FLUORAPATITE FORMATION IN CARBONATED BLAST FURNACE SLAG MIXTURES

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Abstract

The application of sodium monofluorophosphate solution as a surface treatment compound on natural carbonated blast furnace slag cement (BFSC) mortar was studied. The treatment was performed on the surface of mortars either at the age of 10-day or after the one-year natural exposure, described as pre- and post-treatments, respectively. The experimental results show that the treatments evidently improved the frost scaling durability of carbonated BFS mortars. The XRD analysis shows the formation of fluorapatite and carbonate fluorapatite in the carbonated matrix. Pore coarsening due to carbonation shrinkage was reduced accordingly.

1. INTRODUCTION

Using of blast furnace slag (BFS) in concrete industries is widely accepted, particularly in the northern European countries. The superior durability of BFS against aggressive environment promotes this cement as a suitable binder for the concrete exposed to chloride, acid and sulfate attacks. It has been reported that the microstructure of Portland-slag cement pastes is not too different from that plain Portland cement [1]. The major difference consists in a reduced amount of free portlandite (Ca(OH)$_2$; CH). The simplified reactions of Portland cement and BFS can be written as shown below.

\[ \text{OPC} + \text{H}_2\text{O} \rightarrow \text{C-S-H} + \text{Ca(OH)}_2 \]  

\[ \text{BFS} + \text{H}_2\text{O} [+ \text{Ca(OH)}_2] \rightarrow \text{C-S-H} \]

It is clearly seen from above equations that the amount of CH in the matrix would be declined with increasing of slag replacement. It has been found that concrete bearing high amount of BFS has a poor resistance against carbonation because of its significantly low CH content. After carbonation attack, the reduction in CH in BFS concrete can cause depassivation that induces corrosion problems to the steel reinforcement. On the other hand, the carbonation on C-S-H does not show any significant problem on the alkalinity reduction. However, it causes irreversible shrinkage on the surface and reduces the micro-mechanical properties of the BFS matrix drastically due to the conversion of C-S-H to be calcium carbonate and porous silicate products. After several years of exposure, frost salt scaling is
considered as one of the most dangerous treats on BFS-rich concrete infrastructure. The equations of carbonation reaction are as shown below.

\[
\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \tag{3}
\]

\[
\text{C-S-H} + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{SiO}_2\cdot\text{H}_2\text{O} + \text{H}_2\text{O} \tag{4}
\]

In previous studies [2-4], it was reported that sodium monofluorophosphate (Na$_2$FPO$_3$; referred to as Na-MFP from this point on) treatment has a benefit to improve the frost scaling resistance of carbonated blast furnace slag cement (BFSC) mixes. In the studies, a 10% Na-MFP solution was applied on surface of hardened BFSC pastes and mortars, and the influence of the application before or after accelerated carbonation attack was investigated. The results from the experiments reveal that the treatments significantly improve the frost salt scaling durability of carbonated BFSC mortar. However, it has to be remarked that all results were obtained from accelerated test with 3% carbon dioxide concentration. As previously reported [2], there are several mineral types of calcium carbonate phase (calcite, vaterite and aragonite) can be found in carbonated BFS matrix. The results from XRD showed that Na-MFP reacts with vaterite and aragonite, while its interaction with calcite is hardly noticeable. The difference in CO$_2$ concentration between accelerated carbonation test and natural exposure may change the proportion among the types of CaCO$_3$ which may affect the healing ability of Na-MFP. Hence, in this study, the application of Na-MFP solution as a surface treatment compound to improve the frost salt scaling resistance and microstructure of natural carbonated BFS mortar was investigated.

2. EXPERIMENTAL INVESTIGATION

2.1 Materials and Preparation

A BFSC (CEM III/B 42.5 N HSR LH) from ENCI cement manufacturer was used. De-ionized water was used in mixing process throughout the experiment, controlling the w/c ratio in the order of 0.45 by weight. The mixture was designed based on the sand-to-cement ratio of 2.5 by weight. The specimens were cast in plastic containers with 55 mm diameter to a height of about 50 mm. The containers were vibrated for 10 s on a vibrating table. After 24 hours, the specimens were cured in tap water with controlled temperature of 25±2°C for 3 days period. Thereafter, specimens were conditioned in a CO$_2$ free dessicator at 50-55% relative humidity. The specimens were classified into three sets: No Treated Control (NT), Pre-treated (PRE) and Post-treated (POS). After 10 days of the conditioning process, the 10% Na-MFP solution was applied on one set of specimens for 6 times a day by means of a paint brush. This set of mortar was indicated as pre-treated specimens (PRE). De-ionized water was sprayed on treated surface after each Na-MFP treatment to promote the penetration of the solution into the specimens. The treatment period was for 4 days providing 24 times treatments in total while the control (NT) and post-treated (POS) samples received de-ionized water instead of Na-MFP solution. This process was necessary to ensure the identical pore saturation between treated and untreated specimens.

