Application of encapsulated lightweight aggregate impregnated with sodium monofluorophosphate as a self-healing agent in blast furnace slag mortar

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This paper studies the potential of using expanded clay lightweight aggregate impregnated with sodium monofluorophosphate (Na_2FPO_3) solution which is eventually encapsulated by a cement paste layer to produce a self-healing system in blast furnace slag cement mortars. It was found that the technique significantly improved the quality of the interfacial transition zone in mortars subjected to carbonation shrinkage. Consequently the frost salt scaling durability of blast furnace slag mortars was evidently promoted. The findings from ESEM and EDS studies showed that the healing mechanism would be due to the combination of treatment by Na_2FPO_3 solution and calcium hydroxide supplied from the cement paste coating layer.

Keywords: Blast furnace slag cement, capillary water absorption, carbonation, freezing and thawing, sodium monofluorophosphate, self-healing

1   Introduction

Blast furnace slag cement (BFSC) is one of the most important products of the cement industry 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 additive to use in concrete, particularly in low-heat concrete for massive structures. Apart from the low-heat application, the superior durability of BFSC against aggressive environment promotes this cement as a suitable binder for concrete exposed to chloride, acid and sulfate attack. Though using BFS in concrete has several benefits, it is generally known that concrete bearing high amount of BFS has a poor resistance against carbonation shrinkage owing to its significantly low $Ca(OH)_2$ content. Carbonation shrinkage causes micro-cracking and degrades the micro-

mechanical properties and durability of the BFSC concrete drastically. For instance, frost salt scaling is considered as one of the most serious threats to carbonated BFS-rich concrete infrastructure. Because of disintegration of the concrete surface, other types of attack on the structure would have more chance, which can result in a dramatic decrease in durability.

Sodium-monofluorophosphate (Na_2FPO_3; referred to as *Na-MFP* from this point on) treatment is one of the corrosion inhibition agents for reinforced concrete, which is widely studied. The mechanism of Na-MFP on corrosion inhibition has been studied by various researchers [Andrade et al. 1992; Alonso et al. 1996; Ngala et al. 2003]. It was recently reported that Na-MFP treatment is beneficial to improve frost salt scaling resistance of carbonated BFSC concrete. In previous works [Copuroglu et al. 2006; Sisomphon et al. 2009], a solution of 10% Na-MFP was used as a surface treatment compound on hardened BFSC pastes and mortars, and the influence of the application before and after carbonation attack (*pre- or post-treatment*) was investigated. The results from the experiments reveal that the treatments significantly improve the frost salt scaling resistance of carbonated BFSC mortar. Moreover, the carbonation rate and capillary water uptake of the treated mortars were substantially decreased compared with untreated specimens. It was found that the reactions of the free phosphate and fluorophosphate with hydration and carbonation products yield stable amorphous formations analogous to apatite. The XRD results show strong evidence of the presence of amorphous products. The results of pre-treatment are promising with respect to the potential use of Na-MFP as a self-healing agent for BFSC concrete subjected to carbonation and frost salt scaling problems.

In view of microstructure, a significant coarsening of the matrix porosity and increased width of interfacial zones between unreacted slag particles and hydration products has been observed after carbonation attack. With Na-MFP treatment, however, the bonding of hydration products and unreacted slag particles seems stronger and interconnected. A meaningful amount of sponge-like new formations were observed. It was found that the new formations appear in the matrix as well as the interfacial zones. The EDS study shows the presence of fluoride and phosphate along with the existing Ca, Mg, Si and S of the treated paste [Copuroglu et al. 2006].

The XRD results demonstrate three different carbonate polymorphs (calcite, vaterite and aragonite) which existed both before and after the treatment. However, the spectrum

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intensities of the carbonated phases, particularly metastable vaterite and aragonite in treated samples, became lower than in the original untreated carbonated sample. The study results into a hypothesis that the reaction between Na-MFP and vaterite/aragonite phases may lead to a resistant carbonation zone of the BFSC paste against frost salt attack. It was found, however, that there was no reaction between calcite and Na-MFP. Additionally, an increase in the amorphous phase (mainly between 23° and 35° 2θ Cu kα) can be observed in the carbonated samples after the treatment. It was concluded that the main role of Na-MFP treatment probably contributes to an increased tensile strength of the matrix and the interfacial zones. This could be due to the reaction of PO_3F^{2-}, PO_4^{3-} and F- with $Ca(OH)_2$, $CaCO_3$ or porous silicate hydrate which results possibly into fluorapatite ($Ca_5(PO_4)_3F$) or carbonate fluorapatite ($Ca_5(PO_4,CO_3)_3F$). Unknown amorphous humps were often seen in the XRD spectrum after the treatment. The improvement of the microstructure leading to a higher tensile resistance of BFSC systems against frost salt scaling was the conclusion of the study. The theoretical background related to the interaction between Na-MFP and the hydrated products was discussed in detail previously [Copuroglu et al. 2006; Sisomphon et al. 2009].

The aforementioned work revealed a high potential of using Na-MFP as a surface treatment compound to heal carbonated BFSC concrete. However, the surface treatment method may not be convenient in several applications on site. The target of this study is to investigate the possibility of introducing a self-healing ability in BFSC concrete structures which can be potentially affected by carbonation and frost salt scaling. The main objective is to study the effectiveness of using Na-MFP as a self healing agent in the cementitious system, which would enable self-healing of the carbonated microstructure autonomously without any requirement of external application.

2   Experimental investigation

2.1   Materials

A BFSC with a slag content of 67% (CEM III /B 42,5 N HSR LH) from ENCI cement manufacturer was used. The typical chemical and physical properties were presented in Table 1. Two types of fine aggregate, normal quartz sand and expanded clay lightweight aggregate (LWA), were used in this study. The main target of this project was to produce a self-healing medium made of Na-MFP encapsulated in LWA of which the preparation

process will be explained in detail in *Section 2.2*. A treatment solution prepared from 95% purity laboratory grade Na-MFP was used throughout this study.

