste is presented. The results of electron microscopy, mercury intrusion porosimetry (MIP) and X-ray diffraction (XRD) are discussed. It is found that the treatment modifies the microstructure and improves the resistance of carbonated BFSC paste against frost salt attack.

Keywords: Granulated blast-furnace slag (D); Carbonation (C); Freezing and thawing (C); Na-MFP; Microstructure (B)

1. Introduction

BFSC is an important product in the northern European countries such as The Netherlands, Belgium and Germany. In The Netherlands it has a market share of more than 50% and besides many technical advantages; it is an environmental friendly product [1]. However, in comparison with ordinary Portland cement (OPC) its fast carbonation rate is a drawback and as investigated by many researchers, the eventual frost salt scaling resistance is lower than OPC according to the results of laboratory testing [2–4]. It is an important issue to improve the frost salt scaling resistance of BFSC systems from technical and economical point of view.

In order to improve its frost salt scaling resistance of BFSC based materials, several approaches have been taken. The most successful methods known are to decrease the slag content, preventing surface carbonation, air entrainment, and utilization of ternary blends [5]. Modifying the parameters such as water/binder ratio and pore size distribution is also regarded important. However these modifications seem to be inconvenient for technical and economical aspects. Hence it is increasingly becoming important to find new techniques to improve the frost salt scaling resistance of BFSC systems.

2. Research significance

The current investigation was initiated due to lack of information on the effect of Na-MFP on frost salt scaling resistance in the literature. The main aim was to understand the reasons existing for the poor frost salt scaling resistance of carbonated cement based materials rich in slag by studying the

Table 1
Physical and chemical properties of CEM III/B 42,5 N HSR LH

Chemical		Physical	
CaO	45.0%	*Strength of standard mortars*	
SO_3	3.25%	2 days	12.1 N/mm^2
SiO_2	27.6%	7 days	32.7 N/mm^2
Al_2O_3	12.2%	28 days	53.2 N/mm^2
Fe_2O_3	1.27%	Blaine	376 m^2/kg

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Table 2
Physical and chemical properties of CEM I 32,5 R

Chemical		Physical	
CaO	63.9%	*Strength of standard mortars*	
SO_3	2.68%	2 days	22.0 N/mm^2
SiO_2	20.6%	7 days	36.0 N/mm^2
Al_2O_3	5.01%	28 days	49.0 N/mm^2
Fe_2O_3	3.25%	Blaine	285 m^2/kg

interaction of Na-MFP and carbonated BFSC paste. Na-MFP was particularly chosen for this study considering its efficiency on the carbonated cementitious materials [6].

3. Technical background

Na-MFP treatment of concrete is one of the corrosion inhibition techniques for reinforced concrete currently in use. Its positive effect in inhibiting corrosion of steel has been presented by many researchers [6–8]. Generally it is used as a solution and applied on the carbonated concrete surface. It has been reported that factors affecting the kinetics of penetration of Na-MFP into concrete are not well understood. However, it is known that Na_2PO_3F hydrolyses into the pore solution to form PO_4^{3-} and F^- (Eq. (1)). Some authors presented that those anions react with the certain components of the cement matrix to form fluorapatite and fluorite, which are highly insoluble calcium compounds (Eq. (2)) [9]. Furthermore, NaF would also react with more calcium hydroxide to form CaF_2, which has a very low solubility. Additionally this reaction increases the pH of the pore solution [6].

$$PO_3F^{2-} + H_2O \rightarrow F^- + H_2PO_4^- \tag{1}$$

$$5Ca(OH)_2 + 3Na_2PO_3F \rightarrow Ca_5(PO_4)_3(F,OH) + 4NaOH + 2NaF + 3H_2O \tag{2}$$

Douche-Portanguen et al. [10] state that the complex interactions take place between Na-MFP and hardened OPC paste components, especially calcium hydroxide. They observed in the XRD study that this interaction produces an amorphous gel and concluded that Na-MFP treatment modifies the transport properties of OPC concrete.

Copuroglu et al. [11] previously reported the effect of Na-MFP treatment on frost salt scaling durability of BFSC concrete samples with W/C 0.45. They present evidence regarding the possibility of an amorphous gel formed by the interaction between Na-MFP and OPC paste. Additionally, they conclude that the Na-MFP treatment modifies the transport properties of OPC concrete.

The previous investigations focused mainly on OPC and exclusively on corrosion inhibition. No experimental data are known from literature on the interaction between Na-MFP and slag cement paste in relation to frost salt scaling resistance.