Thereafter, all specimens were exposed to the natural environment in two different conditions which were indoor (~25± 2°C, RH 50±5%) and outdoor (Delft, The Netherlands, no shelter). 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 exposed to the environment. After one year exposure, the 10% Na-MFP solution was applied on the surface
of specimens in post-treated series (POS) for 6 times a day. The period of treatment was for 4 days. The method of treatment was similar to that pre-treated scheme explained earlier. The control (NT) and pre-treated (PRE) samples received de-ionized water instead of Na-MFP solution. The treatment and exposure program are given in Table 1.

Table 1: Treatment program

<table>
<thead>
<tr>
<th>Samples</th>
<th>Treatment and exposure program</th>
<th>No treatment (water applied)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (NT)</td>
<td>One year natural exposure</td>
<td>Indoor (~25°C, RH 50±5%)</td>
</tr>
<tr>
<td>Pre-treated (PRE)</td>
<td>Na-MFP treatment</td>
<td>Outdoor (Delft, NL with no shelter)</td>
</tr>
<tr>
<td>Post-treated (POS)</td>
<td>No treatment (water applied)</td>
<td>Na-MFP treatment</td>
</tr>
</tbody>
</table>

2.2 **Analysis and testing methods**

The microstructure of mortars was studied by using environmental scanning electron microscope (ESEM): Philips XL30. The integrity of the samples was maintained by impregnating in 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 weight change. A DBT Diamond Roller and Grinder/86 thin sectioning unit were used for initial preparation of polished sections for ESEM study. Finally, specimens were polished with 6 μm, 3 μm, 1 μm and 0.25 μm diamond pastes, respectively.

A custom frost salt scaling test was adopted with 17 h in -20°C freezing and then 7 h at 25°C thawing cycles conforming ASTM C672. The un-coated surface of mortars was facing downward submerged 5±1 mm into the 3% NaCl solution 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 up to 8 cycles. Eventually, the filter paper with scaling material was oven-dried at 105°C and weighted after 24 hours drying. The scaling weight per unit area of exposed surface can be calculated from the average value of two specimens.

3. **RESULTS AND DISCUSSIONS**

The carbonation depth observed by conventional phenolphthalein test with respect to exposure period of NT mortars under indoor and outdoor exposure conditions is presented in Figure 1. Regarding to Fick’s law of diffusion, it is generally known that the depth of carbonation progresses with square root of exposure duration. In this work, the experimental results reveal that the indoor exposed mortar shows deeper depths of carbonation compared with the outdoor exposure. At one year natural exposure, the carbonation depths were about 10 and 7 mm for indoor and outdoor environments, respectively. An agreeing result has been reported by Thomas and Matthews [5] that concrete stored externally carbonates on average 40% less than the specimens of the same concrete stored indoor.

The relative humidity in the exposure environment plays a role on the rate of carbonation. When the relative humidity is too high, the liquid water saturates the concrete and blocks the capillary pores of the matrix. Hence, the diffusion of gaseous carbon dioxide is hardly
occurring. On the other hand, if the pores are mostly or completely dry, the carbon dioxide can not react with calcium hydroxide (CH) due to the absence of water which is one of the reactants in carbonation reaction. Generally, the gaseous CO₂ has to be dissolved in water to form carbonic acid before reacting to CH. Various works [6-9] reported that the relative humidity between 50-70% yields the highest rate of carbonation.

