Autogenous Self-Healing in Blast Furnace Slag Cement by Sodium Monofluorophosphate

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ABSTRACT

Over the past decade, sodium monofluorophosphate (Na-MFP) has gained large interest as an inorganic self-healing agent, particularly on blast furnace slag cement concrete (BFSC). The superior durability of BFSC against chemically aggressive environments makes this material a suitable binder for concrete exposed to chloride ingress, acid and sulfate attack. However, the carbonation rate of BFSC is a huge drawback compared to ordinary Portland cement (OPC) mixtures and requires a large-scale industrial and feasible solution to keep BFSC equally attractive for the building industry.

Previous work has investigated the influence of Na-MFP as self-healing agent on BFSC systems upon carbonation. Results of these studies have shown that the surface application of Na-MFP as pre- and post surface treatment has the potential to improve the microstructure and surface durability of carbonated cementitious materials with a high BFS concentration.

This study focusses on the influence of cementitious paste pore solutions activated with Na-MFP and their impact to liquid and solid phase formation during carbonation and self-healing in BFS cementitious products. Pore solution analyses of blast furnace slag cement pastes impregnated with aqueous Na-MFP have shown that Na-MFP can recover the pH of a carbonated slag cement paste up to 90% over a reaction period of only 28 days. Simultaneously, Na-MFP reacts under the presence of water with the slag-bearing carbonating paste to form solid cement phases such as secondary ettringite, secondary portlandite and amorphous calcium phosphates (ACPs). The formation of the crystalline phases could be observed by X-ray powder diffraction (XRPD) analyses on the respective cement pastes.

The formation of secondary cement phases and ACP's increase the mechanical quality of the material surface, decrease the pore volume and capillary water uptake and decelerate the carbonation rate of cement products rich in BFS. As a consequence damage through micro coarsening of pore structure and related cracking can effectively be compensated and the frost salt scaling durability of the BFSC products can significantly be increased.

This work provides the basis for an 'autogenous' self-healing mechanism for BFSC.

1. INTRODUCTION

Cements containing between 30% and 90% blast furnace slag, find widespread use in high performance concrete applications due to their chemical and mineralogical characteristics. With the introduction of Na-MFP as a an aqueous self-healing agent on the surface of BFSC binders and building materials about a decade ago, the detrimental effects of carbonation on the microstructure of BFSC products could successfully be recovered [1-8]. With this work we are aiming to understand mineralogical processes of cementitious products prepared from slag rich cement types. In addition we want to provide the basis for an inorganic autogenous self-healing mechanism for the recovery of carbonation-attacked binders prepared from blast furnace slag cement.

2. MATERIALS

Paste specimens were prepared from BFS cement with a slag component of 67% (CEM III/B 42,5 N HSR LH) and ordinary Portland cement (CEM I 32,5 R), both provided by the Dutch ENCI cement fabricator. Pastes were prepared with a water-cement-ratio (w/c) of 0.45 by weight with common tap water. Mixing was performed with a commercial Hobart mixer with one sequence of two minutes low-speed and one sequence of two minutes high-speed mixing. All paste specimens were casted in commercial circular polyethylene jars (d = 35 mm, h = 70 mm) and vibrated for 30 seconds on a vibrating table. The specimens were stored in the closed jars for 24 hours, adjacently removed from the jars and afterwards cured in a fog room at room temperature conditions and 100% relative humidity (HR) for 28 days. Afterwards the pastes experienced chemical treatments such as carbonation of Na-MFP vaccuum impregnation or both.

Carbonation was carried out over a period of 14 days at room temperature in a 3% CO_2 atmosphere at 75% RH. The carbonated samples were stored for 14 more days in a desiccator. Na-MFP treatment was performed once per sample by vacuum impregnation with aqueous solutions of 45 wt% Na-MFP. Afterwards samples were stored for a 28-day reaction time in the desiccator as.

Over the whole experimental period the desiccator atmosphere was adjusted and kept at room temperature conditions and a relative humidity ranging between 50-55%. The atmosphere was obtained by a Sigma Aldrich magnesium nitrate hexahydrate reagent ($Mg(NO_3)\cdot 2.6H_2O$; CAS 13446-18-9) as desiccator agent.

3. METHODS

Pore solutions of all samples were extracted by the exposure of the paste sample to high-pressure of up to 500 tons in a MacBen type block tester. The solutions were gathered with a 10 ml injection device and prepared for analyses on an inductively coupled plasma optical emission spectrometer (ICP-OES). Powder sample aliquots of five gram were taken and fine-grained under ethanol in an agate mortar down to a finish of 5 mm. Samples were prepared as dry powders for X-ray powder diffraction on an aluminum sample holder.

The main element concentrations of the pore solutions were analyzed with a VARIAN Vista 720 ICP-OES. The instrument was calibrated with a 1% v/v HNO_3 blank solution and differently concentrated solutions of the commercial multi-element standard for main elements, trace elements and rare earth elements (111355 Merck

IV). All samples, the standard and the procedural blanks were analyzed in 1% v/v HNO_3.

