Cementitious materials with mineral additions: impact on the self-healing kinetics and the products formation

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ABSTRACT

Ground granulated blast-furnace slags (GGBFS), as a hydraulic binder, are widely used for many years in engineering concretes. The French standards allow substituting 50% of Portland cement by GGBFS. This approach leads to a decrease in the CO_2 emissions produced during clinkerisation process. Portland cement substitution by GGBFS can also improve the workability, decreases the hydration heat and increases the long-term compressive strength. GGBFS can also significantly improve the resistance to sulfate attack. Concrete structures made with GGBFS cement can be cracked at early age due to restrained shrinkage. This cracking can reduce mechanical and transport properties, leading to an increased risk of aggressive agents' penetration. Self-healing of cracks, already observed on building sites, could partially overcome these durability issues.
To understand the effect of GGBFS on self-healing kinetics and the type of self-healing products, five hydraulic binders were studied: two Portland cement (French and Canadian), two GGBFS (French and Canadian) mixed with Portland cement (named GGBFS formulation hereafter) and a French blended cement (62% of slag) named CEMIII/A. Each material was characterized by XRF, XRD, PZD test, fineness Blaine test and TGA. At 7 and 28 days, French and Canadian mortar specimens were cracked respectively to obtain three crack sizes: 50, 100 and 150 µm. The cracked specimens were then stored at 23 °C and 100% R.H for up to 6 months. The evolution of self-healing is followed by X-ray tomography or air-flow measurements. SEM with EDS were performed on the sawed samples to identify and analyze self-healing products.
Results show that two main products are formed: (1) calcite by the carbonation of portlandite in the matrix, and (2) supplementary reaction products (mainly C-S-H with various C/S ratios), formed by the reaction of anhydrous particles. Both GGBFS formulations show a good self-healing potential but the kinetics of the phenomenon are slightly different. Mortar made with French GGBFS presents the best self-healing potential compared to the four others formulations. Mortar with Canadian GGBFS presents a similar behavior as Canadian Portland cement. These results can be explained by the material characteristics but also by their hydration kinetics. A

hydration model is currently developed in order to investigate more deeply these observations.

1. INTRODUCTION

Self-healing of concrete presents a great interest to improve the structure durability after cracking but the improvement of mechanical properties is not yet clear. Some researches have shown a stiffness recovery but there is no agreement about the strength recovery [1, 2]. Moreover, very few studies exist on the effects of blast-furnace slag on self-healing. The latent hydraulic properties of the blast-furnace slag could improve the self-healing potential. To better understand the effect of slag and the impacts of materials characteristics and testing conditions on the chemical and mechanical properties of self-healing products, five cracked mortars were submitted to X-ray Tomography, air-flow measurements, SEM with EDS and nanoindentation measurements.

2. MATERIALS AND METHODS

Five mortars compositions are used: 1) 100% of French Portland cement CEMI 52.5 N CP2 NF; 2) 50% of CEMI 52.5 N CP2 NF and 50% of blast-furnace slag; 3) 100% of CEMIII/A (French industrial cement); 4) 100% of Canadian General Use Portland cement (GU); 5) 50% of GU and 50% of Canadian blast-furnace slag. These compositions are named: CEMI, CEMI+S, CEMIII/A, GU, GU+S respectively. All the mortars have a W/B ratio in the range of 0.50-0.52. The binder content is 563 kg/m^3 in all the mortar mixtures with Portland cement and 539 kg/m^3 for others. The sand used has a normalized size (respectively EN 196-1 for French sand and ASTM C178 for Canadian sand).

Two experimental approaches were used to assess the kinetics of the self-healing phenomenon at early age. The first consists in monitoring the crack size in mortar samples (diameter Ø = 4 cm and height h = 10 cm) with a tomograph. Only the mortars made with CEMI, CEMI+S CEMIII/A binders were tested with this technique. A tensile splitting test at the age of 7 days was used to produce cracks with opening ranging from 71 µm to 289 µm. The cylindrical specimens were confined with a two-component resin reinforced with a fiberglass mat [3]. After cracking and between measurements, samples were stored under tap water at 23°C. The tomography analysis was performed at different ages (cracking day, 7, 14, 21 and 28 days).