![Graph showing carbonation depth vs exposure period](image)

**Figure 1:** Carbonation depth of the control mortars (NT) under indoor and outdoor exposure

Figure 2 shows the microstructure of mortars after one year natural exposure at the depth of 3 mm from the exposed surface. Generally, dark areas show the lowest total atomic value (epoxy) which indicates the porosity of specimen, while the unreacted slag particles could be seen as light grey areas. Unhydrated clinker particles are even lighter. It is clearly seen in Figure 2a and 2c that carbonation induces severely shrinkage which leads to coarsening pore in the matrixes. This would be the result of decomposition of C-S-H phases and formation of porous silica products as shown in Eq. (4). The chemical reaction yields the reduction in volume of the matrix and substantially carbonation shrinkage.

![Microstructure images of mortars](image)

**Figure 2:** Microstructure of mortars after one year natural exposure

In Portland cement paste system, the matrix contains calcium hydroxide (CH) of about 15-20% by weight. The carbonation of CH forms calcium carbonate (CaCO₃) which compensates the pore volume increase due to carbonation shrinkage. The formation of CaCO₃ has another benefit to compensate the strength loss owing to the decomposition of C-S-H. However, because CEM III/B paste contains very low CH (about 1-2% by weight [10]), carbonation attack induces to coarser pore and even weaker microstructure compared with the OPC matrix. The photomicrographs obviously show that the BFSC cement matrix of the
control mortars (NT) were significantly damaged by the carbonation attack. With Na-MFP application, however, it was clearly seen that the pre-treatment obviously reduces the total porosity of the carbonated matrix (Figure 2b and 2d). The pore structures were significantly refined. The presence of Na-MFP in pore solution would improve bonding between the particle and hydration products. This could be a result of the reactions of $PO_3F^2$, $PO_4^{3-}$ and $F^-$ with Ca(OH)$_2$, CaCO$_3$ or porous silica which results possibly into fluorapatite $[Ca_5(PO_4)_3F]$ or carbonate fluorapatite $[Ca_5(PO_4,CO_3)_3F]$ as well as some amorphous formations. In comparison, the Outdoor-PRE has a denser structure than the Indoor-PRE specimen. It would be possible to claim that the external water supply from the environment (i.e. rain) hydrolyzes Na-MFP and promotes the formations of fluorapatite products. Hence, the pore coarsening in Outdoor-PRE was decreased accordingly. On the contrary, lacking of moisture in pore system of Indoor-PRE would cause inefficiency on the apatite formation.

Figure 3 shows the results of scaling weight due to frost salt attack per unit surface area of specimen. The scaling weights were measured after 2, 4 and 8 freezing-thawing cycles. For untreated specimens, indoor mortar had more severe scaling than the outdoor. The results indicate that both Na-MFP pre- and post-treatment methods reduced the frost scaling significantly. All treated specimens were scaled for between 0.6-2.1 kg/m$^2$ after 8 cycles, while the control was scaled for 16.9 and 8.6 kg/m$^2$ for indoor and outdoor exposures, respectively. As discussed earlier, it was found that a significant improvement of the microstructure can be observed only on the pre-treated outdoor mortars (Outdoor-PRE), but not on those pre-treated indoor (Indoor-PRE) specimens. However, in view of frost scaling durability, it would be remarked that it is not only the outdoor specimen but also the indoor exposed mortar showed potential to reduce the frost salt scaling to a comparable extend. A reasonable assumption might be that some apatite products can be formed in a short period of time. When the pre-treated specimen was immersed into the salt solution for the frost scaling test, the formation of apatite and fluorapatite can rapidly take place with supply of external moisture. Hence, the microstructure and frost scaling durability have been improved accordingly. For both indoor and outdoor exposures, it would also be noted that the pre-treatments performed slightly better than those post-treatments under the natural exposure in this work.

Figure 3: Frost salt scaling performance

Figure 4 shows the microstructures of carbonated matrixes under a 2000× magnification at a depth of about 3 mm from the exposed surface. Without treatment (Figure 4a and 4c), it is
clearly seen that the interfacial zone between slag particles and hydrated phases was severely damaged. Significant coarsening of the matrix and increase in the width of the interfacial zone would be due to the loss of chemically bound-water and consequent shrinkage during the carbonation of matrix. With Na-MFP treatment, however, the bonding of hydration products and unreacted slag particles seem quite strong and interconnected (Figure 4b and 4d). Significant amount of new amorphous products can be observed on the interfacial zone indicated by white arrows. Particularly for Outdoor-PRE specimen, the microphotograph shows a very dense microstructure compared with the control. The formation of apatite may probably be the superior contribution to the tensile strength of the matrix and also the interfacial zones.