Table 1. Properties of BFSC used in the experiment

Chemical (%wt)		Physical	
		Strength of standard mortars	
CaO	45.00%	2 days	12.1 N/mm²
SiO$_2$	27.60%	7 days	32.7 N/mm²
Al$_2$O$_3$	12.20%	28 days	53.2 N/mm²
Fe$_2$O$_3$	1.27%		
SO$_3$	3.25%	Fineness (Blaine)	376 m²/kg

The fundamental idea of this study is to provide the Na-MFP solution to the BFSC mixture upon carbonation without any external intervention. In a preliminary trial, it was found that it is impractical to add Na-MFP solution directly into the mixture during the mixing process. The compound significantly retards the time of setting (longer than 2-3 days for initial setting) which furthermore causes serious problems of bleeding and segregation. To prevent those problems, the compound has to be encapsulated which it can be released to the matrix after the mixture has reached an acceptable maturity or degree of carbonation. Ideally, the compound would be perfectly encapsulated inside the LWA until carbonation reaches the capsules.

2.2 *Preparation of encapsulated light-weight aggregate*

The expanded clay lightweight aggregate "*Liapor fit*" which has a maximum size of 4 mm was used as "container" for the healing agent (Na-MFP solution) in this research. Figure 1 shows the water absorption rate of this type of LWA. It can be seen that the LWA has an absorption of about 22% by weight in the first 24 hours upon immersion, and then the absorption remained almost unchanged under atmospheric conditions. With vacuum pressure, however, it was found that the water absorption was raised to as high as 41% by weight within 30 minutes of immersion. After that, no further absorption can be observed. Compared to soaking under atmospheric condition, the absorption was almost doubled by using vacuum.

In the preparation process, the original air-dried LWA was soaked into a 40% Na-MFP by mass solution under vacuum pressure for 30 minutes. After the impregnation, the excess solution was removed by using a thin filter paper, and the aggregate was slightly dried by tissue papers. Then, the LWA was weighted and hand-mixed with cement powder in order to establish a coating around the particles for encapsulation. Two different types of cement, namely CEM I 42,5 R and CEM III /B 42,5 N HSR LH, were used as coating materials. A cement-to-LWA ratio of 0.30 was mainatined throughout the study. During mixing, the particles were sprayed with some deionized water to ensure that there was sufficient moisture available and that all cement was thoroughly attached to the surface of LWA. After that, the container with encapsulated LWA was covered with a damp cloth for 72 hours. Since increasing the temperature raises the rate of cement hydration, the encapsulated LWA was thereafter steam-cured at 65°C and 100% RH for 28 days. The container was agitated from time to time to prevent agglomeration of particles. Vapor condensation causes excess water which has to be drained from time to time. The accelerated high temperature curing provided a thin layer of cement paste which was assumed to be almost completely hydrated. As the paste layer has been thoroughly reacted beforehand, further hydration of the coating layer would be minimized when the encapsulated LWA was mixed into the mortars. The condition of the LWA before and after the encapsulation is shown in Figure 2a and 2b, respectively.
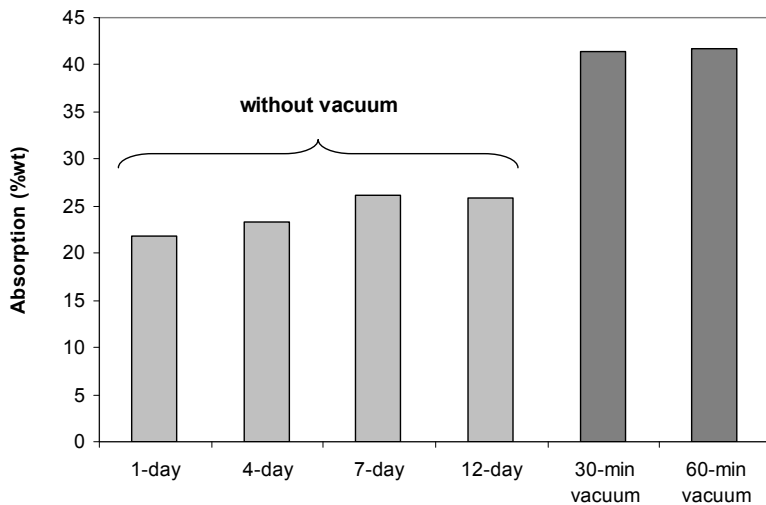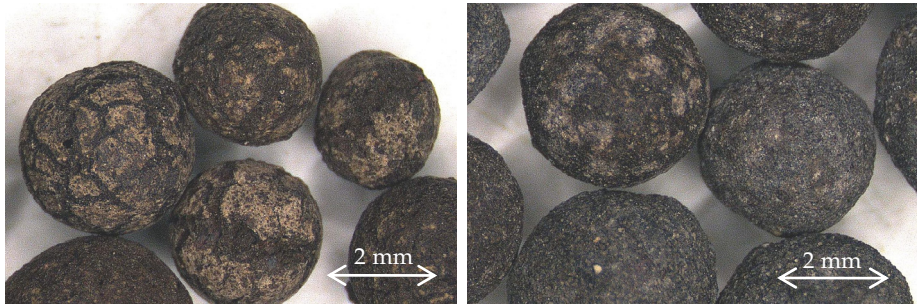

Figure 1. Water absorption of LWA

(a) Original LWA   *(b) Encapsulated LWA (OPC coating)*

Figure 2. Condition of lightweight aggregate

2.3 *Mix design, preparation and testing*

The mortars with water-to-cement ratio of 0.45 were prepared for this study. Blast-furnace slag cement (CEM III /B 42,5 N HSR LH) was used for all mixtures. The control mortar (*mSC*) was designed based on sand-to-cement ratio of 2.5 by mass. In the encapsulated LWA manufacturing, two different types of cement were used as coating materials; namely CEM I 42,5 R and CEM III /B 42,5 N HSR LH. The mortars prepared from these encapsulated LWAs were designated as *mELWA1* and *mELWA3*, respectively. These mortars with encapsulated LWAs were formulated to maintain the volume fraction of aggregate phase similar to the control mix. The encapsulated LWA-to-cement ratio was found to be about 1.086 by weight. The estimated unit weights of mortars can be calculated from mix proportions which were 2203, 1414 and 1321 kg/m³ for *mSC*, *mELWA1* and *mELWA3*, respectively.

