Frost Salt Scaling Resistance Improvement of GGBFS Concrete by Na-MFP Treatment

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Abstract

An investigation has been performed into a treatment of the surface of ground granulated blast furnace slag (GGBFS) cement concrete in order to improve the frost salt scaling resistance. A sodium monofluorophosphate (Na-MFP) solution has been applied. The results show that the resistance is substantially improved. The microstructural characteristics are also discussed. In addition, the effect of various percentages of Na-MFP solution on frost salt scaling resistance of GGBFS mortar phase is presented. It is concluded that the Na-MFP treatment modifies the carbonate phases and improves the early resistance of the GGBFS cement matrix with water to cement ratio of 0.45 against frost salt scaling attack.

Introduction

GGBFS cements produced in the Netherlands contain high percentages of ground granulated slag. Its use reduces the environmental effects of the production of GGBFS cement compared to ordinary Portland cement (OPC). It requires less energy and emits less CO_2 to the environment (Bijen 1998).

The favorable technical, economical and environmental features of GGBFS cement explain its more than 50% market share in The Netherlands and neighbor countries. However, utilization of high amount of GGBFS causes the carbonation of concrete surface faster. Many researchers reported that GGBFS cement concrete shows lower frost salt scaling resistance than OPC (OPC) concrete according to the laboratory testing (Matala 1994; Stark 1997). There are also contradictory results indicating that the field performance of GGBFS cement concrete is comparable to OPC concrete (Lang 2002). It seems that the severe frost salt scaling problem exist especially for the concretes bearing European type CEM III /B or /C cements (GGBFS > 65%). It is an important issue to improve the frost salt scaling resistance of GGBFS cement systems from technical and economical point of view.

In this report, only the normal strength CEM III /B concrete is considered.

Technical Background

In order to improve the frost salt scaling of GGBFS cement concrete, several attempts has been made. The most successful methods have been reported as decreasing the slag content, sealant application, air entrainment and silica fume addition (Vasikari 1983; Virtanen 1990). Parameters such as water/binder ratio

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and pore size distribution are the other important options (Marchand 1994). However modifications on the primarily important parameters seem to be difficult from technical and economical points of view. Hence it is increasingly becoming important to find new techniques in order to improve the frost salt resistance of GGBFS cement systems.

Na-MFP treatment of concrete is one of the corrosion inhibition techniques currently in use. Its positive effect on corrosion inhibition was presented by many researchers (Andrade 1992; Alonso 1996; Ngala 2003). It is generally used in the form of solution and applied on the carbonated concrete surface. It's 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^{3-}_4 and F^- . It seems that those formations react with certain components of the cement matrix to form fluorapatite and fluorite, which are highly insoluble calcium compounds. Additionally this reaction increases the NaOH concentration of the pore solution (Ngala 2003).

The beneficial effect of Na-MFP solution on GGBFS cement paste was investigated by the present authors previously. The effect of Na-MFP on paste microstructure was presented and possible curative mechanisms were discussed (Copuroglu 2005). Under the light of the findings in the above-mentioned study, it's been decided to apply the Na-MFP treatment on concrete samples with w/c ratio of 0.45. It should be noted that according to Dutch codes maximum allowed w/c without air entrainment is 0.45 in severe weather conditions. The effect of the treatment on microstructure and effect of the Na-MFP percentage in the solution were also investigated alongside with the frost salt scaling performance of the GGBFS cement concrete.

Experimental

Blast furnace slag cement with the slag content of 67% (CEM III/B 42,5 N HSR LH) was used from ENCI cement factory of The Netherlands. The chemical and physical properties of the cement are given in Table 1. 15×10cm concrete samples with water cement ratio of 0.45 were prepared (see Table 2). The specimens were prepared with ordinary tap water.