The XRD spectrums of carbonated BFSC matrixes without and with Na-MFP treatment are presented in Figure 5. There was no remarkable new crystalline phase can be observed after Na-MFP treatment. The intensities of the calcium carbonate phases seem to be slightly decreased with the treatment, particularly for aragonite and vaterite. The disappearance of portlandite would be due to the reaction with Na-MFP. It would be noted that a remarkable increasing in the amorphous phase was observed after the treatment. Compared the spectrum to the literatures [11-14], these amorphous humps would show the presence of amorphous fluorapatite phase.

![Figure 4: The interfacial zone between unreacted slag particles and hydration products](image)

In dental research, Na-MFP is best known source of fluoride in toothpastes to protect tooth enamel from attack by bacteria that causes dental cavities. Basically, tooth enamel consists mostly of hydroxylapatite \([Ca_5(PO_4)_3OH]\). Although enamel is a hard and insoluble compound, acid produced especially after a high-sugar meal can attack the enamel. If fluoride ions (F\(^-\)) are present in saliva, fluorapatite \([Ca_5(PO_4)_3F]\) can be formed [15]. Fluorapatite resists attacks by acids better than original enamel itself, so the tooth enamel resists decay better than enamel containing no fluoride. For this reason, toothpaste typically contains a source of fluoride ions. The equation of fluorapatite formation on enamel is as shown below.

\[
Ca_5(PO_4)_3OH + F^- \rightarrow Ca_5(PO_4)_3F
\] (5)

The reaction of Na-MFP to carbonated BFSC matrix is quite similar to the tooth decay protection. In dental, Na-MFP supplies fluoride to form fluorapatite on enamel. In carbonated BFSC matrix treatment, however, Na-MFP hydrolyzed into the pore solution to form phosphate and fluoride ions. Eventually, these ions react with portlandite and calcium carbonate phases (aragonite and vaterite) to form fluorapatite and carbonate fluorapatite. Different than the tooth decay protection, not only fluoride, the paste matrix requires fluoride and also phosphate ions to create the fluorapatite. The amorphous humps (at about 32°, 39°
and 48° 20 Cu Kα) found in Na-MFP treated specimen (Figure 5b) was very well accorded to
the XRD pattern of natural amorphous fluorapatite found in tooth enamel reported by various
dental research works [11-14]. Hence, it can be confirmed that the amorphous product found
in Na-MFP treated matrix (Figure 4) would be amorphous fluorapatite. Regarding to the
Mohs scale of mineral hardness [16], apatite has a hardness of about 5, while the calcium
carbonate is only about 3. It would be noted that the Mohs hardness is an ordinal scale. The
absolute hardness of apatite measured by sclerometer is between 5-6 times as hard as calcite
[15]. This transformation would increase the strength and improve the frost scaling durability
of carbonated BFSC matrix. Apart from the transformation of carbonate phases, the
improvement of bonding between the unreacted particles and hydration products due to
apatite formation would be also another factor which promotes the micro-mechanical
properties of carbonated BFSC matrix.

![Figure 5: XRD diffractograms of carbonated BFSC pastes [2]](image)

From the experiments, both Na-MFP pre- and post-treatment methods are promising to
prevent frost scaling problem on BSFC mixes. However, in practice view, the methods of
Na-MFP pre-treatment performed during the construction period would be more convenient
than the surface post-treatment which has to be performed during the service of structure.
Apart from frost scaling problem, the application of Na-MFP would have a potential to
promote other mechanical properties of BFSC concrete, particular the surface strength. The
improvement on abrasion and erosion resistances of the concrete might be able to expect, and
would be studied in future works.

4. CONCLUSIONS

The using of 10% Na-MFP solution as a surface treatment compound for carbonated 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 with the
untreated control. The pore coarsening of carbonated matrix was considerably reduced, and
the quality of the ITZ between sand and matrix was improved. The mortars with Na-MFP
treatment showed significantly better frost salt scaling durability compared with the untreated
control. The study on microstructure shows the presence of sponge-like amorphous phase in
treated matrix bonding the hydration product and unreacted slag particles. The results from
XRD analysis and some literatures in dental research suggested that the sponge-like mineral
would be amorphous fluorapatite and carbonate fluorapatite.
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