For mortar mixing, the mixing sequence was 2 minutes low speed followed by 2 minutes medium speed mixing with a 5-litre commercial Hobart mixer. The specimens were cast in plastic containers with 55 mm diameter to a height of about 50 mm. The containers with fresh mortar were vibrated for 10 s on a vibrating table. Then, the containers were capped and stored in laboratory air. After 24 hours, the moulds were removed, and the specimens were submerged in tap water with a controlled temperature of 25±3°C for 3 days.

Thereafter, all specimens were pre-conditioned in a dessicator with CO_2 free environment and 50-55% relative humidity until an age of 28 days. The circumference surface and the bottom area were coated with epoxy. The top trowel surface was the only area which was exposed to the environment. Accelerated carbonation was performed on the specimens

after pre-conditioning. The accelerated carbonation environment provides a carbon dioxide concentration of 3% by volume, with 65% relative humidity and 25°C. Eventually, the carbonation zone can be visualized by spraying phenolphthalein indicator on a freshly broken surface.

After 28 days accelerated carbonation and then 28 days air drying, the uncoated surface was facing downward immersed into the water pond which was kept to a constant level at about 5 mm above the specimen surface to investigate the rate of capillary water uptake. The specimens were placed on glass rods to allow free access of water. Each specimen was weighed and returned to the pond within 30 s in each investigation. Before weighing, the excess water on the surface was wiped off with clean damp tissue paper. Because the water penetration is mainly due to capillary force, the clock was not paused during the measurement. The weight change of each specimen was monitored with respect to immersion time to determine the rate of water uptake.

Another set of specimens was subjected to frost salt scaling tests conforming ASTM C672 freezing-thawing cycle, which consists of 17 h freezing at -20°C and then 7 h at 25°C. The uncoated specimen surface was facing downward submerged into a 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 using a filter paper up to 7 cycles. The scaling material was weighed after 24 hours drying at 105°C.

The microstructure of mortars was studied using environmental scanning electron microscope (ESEM), equipped with energy dispersion spectroscopy (EDS). The specimens were vertically cut to a thickness of about 5 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 was used for preparing perfectly smooth ESEM specimens. Then, the specimens were polished with 6 μm, 3 μm, 1 μm and 0.25 μm diamond pastes, respectively. Low viscosity epoxy was used to maintain the integrity of the samples and the matrix. In addition to the microstructure, the presence of Na-MFP was evaluated by determining the element contents in the surrounding matrix, which elements were taken as indicators.

*2.4   Principle of encapsulation and healing processes*

As shown in Figure 3, the mechanisms of encapsulation and healing in carbonated BFSC mortars with the encapsulated LWA can be explained as follows:

i.   The LWA is impregnated with Na-MFP solution by the method presented in *Section 2.2*. The particles are coated with a cement paste layer to prevent the undesirable early reaction between the compound and the matrix.

ii.   After steam curing, the encapsulated LWA is ready to be used as a healing medium in mortar or concrete. When the LWA is introduced to the mixture, any further hydration of the coating paste layer has been minimized due to pre-curing at high temperature.

iii.   In the long term, gaseous CO_2 diffuses into concrete, and carbonation attack damages the microstructure of the matrix.

iv.   When the carbonation front reaches the encapsulated LWA, the porosity of the coating layer also becomes coarsened due to carbonation shrinkage. The permeability of the coating layer would be increased. With presence of moisture, the Na-MFP solution diffuses into the matrix, and the healing process would take place.

v.   Apatite products are formed and the microstructure of the matrix becomes denser and stronger.

3   Results and discussion

Figure 4 shows the microstructure of the control mortar (*mSC*) investigated by ESEM in the backscattered electron (BSE) detector mode. The photomicrographs show that the CO_2 attack on the BFS rich matrix causes a substantial shrinkage, which induces pore coarsening. The phenolphthalein test was used for determining the carbonation zone. The dense microstructure can be observed in the area where the mortar has not been carbonated. NB: The dark areas in the BSE micrograph represent the porosity. Unreacted slag can be seen as light grey areas, while unreacted clinker particles are rather bright. At 500× magnification, coarsening of the pore structure can be observed particularly in the interfacial transition zone (ITZ) between aggregate and carbonated matrix. The severe coarsening can be seen in the first 100 µm distance from the aggregate surface.