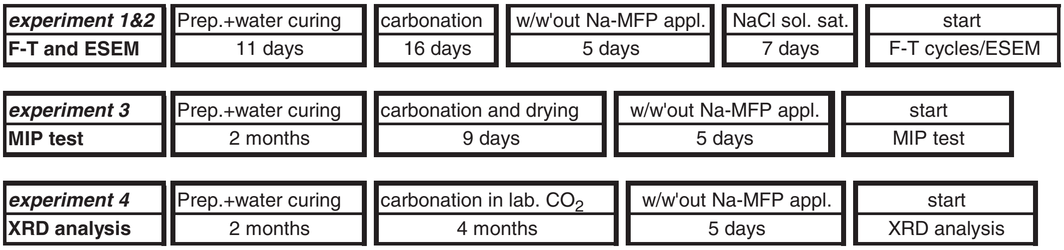
4. Experimental data

4.1. Materials and preparation techniques

A BFSC with a slag content of 67% (CEM III/B 42,5 N HSR LH) and an OPC CEM I 32,5R were used from ENCI cement factory of The Netherlands. The chemical and physical properties of the cements are given in Tables 1 and 2. Paste samples with water to cement ratio of 0.45 were prepared. Ordinary tap water was used in the mixtures. The mixing sequence was 2 min low speed and 2 min high speed mixing with a commercial HOBART mixer. Then the mixtures were poured into a PVC pipe with 90 mm diameter and 30 cm length. The pipes were vibrated for 15 s on a vibrating table. The pipe was then rotated at a speed of 4 rotations per minute for 24 h at room temperature and placed in tap water for the water curing.

The samples were kept in water for 10 days. Consequently the samples were demoulded and cut into 3 cm thick discs. Then the discs were put in the environment with 0%, laboratory air and 3% carbon dioxide for 16 days. 0% carbonation was reached by a blend of NaOH and $Ca(OH)_2$, sodalime pellets with absorption capacity of 28% for CO_2 in a dessicator. In all cases the relative humidity of the environment was kept in the range of 50–55%. The 0% CO_2 environment was realized by storing the specimens in a dessicator and the mentioned relative humidity was obtained by $Mg(NO_3)_2{\cdot}6H_2O$.

The drying and carbonation period was followed by the Na-MFP treatment. 10% Na-MFP solution was applied on the specimen surfaces 5 times per day by means of a paint brush. Demineralised water was applied after each Na-MFP treatment to enhance the penetration of the solution into the specimen. The surfaces were allowed to become visibly dry between each application. The Na-MFP treatment took 5 days providing 25 times treatments in total and the control specimens were treated with demineralised water instead of Na-MFP solution. Finally the specimens were exposed to freezing and thawing cycles.



experiment 1&2 / **F-T and ESEM** | Prep.+water curing 11 days | carbonation 16 days | w/w'out Na-MFP appl. 5 days | NaCl sol. sat. 7 days | start F-T cycles/ESEM

experiment 3 / **MIP test** | Prep.+water curing 2 months | carbonation and drying 9 days | w/w'out Na-MFP appl. 5 days | start MIP test

experiment 4 / **XRD analysis** | Prep.+water curing 2 months | carbonation in lab. CO_2 4 months | w/w'out Na-MFP appl. 5 days | start XRD analysis

Fig. 1. Summarization of the curing regimes.

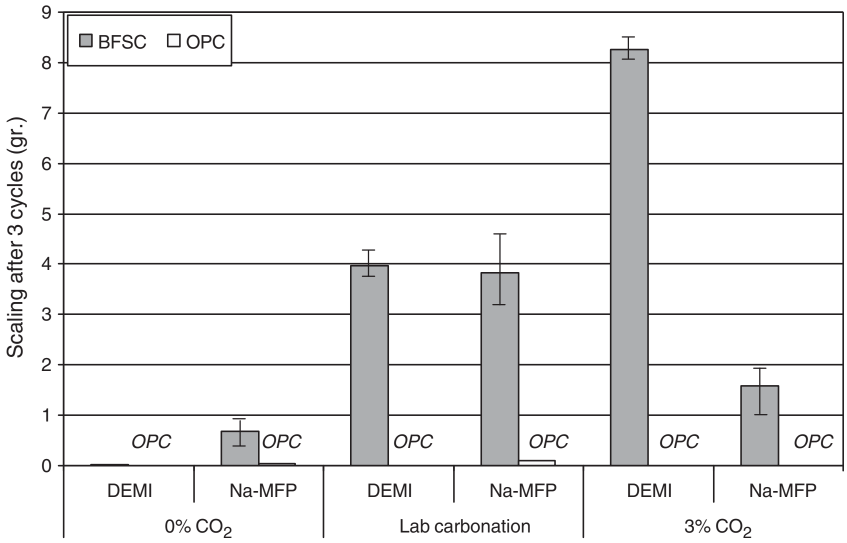


Fig. 2. Frost salt scaling performances of the BFSC and OPC pastes with W/C = 0.45 after 3 freezing–thawing cycles (DEMI: demineralised water treatment). All samples have identical surface area.