XRPD was performed on a Philips PW 1830/40 powder. The machine is operated with an acceleration voltage of 40 kV and an X-ray beam current of 30 mA. The X-ray source is a Cu-tube working with characteristic CuKa wavelength. The machine is equipped with a Ni-filter. Analyses were performed in air on hydrated, carbonated and on Na-MFP treated and fine grained paste powders with a stepsize of 0.02° for a 2Θ angle range between 5° and 70°. Every step was analysed for 10 seconds.

4. RESULTS

The pH of an untreated paste pore solution was analysed with 13. After carbonation the pH decreases to 8.8. With the vaccuum impregnation after carbonation the pH recovers to a value of 10. Results of the ICP-OES analyses have shown that the pore solution composition of a slag bearing cement paste changes in dependency of the chemical environment to which the sample is exposed (figure 1).

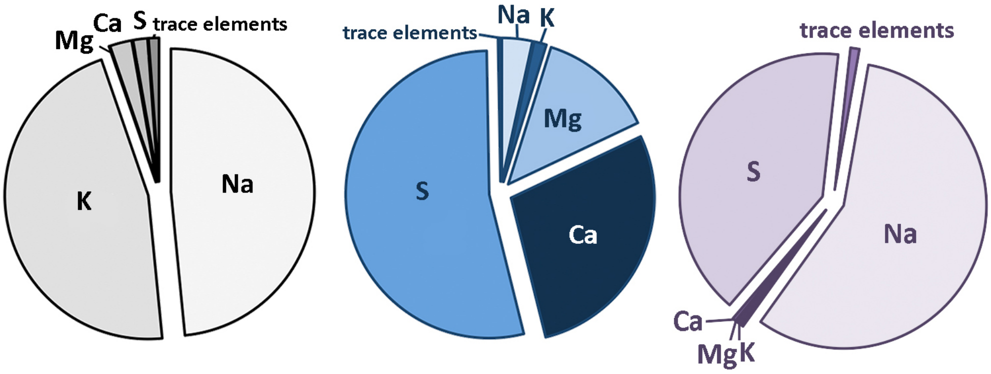

Figure 1: Main element concentrations of slag-rich cement paste pore solutions in percent; left: untreated CEM III /B; middle: carbonated CEM III /B; right: carbonated and subsequently Na-MFP impregnated CEM III /B.

The pore solution composition and pH have direct influence to the formation of solid cement phases.

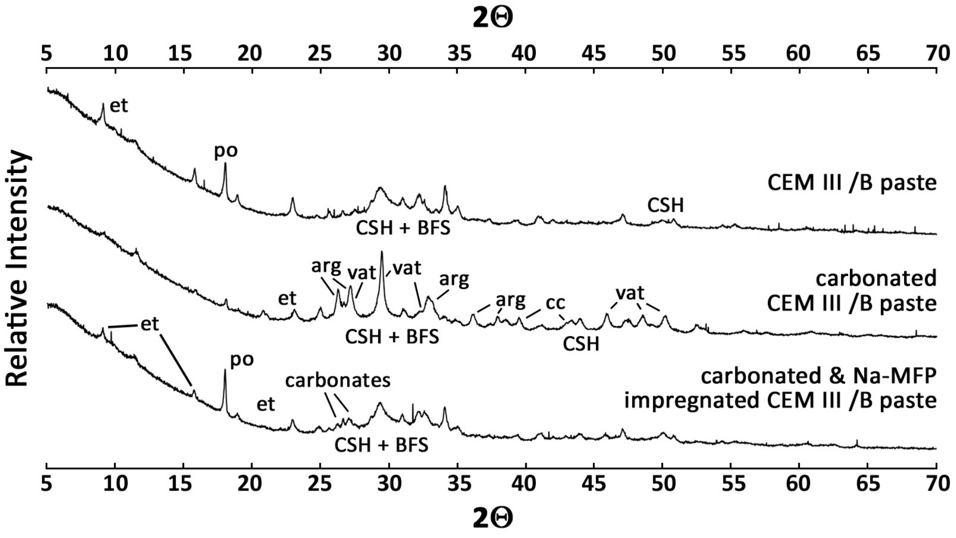

Figure 2: X-ray powder diffractograms of CEM III /B cement pastes; Na-MFP treatment after carbonation causes the formation of secondary cement phases.

X-ray powder diffraction analyses show an ettringite (et) breakdown during carbonation. This sulfur-bearing mineral releases sulfur to the pore solution by destabilising (figure 1). Remaining calcium oxide and portlandite (po) form carbonates such as vaterite (vat) aragonite (arg) and calcite 9 (cc) during carbonation. After vaccum impregnation with Na-MFP the carbonates break down with the recovery of the pH of 90% after only 28 days and form secondary ettringite and portalndite as well as amorphous calcium phophates.

5. CONCLUSIONS

Results of this work contribute to a clear understanding of the processes taking place during carbonation and simultaneous self-healing in BFS cement mixtures. Laboratory studies have shown that the inorganic self-healing agent Na-MFP has a favorable effect on the repair of BFS cement products by surface application. As a macroscopic result frost salt scaling resistance can strikingly be improved for BFSC based building materials. Future work will focus on elaborating a pH-sensitive coating material to encapsulate Na-MFP for outdoor applications.

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