In encapsulated LWA systems, very dense coating paste layers around LWA particles can be observed as seen in Figure 5(a) and 5(c) for *mLWA1* (*OPC coating*) and *mLWA3* (*BFSC coating*), respectively. The protective layer prevents the Na-MFP compound leaching to the
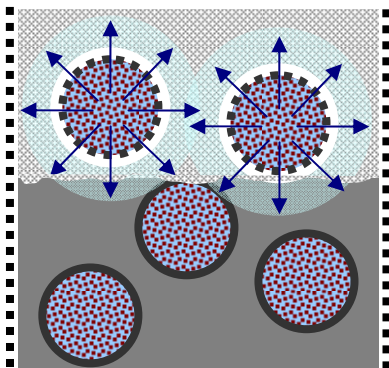
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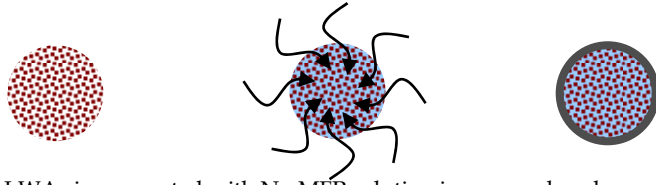
(I) LWAs impregnated with Na-MFP solution is prepared under vacuum. Then, the particles are encapsulated in a cement paste layer.
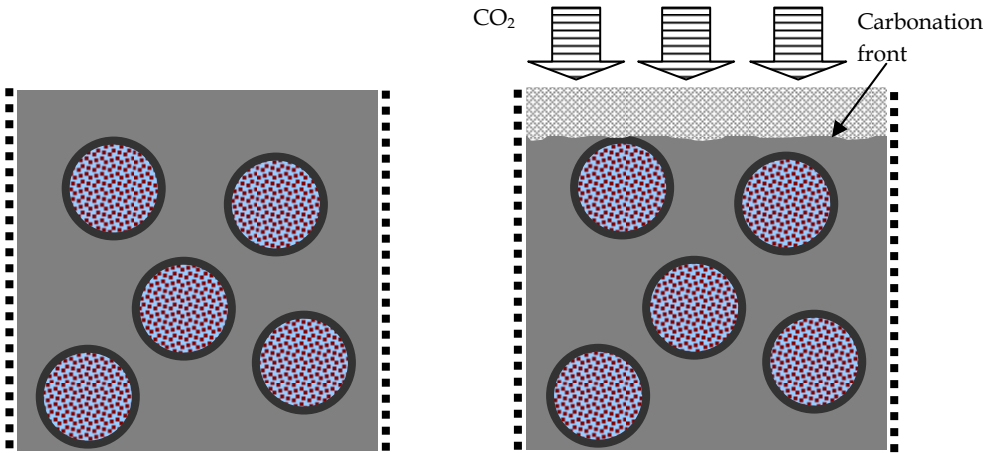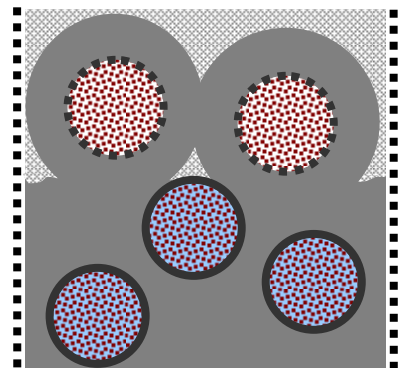
(II) Encapsulated LWA embedded in the matrix

(III) Carbonation coarsens the matrix porosity

(IV) Carbonation damages the coating layer. Na-MFP is released to the matrix

(V) Healing takes place. The microstructure of the matrix is improved.

Figure 3. Mechanisms of encapsulation and healing process

matrix. After carbonation, the porosity coarsening took place not only in the matrix zone, but also on the coating layer of LWA. This phenomenon would induce a carbonation triggered mechanism which allows the encapsulated Na-MFP to become released to the matrix after the coating paste layer has been attacked by CO_2. The influence of carbonation attack on the microstructure of the coating layer and the interfacial transition zone (ITZ) can be clearly seen in Figure 5(b) and 5(d) for *mLWA1* and *mLWA3*, respectively. In the presence of moisture, leached-out Na-MFP solution would diffuse to the surrounding matrix. Eventually, not only the denser ITZ can be observed (Fig. 5), but the quality of the bulk matrix in the carbonated zone was also significantly improved (Fig. 6).
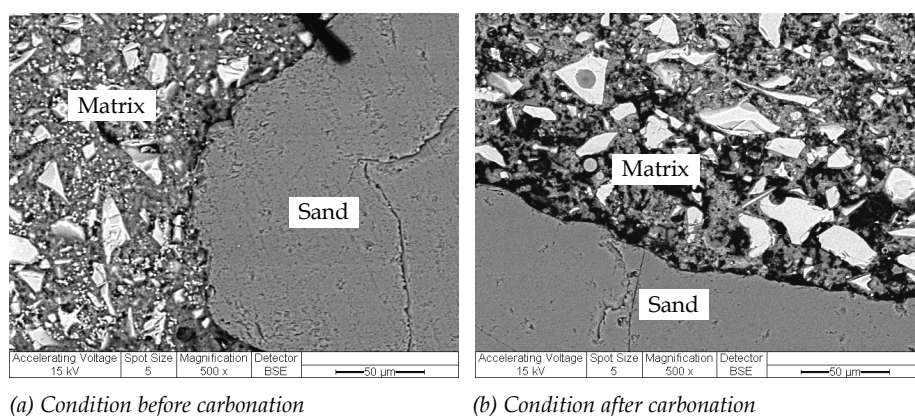

(a) Condition before carbonation   *(b) Condition after carbonation*

Figure 4. ITZ of control mortar (mSC) before and after carbonation

It was reported in previous studies [Copuroglu et al. 2006; Sisomphon et al. 2009] that carbonation causes shrinkage of the matrix of BFSC mixtures due to the low portlandite (CH) content. The decomposition of C-S-H phases and formation of porous silica gel introduce shrinkage during carbonation of the matrix. Generally, BFSC (CEM III /B 42,5 NWHS NA) produces a paste that contains CH as low as 1-2% by mass, while the paste made of OPC (CEM I 42,5 R) contains CH up to 20% [Sisomphon and Franke 2004]. Owing to the low CH in CEM III /B paste, the carbonation process induces a coarser and even weaker microstructure compared to OPC [Wowra 2002]. It is known that the presence of CH in a given cement system is regarded as a favorable property with respect to carbonation. Copuroglu [Copuroglu 2006] studied the influence of CH addition to BFSC mixtures on carbonation and frost salt durability. However, the experimental results reveal that there was no significant difference for BFSC mortars with and without CH addition against frost salt scaling. One of the reasons of the unsatisfactory performance could be

because of the inefficiency of the preparation method. In the study, pure CH was mixed with CEM III /B powder during mixture preparation. However, in the course of Portland cement hydration normally relatively well-distributed portlandite crystals (CH) are produced over the entire volume. This might enable uniform calcite formation and avoids agglomeration in certain locations. Agglomeration leaves space for a coarsening carbonation reaction of the calcium silicate phases. It would be also remarked that CH is a substance which has relatively low water solubility (~ 1.5-1.7 g/l at 25°C [Duchesne and Reardon 1995]). In concrete pore solution, the solubility of CH would become even lower with presence of alkali, i.e. sodium and potassium. It might be impossible to dissolve and well-distribute CH all over the mixture during the mixing process. Moreover, another problem might be the precipitation of carbonate micro-crystals on the surface of CH [Groves et al. 1991]. Thus, the surface of CH clusters is covered by secondary carbonate micro-crystals, and this formation prevents further carbonation of remaining CH crystals.