A DBT Diamond Roller and Grinder/86 thin sectioning machine was used for the preparation of the perfectly flat ESEM specimens. Then the specimens were polished with 6 μm, 3 μm, 1 μm and 0.25 μm diamond paste. Low viscosity epoxy was used to maintain the integrity of the samples during the preparation and for distinguishing the porosity and the matrix in the photomicrographs.

4.2. Testing and analysis procedures

The ASTM C672 freezing–thawing cycle consisted of 16 h in −20 °C freezing and then 8 h at 20 °C was used. Approximately 3 mm of 3% NaCl solution was maintained on top of the paste samples during the freezing–thawing cycles.

The BFSC samples with W/C = 0.45 were examined by ESEM in backscattered electron (BSE) mode before carbonation, after carbonation and after the Na-MFP solution treatment.

The effect of Na-MFP treatment on the pore structure of W/C = 0.45 BFSC pastes were measured by the MIP method. The MIP test samples were water cured for 2 months. After the water curing period, non-carbonated samples were immediately cut into small pieces and put in the freeze dryer in which the temperature and air pressure kept at −24 °C and 10^{-1} Pa, respectively, until the day of testing. The carbonated samples were put in the 3% CO_2 and 50% R.H. chamber until they were completely carbonated. The carbonation front was monitored by phenolphthalein method. After the completion of the carbonation, half of the samples were put in the freeze dryer. The rest was treated by 10% Na-MFP solution for 5 days and also put in the freeze dryer until the samples were completely dry.

For the XRD analysis of carbonated and carbonated/Na-MFP treated BFSC pastes, a Philips PW3710 diffractometer with Cu tube and Ni filter was used. The 2θ diffraction range was from 0 to 80°. The paste samples examined were cured under water for 2 months and then sawn in slices of 1–2 mm thickness to be exposed to an additional 4 months of laboratory carbonation prior to the XRD analysis.

Each experimental study was designed for the A/B comparison of the treated/non-treated carbonated samples at the end of certain curing regimes. The aim for using different curing regimes was to see the efficiency of Na-MFP treatment at different ages

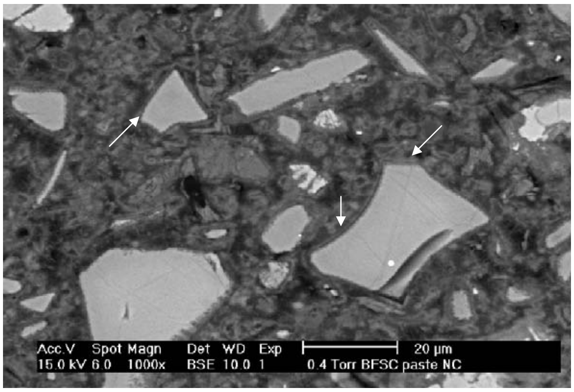


Fig. 3. BSE photomicrograph of the non-carbonated BFSC paste with W/C = 0.45. Mg rich interfacial zone is indicated by the white arrows.

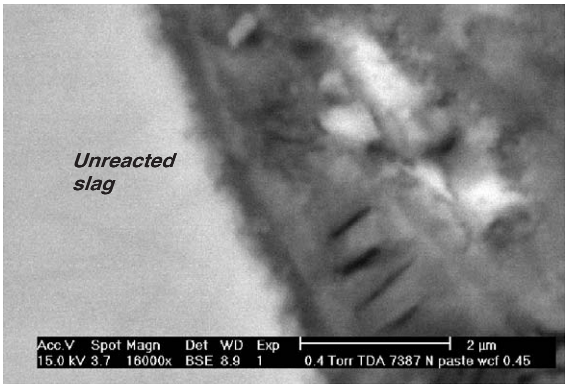


Fig. 4. Detailed BSE photomicrograph of the Mg rich interfacial transition zone between unreacted slag and hydration products. Non-carbonated BFSC paste W/C = 0.45.