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	MPa	12.1
SiO_2	%	27.6	7 days	MPa	32.7
Al_2O_3	%	12.2	28 days	MPa	53.2
Fe_2O_3	%	1.27	Blaine	m^2/kg	376

Table 2: Mixture proportions of concrete (kg/m^3)

w/c	Cement	Water	Sand[a]	Aggregate[a]	SP[b]
0.45	350	159	951	915	1.75

[a] *Commercial river sand and river gravel Dmax=16mm*

[b] *Cugla SL-01 commercial superplastisizer*

The curing periods were performed as follows;

Lab carbonation :	- 1 day in mould in fog room - 6 days under water - 14 days at 21°C, 50-55% R.H. lab. condition - 5 days surface treatment by water or10% Na-MFP solution - 7 days 3% NaCl solution saturation
Accelerated carbonation:	- 1 day in mould in fog room - 6 days under water - 14 days at 21°C, 50-55% R.H., 3% CO_2 chamber - 5 days surface treatment by water or 10% Na-MFP solution - 7 days 3% NaCl solution saturation

The Na-MFP solution was applied on the specimen surfaces 5 times per day by means of brushing. Each application was followed by demi water brushing in order to ease the penetration of the solution. The surfaces were allowed to become visibly dry between each application.

Additionally the effect of $Ca(OH)_2$ addition to Na-MFP solution was studied. 0.1 gram $Ca(OH)_2$ was mixed with 1 mL of 10% Na-MFP solution. The intention was to enable the further apatite formation. Finally the specimens were exposed to freezing and thawing cycles.

The effect of the concentration of Na-MFP solution on the frost salt scaling resistance was also studied on 10 cm GGBFS cement mortars cubes w/c 0.45. Solution percentages of 1%, 3%, 5% and 10% were considered. The curing history, method of Na-MFP solution treatment and freezing - thawing testing were kept identical to the ones for accelerated carbonation concrete specimens.

ASTM C672, *Standard Test Method for Scaling Resistance of Concrete Surfaces Exposed to Deicing Chemicals* was used for the frost salt scaling testing. 15 freezing - thawing cycles were performed.

The GGBFS concrete samples were examined by ESEM in backscattered electron (BSE) mode before carbonation, after carbonation and after the Na-MFP solution treatment.

Results

The phenolphthalein measurements showed that at the end of the curing period in case of accelerated carbonation, the depth of carbonation of the concrete samples was about 1 cm. Almost no depth of carbonation could be traced in normal carbonated concrete samples (<1mm).

The frost salt scaling performances of the GGBFS concrete samples are presented in Figure 1. As it was expected, the highly carbonated samples (HC) showed the highest mass scaling. Normal (lab) carbonated samples (NC) had the second worst performance. By far, the Na-MFP treated high carbonated samples (HC-MFP) had the best resistance among the series.

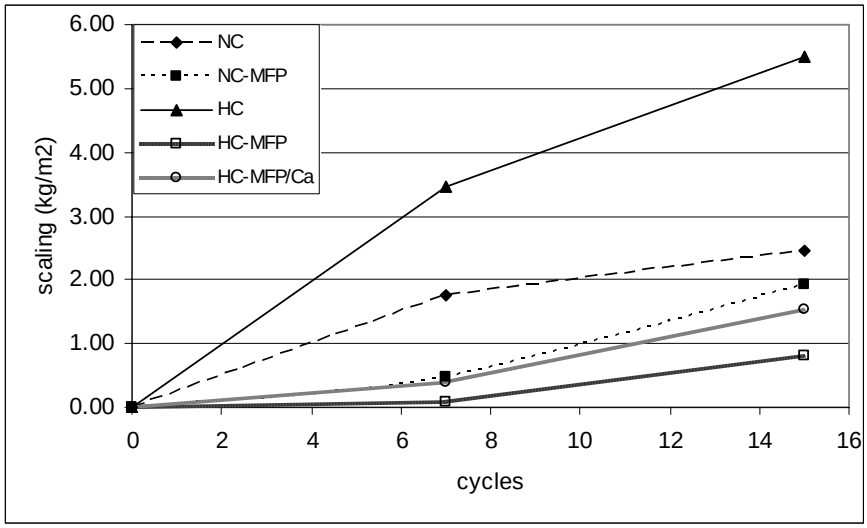


Figure 1: Frost salt scaling performances of the GGBFS concrete samples with w/c 0.45 after 15 freeze-thaw cycles. *(NC: normal carbonation, NC-MFP: normal carbonated / treated with Na-MFP solution, HC: highly carbonated, HC-MFP: highly carbonated / treated with Na-MFP, HC-MFP/Ca: highly carbonated / treated with $Ca(OH)_2$ and Na-MFP mixture solution)*

The surface conditions of the specimens after 7 freezing thawing cycles can be seen in Figure 2 to Figure 5.