(a) mELWA1 before carbonation *(b) mELWA1 after carbonation*

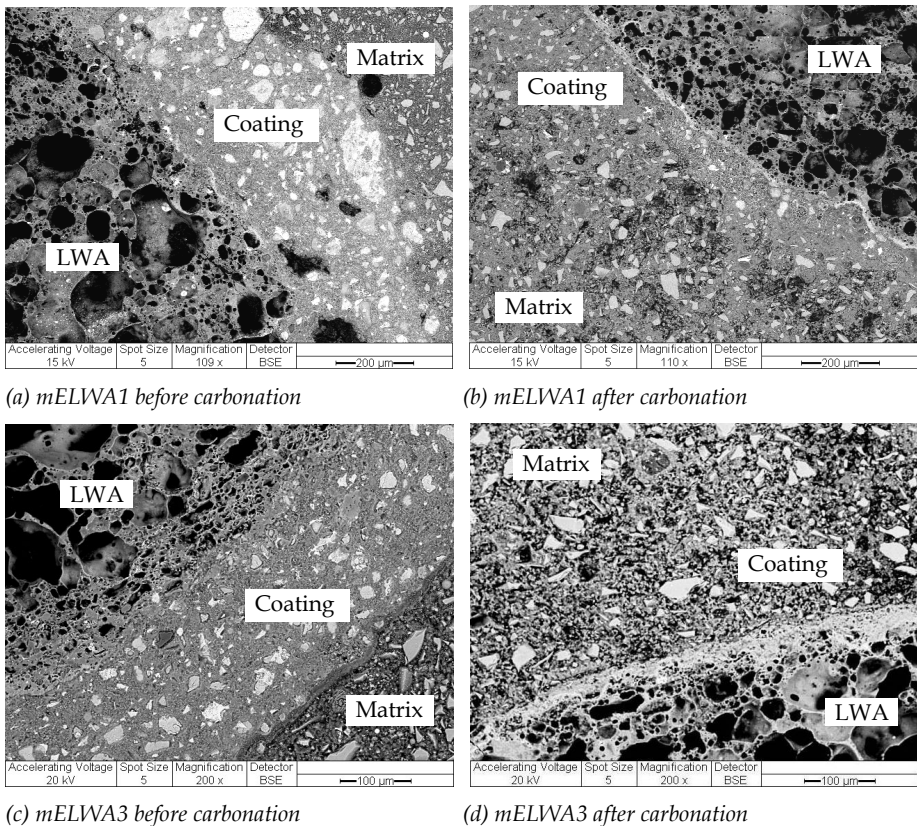*(c) mELWA3 before carbonation* *(d) mELWA3 after carbonation*

Figure 5. ITZ of encapsulated LWA mortars before and after carbonation

At first sight, it seems a possibility that CH addition into the BFSC mixture would decrease carbonation propagation and frost salt scaling. Nevertheless, the effect of introducing CH into BFSC mixtures is still ambiguous. In the present study, the role of OPC paste coating on encapsulated LWA (*in mELWA1*) is not only for encapsulation purpose, but also to supply CH to the matrix. The carbonation of CH forms calcite which compensates the pore volume increase due to porous silica formation. As the source of CH was attached to the surface of fine aggregate, it would be more effective to obtain well-distributed CH in the matrix than adding pure CH powder to the fresh mix directly. In future studies, this idea might be extended to the method of using OPC concrete debris as recycled aggregate to supply CH to BFSC concrete or other pozzolan mixtures to suppress carbonation.

Although the OPC coating has a benefit to supply CH to the matrix, BFSC coating also has an advantage in another aspect as it is more vulnerable to carbonation. As seen in Figure 5 (d), the BFSC coating layer was severely coarsened, and the encapsulated Na-MFP solution would more easily be released. In Figure 7, the result of EDS analysis performed on specimens in carbonated and non-carbonated zones was presented. The results showed that some leaching of the compound can be detected as increments of Na, P and F in the matrixes of *mELWA1* and *mELWA3* mortars. At 500× magnification, the concentration of Na-MFP in the matrix area at the position about 500 μm apart from the LWA surface was determined. The concentration was measured at 10 different randomly selected paste locations through the area. The measurements were performed at a depth of 7 mm from the mortar surface to represent the carbonated zone, and at a depth of 12 mm for the non-carbonated zone. The results indicate that the encapsulated LWA releases a significant amount of Na-MFP. As reference datum, it would be noted that the phosphorous concentration determined from *mSC* was only about 1% by weight. For *mELWA3*, the phosphorous concentration of about 14% by weight can be detected in the carbonated area, while an obviously lower concentration (about 4% by weight) was observed in the non-carbonated area. This result would confirm the efficiency of a carbonation triggered mechanism of the encapsulation system. The encapsulated compound was released after the matrix and coating layer have been attacked by carbon dioxide. In non-carbonated areas, however, the coating layer protected the encapsulated compound well. Also for *mELWA1*, the leaching of encapsulated Na-MFP after carbonation can be observed. However, the phosphorous concentration was significantly lower compared to that in the carbonated *mELWA3*. This might be possibly due to higher physical and also chemical