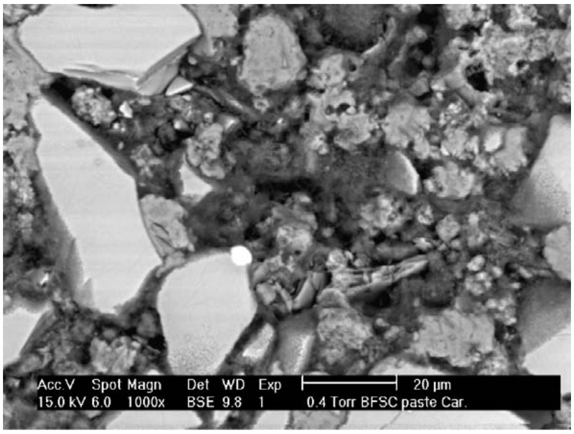


Fig. 5. BSE photomicrograph of 3% CO_2 (accelerated) carbonated BFSC paste with W/C = 0.45.

and degrees of carbonation of the paste samples. A summary of the curing regimes in the experiments is presented in Fig. 1.

5. Results

The initial frost salt scaling performances of the OPC and BFSC pastes are presented in Fig. 2. The scaling values represent the average of two samples. OPC cement paste showed in all cases an excellent performance after 3 cycles. The small amount of scaling, which is seen in the results was just a local pop-out and cannot be generalised for the whole surface. The results show that high carbonation has improved the resistance of OPC cement paste even further.

The performance of the non-carbonated BFSC pastes was somewhat comparable to the OPC ones. The effect of Na-MFP treatment showed no significant effect on laboratory carbonated BFSC pastes after 3 freezing–thawing cycles probably because of very low depth of carbonation (only surface carbonation). However the positive contribution of Na-MFP treatment was apparent for highly carbonated BFSC paste samples under 3% CO_2 (carbonation depth of 4.1 mm, measured by phenolphthalein method). The improvement of frost salt scaling resistance was some 75%.

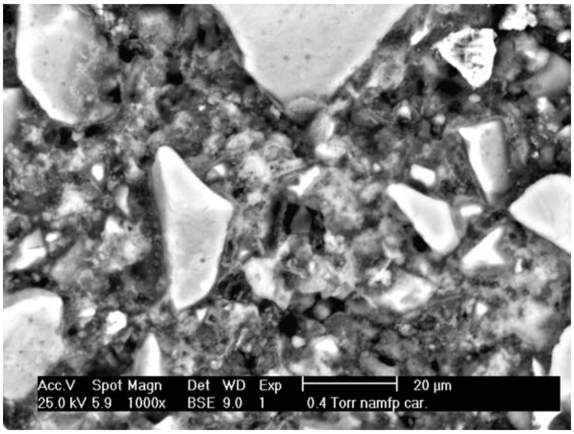


Fig. 6. BSE photomicrograph of the (3% CO_2) accelerated carbonated BFSC paste with W/C = 0.45 treated with 10% Na-MFP solution, to be compared with Fig. 7.

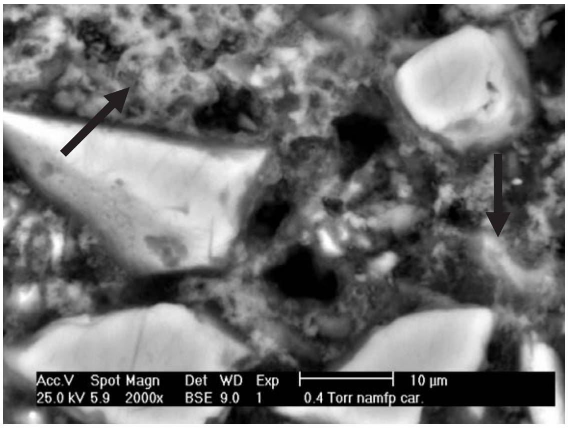


Fig. 7. BSE photomicrograph of the (3% CO_2) accelerated carbonated BFSC paste treated with 10% Na-MFP solution.

In Figs. 3 and 4, the microstructural condition of a non-carbonated BFSC paste with W/C = 0.45 can be seen. The bonding of hydration products and unreacted slag particles seem quite strong and interconnected. Approximately 0.20 µm thick reacted zone penetrates from Mg rich interfacial transition zone into the unreacted slag particles [12].

The effect of carbonation on BFSC paste with W/C 0.45 is clearly visible in Fig. 7. Significant coarsening of the matrix and increase in the width of the transition zones can be observed. The reason of the observed formation is due to the loss of water and consequent shrinkage during the carbonation of matrix. This happens due to the decomposition of CSH phase and formation of porous silica gel [13]. It can be expressed by the following reaction;

$$(\mathrm{CaO})_x \cdot (\mathrm{SiO_2})_y \cdot (\mathrm{H_2O})_z + x\mathrm{CO_2} \rightarrow x\mathrm{CaCO_3} + (\mathrm{SiO_2})_y \cdot (\mathrm{H_2O})_{z-w} + w\mathrm{H_2O} \quad (3)$$

The role of calcium hydroxide (CH) in the carbonation of cementitious materials is quite important. The carbonation of CH leads to a pore volume decrease and (depending on its