The second experimental approach consists in measuring air flow to assess self-healing in mortars cracked at 7 days with a mechanical expansive core [3]. Only the mortars made with GU and GU+S were tested with this technique. Mortar samples were cylindrical disks with a central hub (diameter Ø = 15 cm and height h = 5 cm). A mechanical expansive core was inserted in the sample hub to create a radial crack of controlled opening. All mortar disks were stored in a100% RH – 23 °C room for the initial 7-day curing before cracking and for up to 3 months after cracking (self-healing environment). Measurements of the air-flow in the cracks were performed at one and three months after the cracking. Before each air-flow measurement mortar disks were stored at35°C for 24 h to remove water in the crack volume.

In parallel, thermogravimetrical analysis was performed to assess the hydration degree. At the end of the elf-healing testing program, mortar specimens were broken to take samples for characterization of the healing products by SEM - EDS analysis. Moreover, one mortar specimen was observed and analyzed using a nanoindentator installed in the internal chamber of an SEM. These measurements were performed to assess the some other mechanical properties of the healing products.

3. RESULTS

The tomography allows observing in 3D the evolution of the cracks characteristics (density, length, opening, percolation …), for crack larger than the voxel size of about 20 µm. Figure 1 shows the evolution of the volume of the healing-products for mortars made with CEMI, CEMI+S and CEMIII/A binders. The evolution of the air-flow measurements for mortars made with GU and GU+S binders is shown in Figure 2. Figure 3 shows hydration degree results for all compositions.

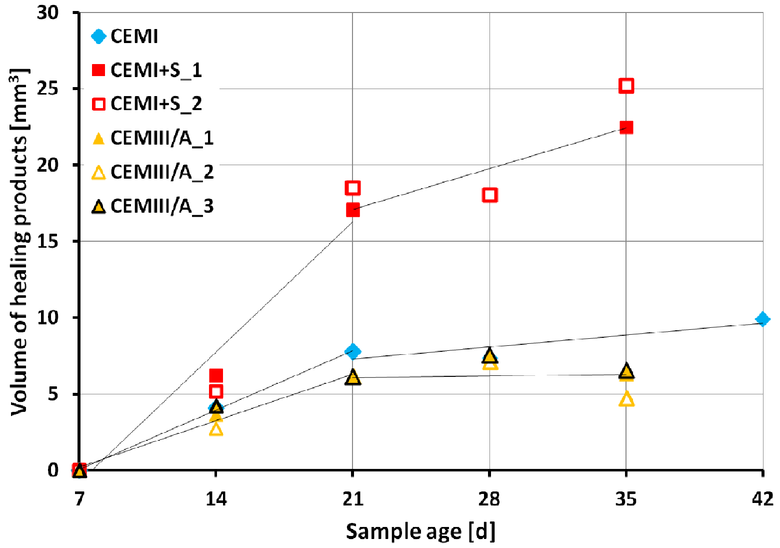


Figure 1. Evolution of the volume of the healing products for mortars made with a slag binder (CEMI+S and CEMIII/A) and for the reference mortar without slag (CEMI)