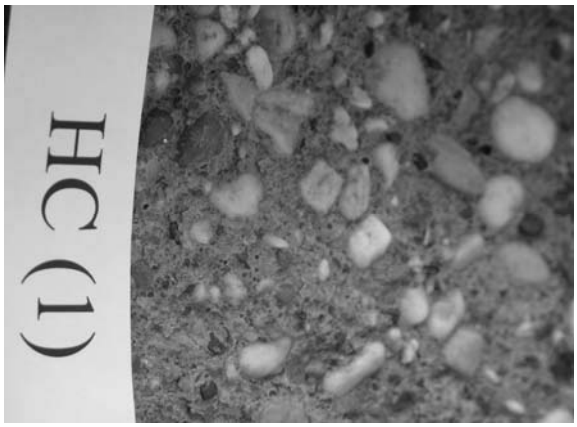


Figure 2: Surface condition of highly carbonated concrete (w/c 0.45) after 7 F-T salt cycles.

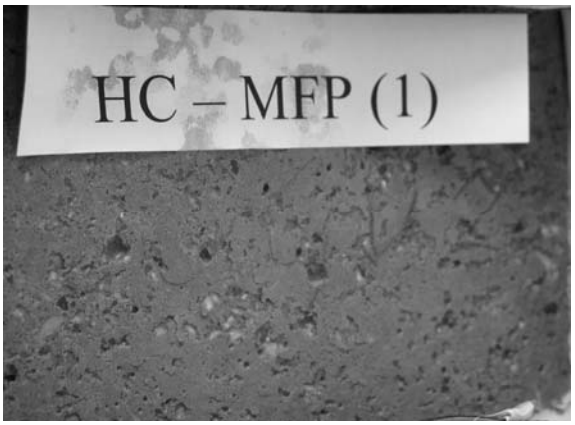


Figure 3: Surface condition of Na-MFP treated-3% CO_2 (highly) carbonated concrete (w/c 0.45) after 7 F-T salt cycles.



Figure 4: Surface condition of lab carbonated concrete (w/c 0.45) after 7 F-T salt cycles.

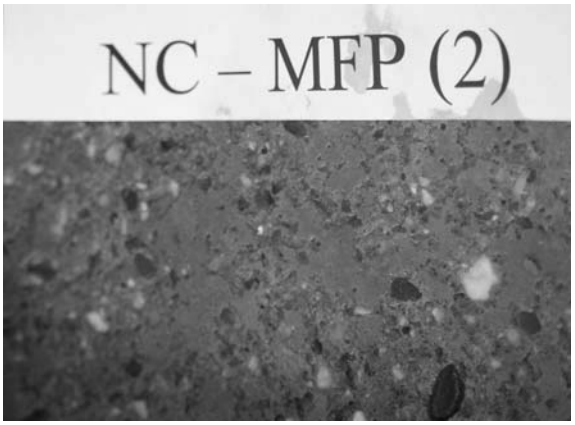


Figure 5: Surface condition of MFP treated - lab carbonated concrete (w/c 0.45) after 7 F-T salt cycles.

The effect of solute concentration on the effectiveness of the treatment for mortars is summarized in Figure 6. Weak solutions give relatively less contribution to the frost salt scaling resistance of the mortars. Mid-level solutions

showed similar performances while strong Na-MFP solution gave the highest reduction in mass scaling.