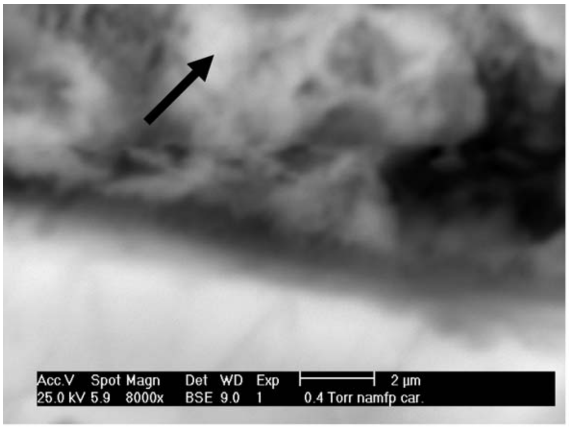


Fig. 8. BSE photomicrograph of the (3% CO_2) accelerated carbonated BFSC paste treated with 10% Na-MFP solution.

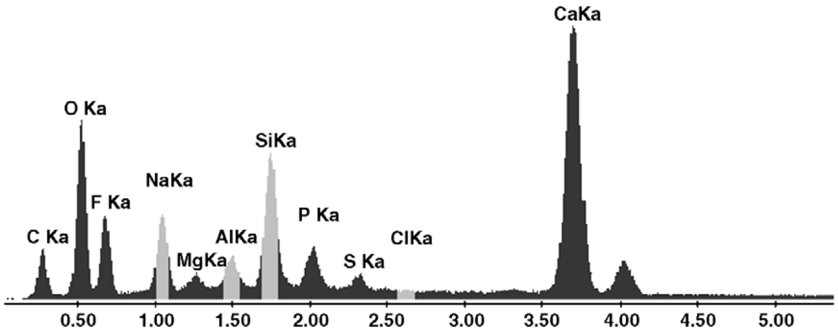


Fig. 9. EDX spectrum of a Na-MFP treated carbonated BFSC paste.

amount) it compensates the pore volume increase due to porous silica formation (Eq. (3)). With regard to OPC, having less than half amount of CH in BFSC, carbonation process results to a coarser and even weaker microstructure [14]. The authors have previously discussed that this process especially affects the interfacial zones in cement pastes rich in slag, possibly leading to a lower resistance against frost salt attack [15] (Fig. 5).

The condition of the carbonated BFSC paste after the Na-MFP treatment is presented in Figs. 6, 7 and 8. The authors interpret that the solute undergoes a reaction with only carbonated cement paste and may form a stable phase according to the scaling results.

Significant amount of sponge-like new formations are observed on the Na-MFP solution treated paste samples. These formations are indicated by black arrows in Figs. 9 and 10. It seems that the new formations appear in the matrix as well as the transition zones between unreacted slag particles and hydration products.

The EDX analysis of the Na-MFP treated paste revealed that the resulting paste consists of fluorine and phosphate elements along with the existing Ca, Mg, Si and S peaks of the BFSC paste (Fig. 9).

The effect of Na-MFP treatment on the pore structure of the BFSC paste was also investigated. The results are presented in Figs. 10 and 11.

The results show that Na-MFP treatment increases the cumulative intrusion volume compared to the carbonated sample slightly. However, the most remarkable result from MIP measurements is the pore size distribution. It can be seen that the Na-MFP treatment decreases the volume of the pores smaller than 0.1 μm and slightly increases the pore volume in the portion of 0.1–1 μm in comparison with carbonated paste.

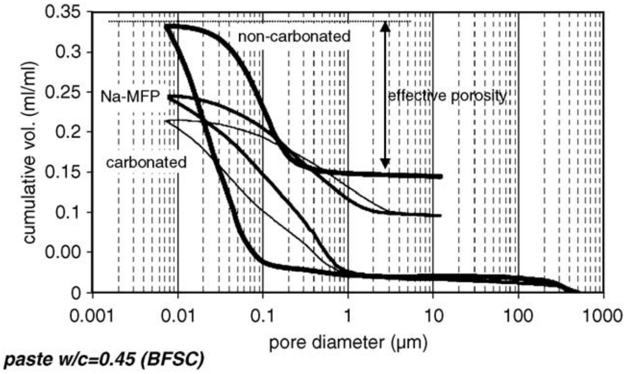


Fig. 10. The effect of Na-MFP treatment on the cumulative intrusion volume of BFSC paste with W/C=0.45.