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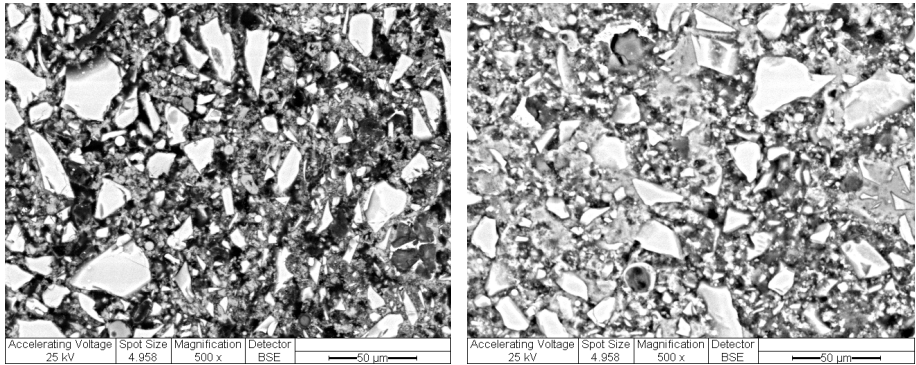
(a) Matrix of mSC

(b) Matrix of mELWA1
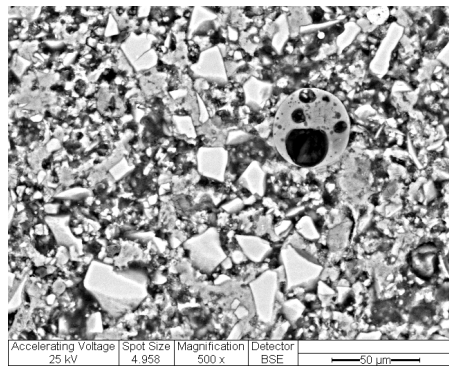
(c) Matrix of mELWA3

Figure 6. BSE photomicrographs of the carbonated matrix

binding abilities of OPC paste coating. As clearly seen in Figure 5, the coating layer in *mLWA1* was less damaged compared to that in *mLWA3*.

A frost salt scaling test was started when the mortars had been carbonated for 28 days. It should be noted that the mortars studied in this experiment had significant differences in unit weight. As the specific gravity of quartz sand and LWA are rather different, it may not be appropriate to compare the condition of scaling among mortars directly by weight, as is the usual practice. The results are evaluated and compared here in terms of scaling volume or scaling depth and visual surface characteristics. As the unit weight of each mortar (reported in *Section 2.3*) can be estimated from the mix proportion, the scaling weights can be converted to the scaling volume. Eventually, the scaling depth can be determined as the results shown in Figure 8. It is clearly seen that the mortars with encapsulated LWA had significantly lower scaling depths compared to the control. The *mELWA1* mortar showed

slightly lower depth of scaling compared to *mELWA3*. The conditions of mortars after 2-cycle frost scaling are shown in Figure 9. There was almost no scaling that can be observed on the mortars with encapsulated LWA, while the top surface area of the control mortar was severely damaged. Figure 10 compares the amount of capillary absorbed water into the mortars. Though LWA is originally more porous than quartz sand, it is clearly seen from the experimental results that *mELWA1* and *mELWA3* specimens absorbed less water than the control mortar. At 8 hours immersion, the relative amounts of water uptake were about 83% and 76% for *mELWA1* and *mELWA3*, respectively, compared to 100% for the control mortar (*mSC*). The reduction in the capillary water absorption can result in an improvement of the durability of concrete exposed to severe environments.

For the *mELWA1* mortar, it appears that the carbonation of CH would reduce the volume of pore coarsening. However, the role of Na-MFP is also important as it increases the tensile strength of the matrix by transforming vaterite and aragonite to stable amorphous phases [Copuroglu et al. 2006]. In future studies, the coating layer of encapsulated LWA could be modified to promote diffusion rate of Na-MFP. An optimized healing process would be achieved by balancing supplies between CH and Na-MFP. In addition, the particle size-distribution of encapsulated LWA could be also optimized to improve the
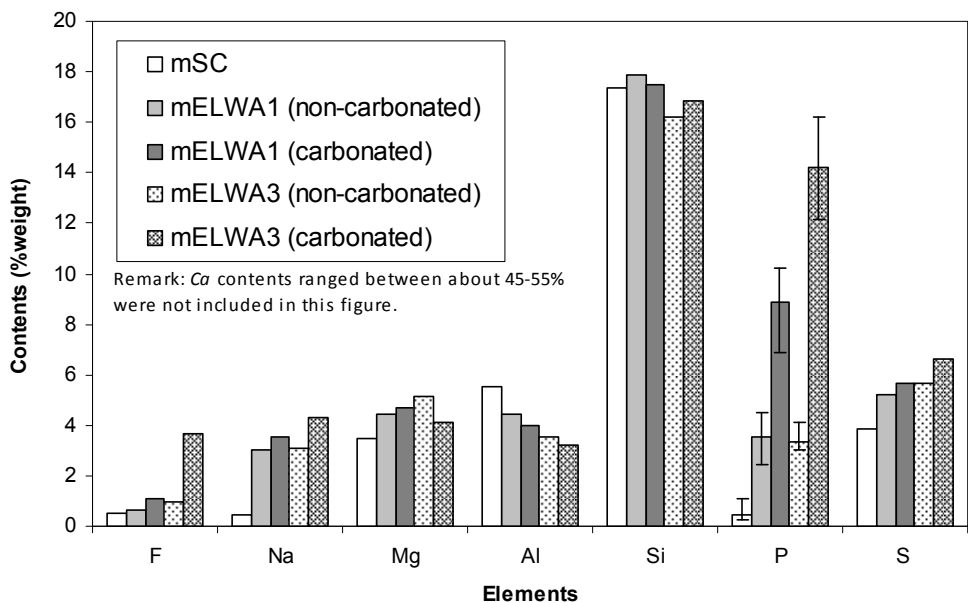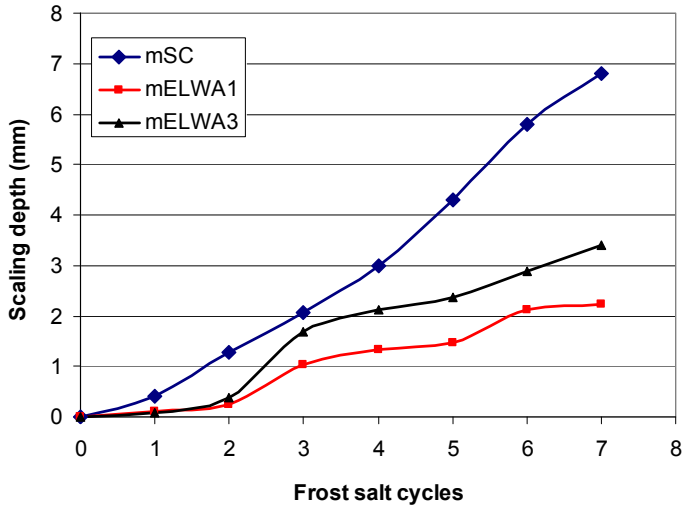