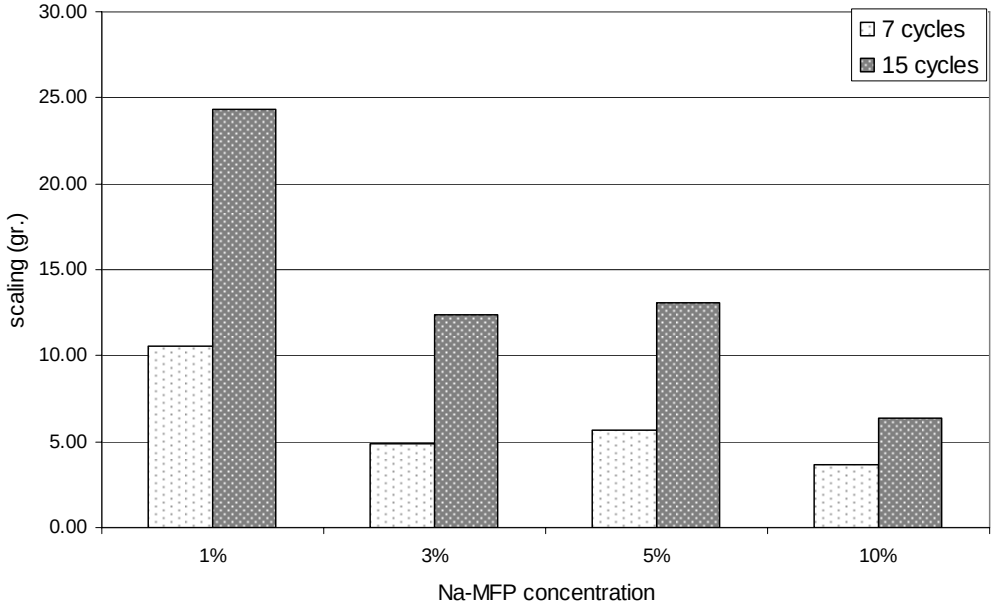


Figure 6: Effect of Na-MFP solution concentration on the frost salt scaling of GGBFS cement mortars.

The microstructural characteristics of the concrete samples after Na-MFP treatment are presented in Figure 7 to Figure 10. A sponge-like mineral formation is nestled inside the pore structure of concrete. Drying cracks are also visible in the matrix of the system.

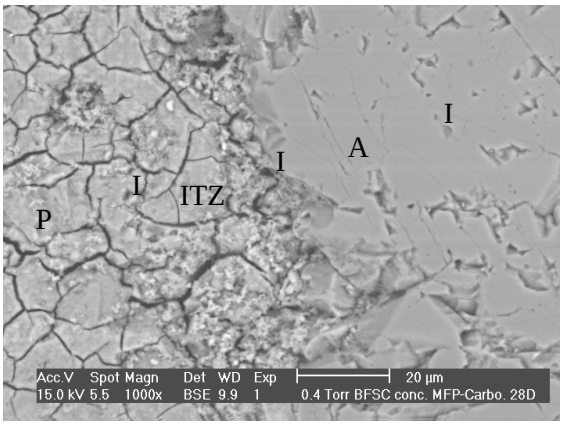


Figure 7: The interfacial transition zone (ITZ) between aggregate (A) and cement paste (P).

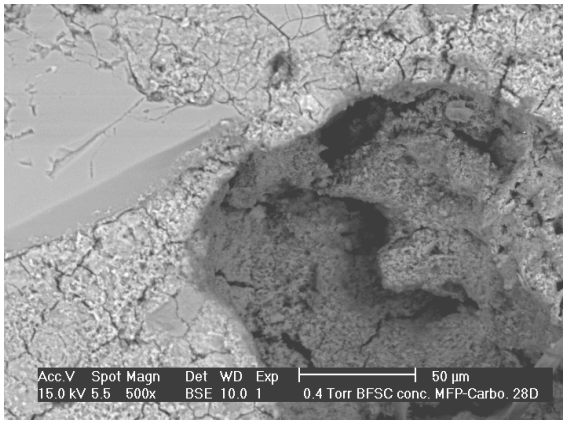


Figure 8: A pore partially filled by the reaction products after the Na-MFP treatment