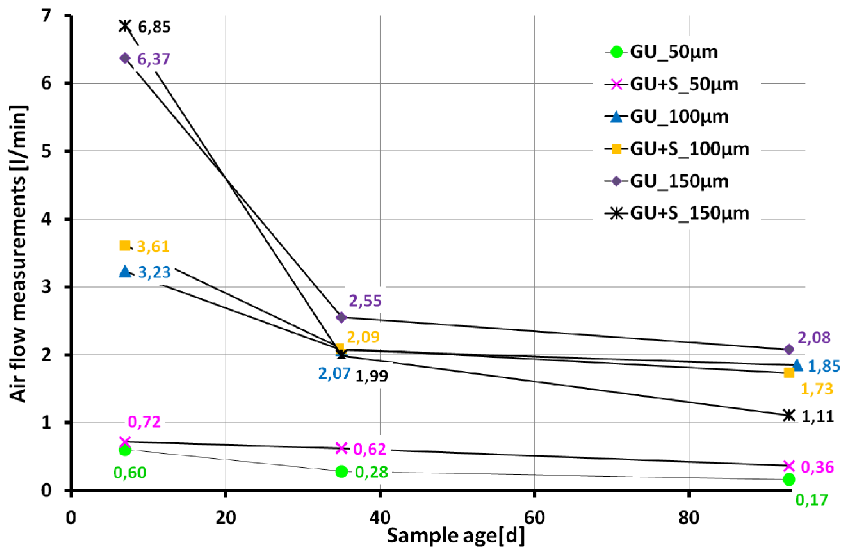


Figure 2. Evolution of the air-flow over time for mortars made with GU and GU+S binders.

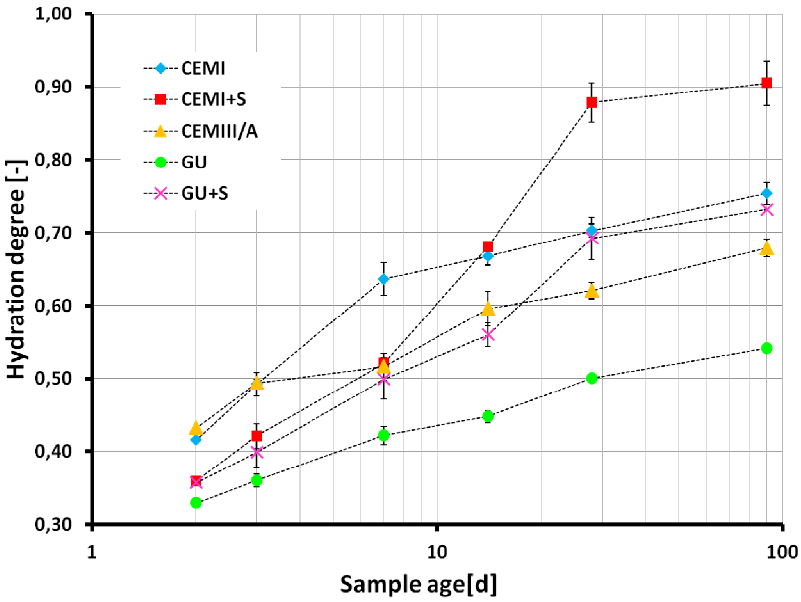


Figure 3. Evolution of the hydration degree over time for mortars with and without slag

The curves of Figures 1 and 2 show a two-stage evolution for the self-healing kinetic. For the first stage, self-healing is faster as the volume of the healing products increases rapidly during the first 14 days (Figure 1) and the air-flow decreases rapidly during the first month (Figure 2). For the second stage, the kinetic of self-healing is slower. A similar behavior was found by Gagné and Argouges for mortars made of pure Portland cement [2].