Figure 7. Element contents in the matrixes

Figure 8. Scaling depth of carbonated mortars subjected to frost salt scaling

healing mechanism. It is expected that a smaller size of encapsulated LWA would enhance the healing mechanism. Apart from frost scaling durability, the application of Na-MFP would have a potential to promote other mechanical properties of BFSC concrete, in particular the surface strength. An improvement of abrasion or erosion resistances of the concrete might be expected, and should be studied in future work. Moreover, inspired by the OPC coating on encapsulated LWA, the idea might be extended to the method of partially using (Portland cement) concrete debris as crushed to fine aggregate to supply CH for pozzolanic mixtures.

As discussed in previous work [Copuroglu et al. 2006], the reaction between Na-MFP and the calcium compounds in the matrix results possibly into fluorapatite or carbonate fluorapatite which would have a superior contribution to the tensile strength of the matrix. The XRD spectra of carbonated BFSC cement pastes without and with Na-MFP treatment are presented in Figure 11(a) and (b), respectively. 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 increase in the unknown amorphous phase was observed after the treatment. Comparing the spectra from literature [Nelson et al. 1984; Ishikawa et al. 1994;

(a) mSC
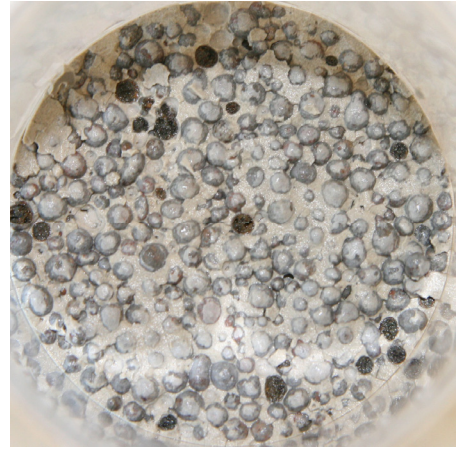
(b) mELWA1
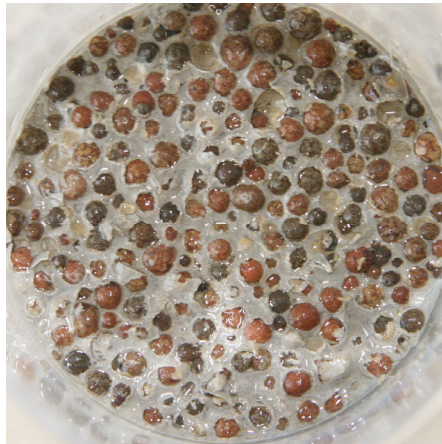
(c) mELWA3

Figure 9. Condition of carbonated mortars after 2 cycles of frost scaling

Legfros et al. 1996], these amorphous humps could show the presence of amorphous fluorapatite.

In dental research, Na-MFP is the best known source of fluoride in toothpastes to protect tooth enamel from attack by bacteria that cause dental cavities. Basically, tooth enamel consists mostly of hydroxylapatite [$Ca_5(PO_4)_3OH$]. Even though 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. Fluorapatite resists attack by acids better than the original enamel itself, so the fluoride-

modified tooth enamel resists decay better than enamel containing no fluoride [Davis et al. 1999]. For this reason, toothpaste typically contains a source of fluoride ions. The equation of fluorapatite formation on enamel is as shown below.

$$Ca_5(PO_4)_3OH + F^- \rightarrow Ca_5(PO_4)_3F + OH^- \tag{1}$$
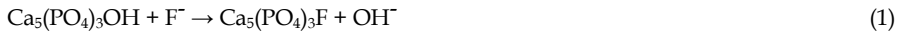
The reaction of Na-MFP in carbonated BFSC matrix is comparable to tooth enamel decay protection. In dental protection, Na-MFP supplies fluoride to form fluorapatite on enamel. In carbonated BFSC matrix treatment, however, Na-MFP hydrolyzes into the pore solution to form phosphate and fluoride ions. Eventually, these ions react with portlandite and calcium carbonate phases (*aragonite and vaterite*) to form fluorapatite and carbonate fluorapatite. Different from tooth decay protection, the paste matrix requires fluoride and also phosphate ions to create fluorapatite. The amorphous humps (at about 32°, 39° and 48° 2θ Cu Kα) found in the Na-MFP treated specimen (Fig. 11b) correspond well to the XRD pattern of natural amorphous fluorapatite found in tooth enamel reported by various dental research works [Nelson et al. 1984; Ishikawa et al. 1994; Legfros et al. 1996]. Hence, it can be confirmed that the amorphous product found in Na-MFP treated matrix would be amorphous fluorapatite. Regarding to the Mohs scale of mineral hardness [Wilkes et al. 2005], apatite has a hardness of about 5, while calcium carbonate is only about 3. This
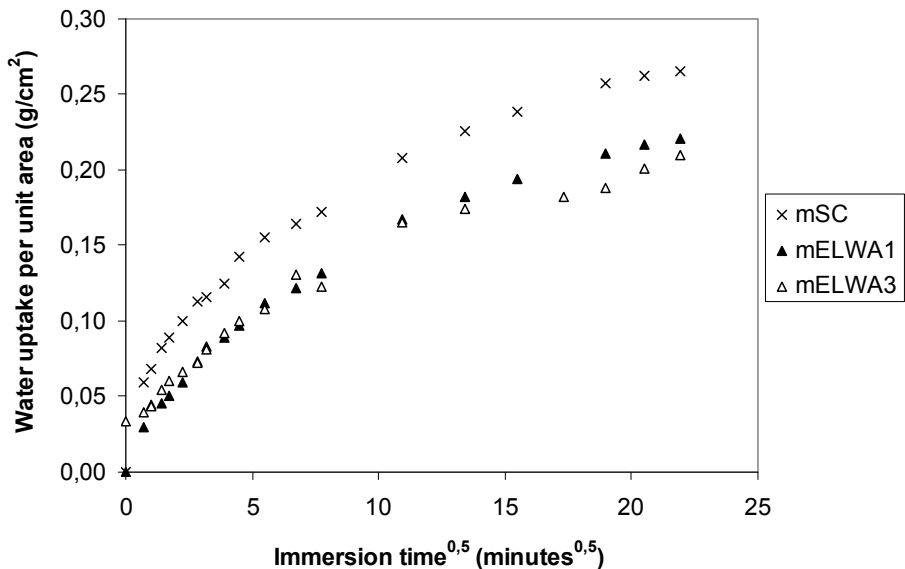