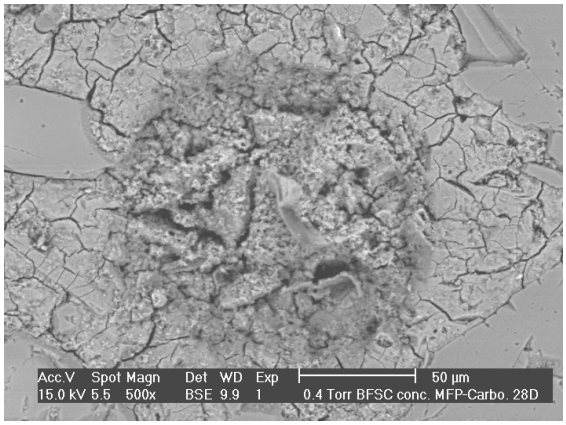


Figure 9: A pore completely filled by the reaction products after the Na-MFP treatment.

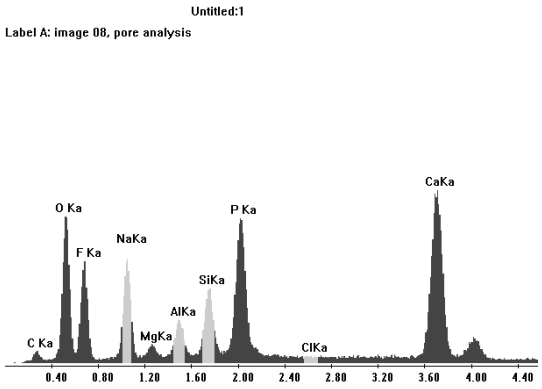


Figure 10: The EDX analysis of pore filling material.

Discussion

The results from the previous study of the authors on the effect of Na-MFP on GGBFS cement pastes are confirmed by this study on concrete. It was observed that the Na-MFP treatment is extremely effective for the highly carbonated concrete surfaces with water cement ratio of 0.45. The increase in the frost salt scaling resistance was 98% after 7 cycles and 85% after 15 cycles.

This impressive improvement should be evaluated not only by numerical means but also aesthetically. As can be seen in Figure 3, almost no sign of massive scaling is visible and the skin is generally intact. Although the frost salt scaling performances of the concrete samples are determined by weighing the scaled mass, it is the appearance of the concrete surface, which draws the attention in reality. A scaling performance of more than 1.5 kg/m^2 generally presents a surface with exposed coarse aggregates. This is obviously not acceptable for concrete road and pavement structures.

The $Ca(OH)_2$ and Na-MFP mixture solution was somehow not so successful as much as the solution prepared only with Na-MFP. This was probably because the reaction between Na-MFP and certain $CaCO_3$ phases (vaterite and aragonite) contributes more to the frost salt scaling resistance compared to the reaction between Na-MFP and $Ca(OH)_2$. It was previously reported that no reaction takes place between calcite and Na-MFP (Copuroglu 2005).

It seems that the Na-MFP treatment works also for slightly carbonated surfaces, especially during the initial stages of frost salt attack. It was found that after 7 freeze thaw cycles the salt scaling resistance improvement of lab carbonated samples was some 73%. However, it is necessary to study the long term effect of Na-MFP treatment

In Figure 7 the interfacial zone between an aggregate particle and GGBFS paste is presented. The interfacial zones are filled or modified with the reaction products of Na-MFP and $CaCO_3$. Superior frost salt scaling resistance of the concrete samples may be because of this modification. These reaction products do also fill the air voids (see Figure 9). The EDX analysis revealed that those new formations have mainly F, Na, P and Ca peaks. It might be useful to emphasize that the chemical formula of the apatite mineral is $Ca_5(PO_4,CO_3)_3F$.

Currently, the existence of the drying mark types of cracks cannot be explained. Their existence leads us expecting a lower durability of the concrete. However the performance is superior. This point is yet to be investigated.

Conclusions

The Na-MFP solution treatment increases the initial frost salt scaling resistance of carbonated GGBFS concrete w/c 0.45. The solution is effective especially for the highly carbonated surfaces and at higher concentrations.

The ESEM study provides evidence that Na-MFP solution modifies the GGBFS cement matrix, pore structure and the interfacial zones. It is a possibility that the Na-MFP hydrolysis products react with the certain carbonated phases (aragonite and/or vaterite) of GGBFS cement paste.

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