The XRD diffractograms of carbonated and carbonated/Na-MFP treated slag pastes are presented in Figs. 12 and 13. It was not possible to identify any new crystalline formations. Three different carbonate phases still existed after the treatment. However the intensities of carbonate phases seem to be slightly lower after the Na-MFP curing. Additionally, an increase in the amorphous phase (mainly between 23° and 35°) of carbonated slag paste was observed after the Na-MFP treatment (Fig. 12 vs. Fig. 13). Most remarkable result is the disappearance of portlandite mineral. This result was expected because portlandite has a high tendency to react with Na-MFP and create apatite (Fig. 14). However no reaction was found between separate calcite phase and Na-MFP (Fig. 15).

6. Discussion

An improvement of initial frost salt scaling resistance was achieved by Na-MFP solution treatment on the highly carbonated BFSC paste samples. This improvement was initially expected from the reaction between the formations due to Na-MFP hydrolysis and the $CaCO_3$ phase of the paste. However, the XRD results showed that there is no significant reaction between calcite and Na-MFP. The only reaction identified was the CH+Na-MFP creating possibly the highly soluble fluoroapatite. There is a possibility that Na-MFP reacts with other mineral types of calcium carbonate, like vaterite and aragonite since the XRD peaks of those phases appear to decrease slightly after the treatment. It is not likely that the

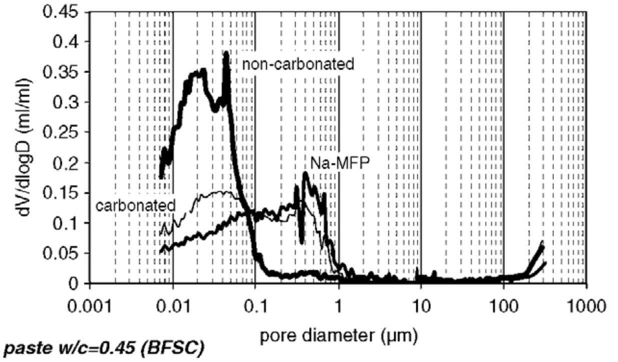


Fig. 11. The effect of Na-MFP treatment on the pore size distribution of BFSC paste with W/C=0.45.

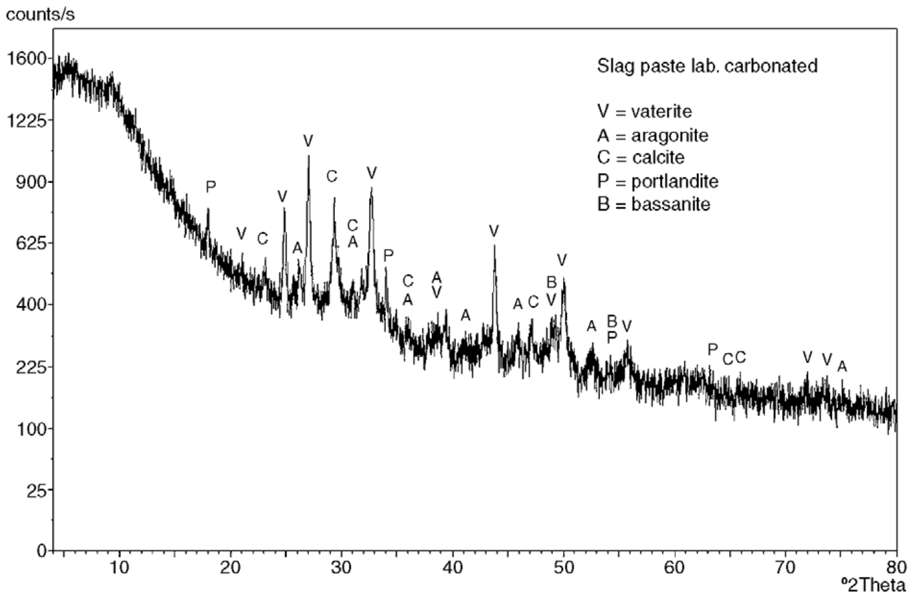


Fig. 12. XRD diffractograms of 4 months laboratory carbonated BFSC paste.

improvement of frost salt scaling is due to the apatite formation because the significant improvement was achieved on highly carbonated samples, which possess almost no portlandite. According to the XRD analysis results the improvement may be generated by the formation of amorphous phase (see Fig. 13).