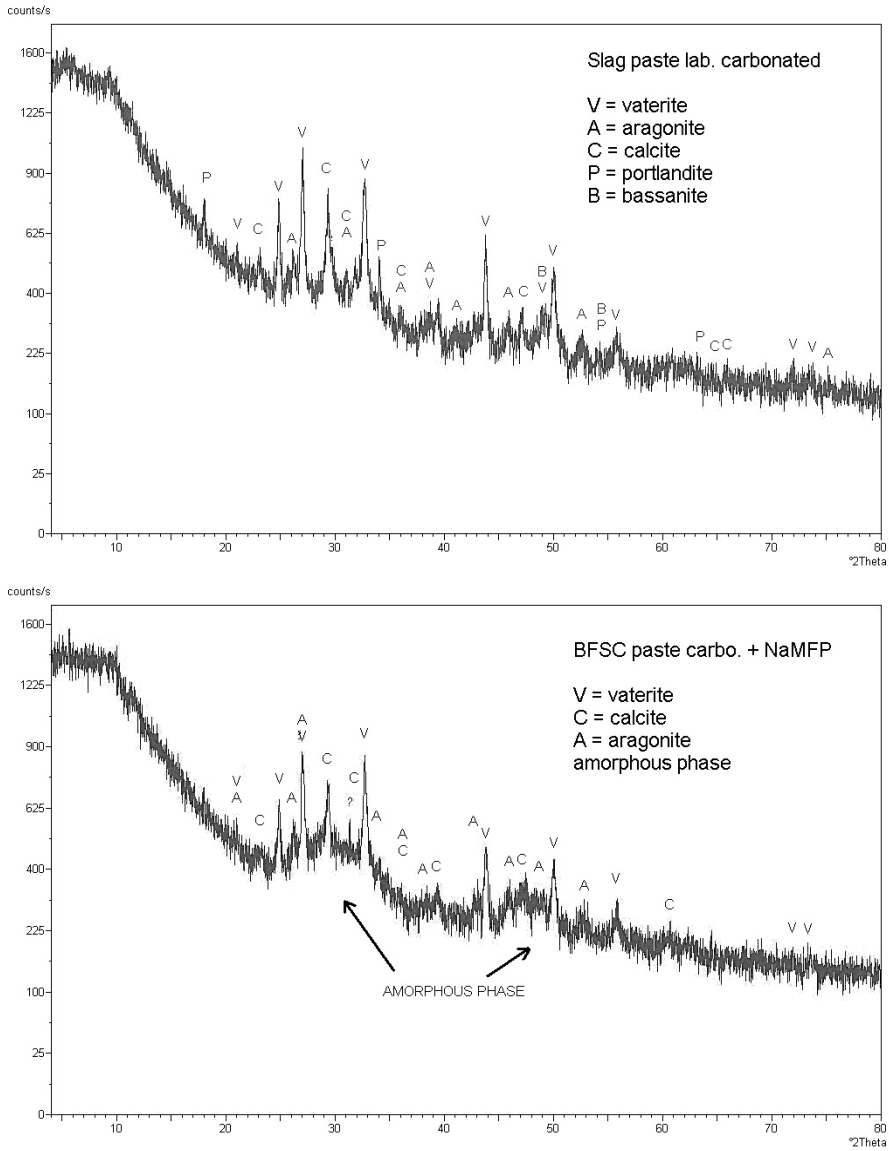*Figure 10. Capillary water uptake of carbonated mortars*

Figure 11. XRD diffractograms of carbonated BFSC pastes [Copuroglu et al. 2006]

transformation would increase the strength and improve the frost scaling durability of carbonated BFSC matrix. Apart from the transformation of cement phases, the improvement of bonding between the unreacted particles and hydration products due to apatite formation would be also another important factor which promotes the micro-mechanical properties of carbonated BFSC matrix.

30

4   Conclusion

A self-healing system for carbonated blast furnace slag mixtures subjected to carbonation and frost salt scaling attack was proposed. Expanded clay lightweight aggregate impregnated with Na-MFP solution which is subsequently coated with a cement paste layer was used as a healing medium. The experimental results from freezing and thawing tests reveal that the mortars with encapsulated LWA showed a better resistance against frost salt attack. The capillary water absorption was obviously decreased compared to the mortar with normal fine aggregate. The ESEM results showed an improvement of the pore structure of the carbonated matrix particularly on the aggregate/cement paste interfacial transition zone. From EDS results, significant sodium, phosphorous and fluoride leaching from encapsulated LWA to the matrix can be observed. The healing mechanism would be due to the reaction of Na-MFP compound and CH supplied from the coating Portland cement paste layer.

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