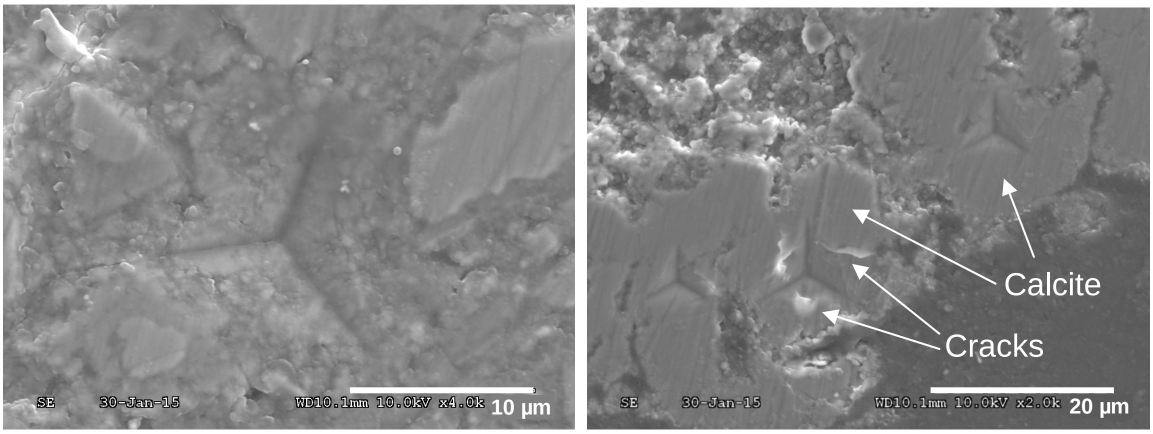
The mortar made with CEMI+S showed a better self-healing potential than the CEMI and CEMIII/A mortars. This can be explained by the latent hydraulic properties of slag. At early age (before 7d), the hydration degree of the CEMI+S mortar is lower than the one of the CEMI and CEMIII/A mortars. The higher amount of anhydrous binder in CEMI+S at the time of cracking explained the better self-healing behavior. The three tests performed with CEMIII/A show a good repeatability for the tomography procedure used to assess the volume of the self-healing products in the crack (Figure 1).
Both GU and GU+S mortars show a very similar evolution of the air-flow over time (Figure 2) Before 7 days, these two mortars have the lowest hydration degrees. Therefore, GU and GU+S mortars contain a higher amount of anhydrous binder. The consequence is that, both formulations have a good self-healing potential. The standard deviations of the air-flow measurements are between 0.07 and 2.2.

All the mortar specimens were observed by SEM with EDS to identify self-healing products. Evidence of C-S-H formation was found in the cracks for CEMI, CEMI+S and CEMIII/A mortars Water storage allowed the formation of new hydrates by the hydration of anhydrous binder available at early age. Most of the self-healing products found in the cracks of the GU and GU+S mortars were calcite. The storage in a humid chamber, where the amount of CO_2 is higher than in water (dissolved CO_2), could explain the calcite formation in the GU and GU+S mortars compared to the C-S-H mainly found in the cracks of mortars stored under water (CEMI, CEMI+S and CEMIII/A) The formation of C-S-H and calcite after self-healing is in agreement with [5] and [6].

The GU+S mortar was observed with the SEM equipped with the nanoindentation apparatus. Average hardness results are presented in Table 1. Figures 4 and 5 show an indent imprint in the matrix (C-S-H) and in a healing product (calcite). The anhydrous particles hardness (2.4 ± 0.4 GPa) is higher than the two others products (C-S-H matrix and healing products). The healing product (calcite) has a higher hardness (1.1 ± 0.7 GPa) than C-S-H matrix (0.5 ± 0.3 GPa). However, SEM observations showed crack formation in calcite after the nanoindentation test. This cracking behavior was not observed for others products (matrix and anhydrous particles). Moreover, the standard deviation for calcite is 2-3 times higher than those for anhydrous particles and C-S-H matrix. This result emphasizes the higher dispersion of healing products hardness. During the nanoindentation test, calcite cracked easily and the indent may measured the hardness of products around calcite (volume of matter: 5 μm^3, [7]). This can explain that near the resin, hardness calcite was close to the resin hardness and near matrix/anhydrous particles, hardness calcite was close to these products.

	Hardness HM [GPa]
Anhydrous particle	2.4±0.4
C-S-H matrix	0.5 ± 0.3
Calcite (self-healing product)	1.1 ± 0.7

Table 1. Average hardness of matrix products and healing products in GU+S.



Figures 4 and 5. Indenter observations in the matrix (C-S-H) and self-healing products (calcite) for GU+S.

4. CONCLUSIONS

Thanks to the use of tomography and air flow test, we have seen that it is possible to observe and quantify the self-healing capacity of different types of cementitious materials. For French materials, the slag composition CEMI+S presents greater self-healing potential. For Canadian formulations, the same self-healing potential is observed. For all compositions, results could be explained by the hydration degree evolution. The difference in storage conditions (water or damp chamber), explained the difference between self-healing products for French and Canadian compositions which were respectively C-S-H and calcite. Finally, SEM with nanoindentation revealed that calcite (healing products for GU+S) seems to have better mechanical properties than the initial matrix products. However, lots of cracks observed in calcite after the test could reveal that this product had a brittle behavior.

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