Looking at the interfacial zones between unreacted slag particles and matrix, we see that Na-MFP does not reduce the openings significantly. Considering the current results, the main role of Na-MFP treatment may probably be the superior contribution to the tensile strength of matrix and the interfacial zones. This could be realized with the reaction of PO_3F^{2-}, PO_4^{3-} and F^- with $Ca(OH)_2$, $CaCO_3$ or porous silica which results possibly into fluoroapatite ($Ca_5(PO_4)_3F$) or carbonate fluoroapatite ($Ca_5(PO_4,CO_3)_3F$) as well as unidentified amorphous formation(s). An X-ray analysis made by Farcas et al. [9] on OPC paste shows that the resulting mineral could be calcium apatite (fluoroapatite or hydroxylapatite). It should be noted here that the possible reaction product hydroxylapatite is the major component of tooth material [16] and the solubility of apatite is extremely low in that the solubility product constant values (Ksp) are 3.16×10^{-60} and 2.34×10^{-59} for fluorapatite and hydroxylapatite, respectively. Farcas et al. also state that the exact nature of the calcium apatite cannot be figured out from their X-ray data. Since $Ca(OH)_2$ minerals can hardly be found in (especially carbonated) BFSC paste and it is observed that there was no reaction between calcite and Na-MFP (Fig. 13), it is likely that the remaining carbonates (vaterite and/or aragonite) of the carbonated BFSC paste may take part in the production of new stable formations up to certain extend.

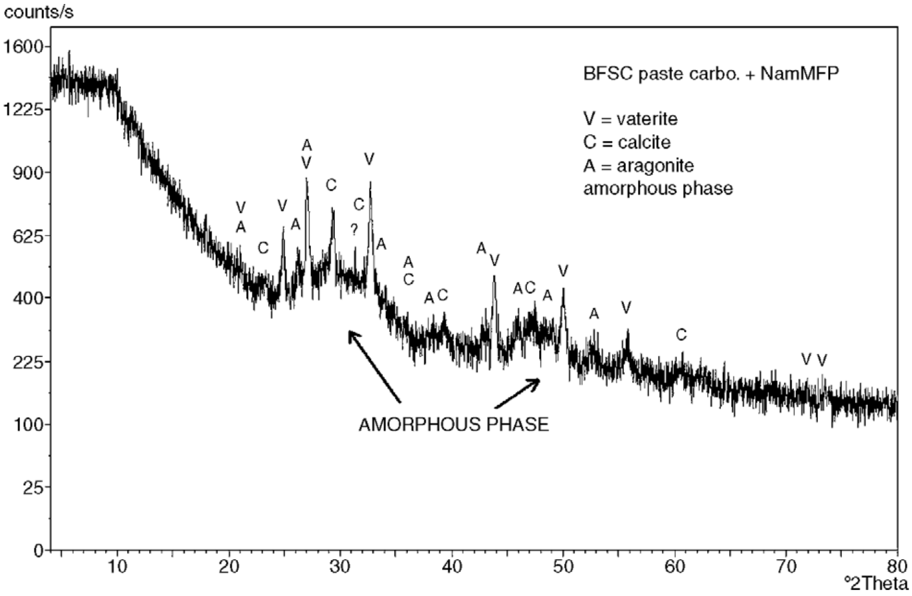


Fig. 13. XRD diffractograms of 4 months laboratory carbonated/Na-MFP treated BFSC paste.

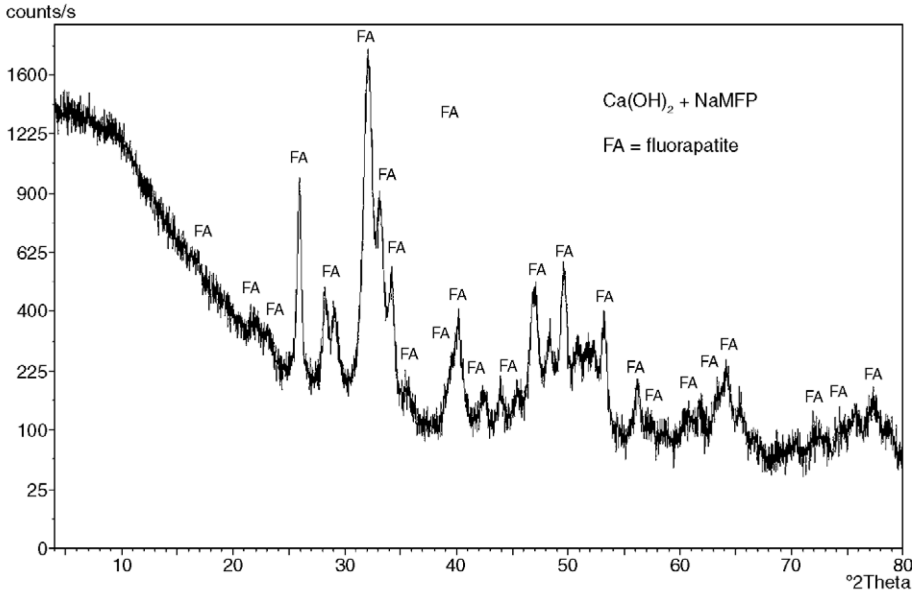


Fig. 14. XRD diffractograms of CH+Na-MFP reaction product.

Apparently the Na-MFP treatment leads to pore structure change in BFSC paste. The results show that there is a slight increase in the total intrusion volume after the treatment. The change in pore size distribution is noteworthy from a point of the roles of the micro-capillaries ($d < 0.1$ µm) in frost salt attack. It was expected that the action of Na-MFP should be to decrease the portion of the macro capillaries ($d > 0.1$ µm) and increase the portion of the micro capillaries. By this way freezable NaCl solution content could have been decreased. However according to the MIP test results the effect of Na-MFP is the opposite. It increased the portion of macro-capillary volume and decreased the micro-capillaries significantly and yet, an improvement in frost salt scaling is achieved. An explanation to this situation could be the interaction between the phases in the transition zones and Na-MFP. It is a possibility that as a result of the above-mentioned reaction(s) the bonding quality and the tensile strength of the interfacial zones between unreacted slag particles and matrix improves significantly. This improvement should lead to a much higher resistance of BFSC systems against frost salt scaling since tensile strength is related to the frost salt scaling resistance of cementitious materials [17]. However, current study suggests that mineralogical modifications should be seriously considered in order to achieve a better frost salt scaling resistance of BFSC based materials.

It should also be stressed that mercury porosimetry may destruct the mineral phases which causes an over-estimation of pores [18].

Increased ion concentration due to Na-MFP application may decrease the freezing point of pore water. However, it is not

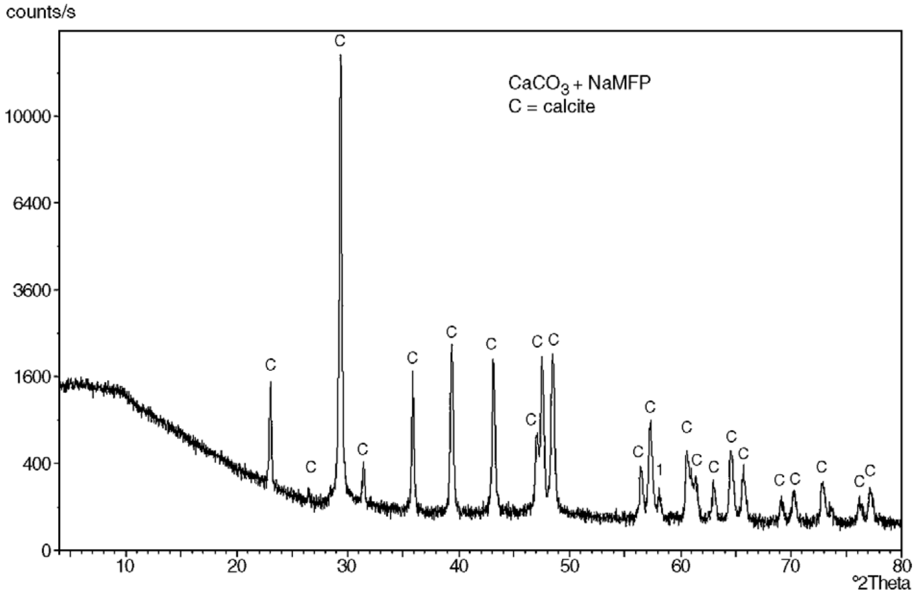


Fig. 15. XRD diffractograms of pure calcite and Na-MFP reaction products.

possible to attribute the improvement to the increased ion concentration of pore solution since the application is much more effective for highly carbonated samples than for the normal carbonated ones.

Another explanation can be made from chemical point of view. According to Stark and Ludwig the responsible phases are aragonite and vaterite minerals regarding the poor frost salt scaling resistance of carbonated cement paste rich in slag [19]. They claim that in case of frost salt attack, the crystal structure of the minerals transforms into a much poorer state. Assuming that their hypothesis is correct, Na-MFP treatment may be preventing the transformation of vaterite and aragonite minerals under the combined attack of frost and deicing salts. However, it is necessary to do further research in order to clarify this hypothesis.

7. Conclusions

10% of Na-MFP solution treatment increases the initial frost salt resistance of carbonated BFSC paste with a W/C = 0.45 substantially. The solution is effective especially for highly carbonated surface since a thick resistant zone can be created by the application.

The study results into a hypothesis that the reaction between Na-MFP and vaterite/aragonite phases may lead to a resistant carbonated zone of the BFSC paste against frost salt attack. It is also possible that the porous silica gel may undergo a similar reaction according to the XRD analysis results.

The Na-MFP treatment appears to modify the pore structure of the BFSC paste. An increase in macro-capillary intrusion volume and decrease in micro-capillary intrusion volume was found. The treatment also slightly increases the total intrusion porosity.

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