Early-age self-healing of cementitious materials containing ground granulated blast-furnace slag under water curing
Avéline Darquennes, Kelly Olivier, Farid Benboudjema, Richard Gagné

Related Papers Click to Download full PDF!

XRD/Rietveld analysis of the hydration and strength development of slag and limestone blended cement
Seiichi Hoshino, Kazuo Yamada, Hiroshi Hirao

Shrinkage cracking resistance of blast furnace slag blended cement concrete - Influencing factors and enhancing measures
Tetsushi Kanda, Haruki Momose, Keiichi Imamoto

Quantitative Evaluation of Crack Resistance Mechanism of Blast Furnace Slag Blended Cement Concrete via Restrained Shrinkage Stress Analysis
Tetsushi Kanda, Haruki Momose, Keiichi Imamoto, Chizuru Kiyohara

Impacts of trace additives and early-stage curing conditions on the shrinkage cracking resistance of blast-furnace slag cement concrete
Tetsushi Kanda, Haruki Momose, Kohsuke Ishizeki, Keiichi Imamoto

Click to Submit your Papers
Japan Concrete Institute http://www.j-act.org
Early-Age Self-Healing of Cementitious Materials Containing Ground Granulated Blast-Furnace Slag under Water Curing

Kelly Olivier¹, Aveline Darquennes²*, Farid Benboudjema³ and Richard Gagné⁴

Received 21 July 2016, accepted 30 October 2016 doi:10.3151/jact.14.717

Abstract

In order to limit the release of CO₂ emissions produced by cement manufacturing, clinker, the major cement component, is often partially replaced by mineral additions such as Ground Granulated Blast-Furnace Slag (GGBFS). Civil-engineering structures made with GGBFS cement can however present cracking at early age (< 28 days) due to restrained shrinkage that significantly affects their durability and their material transport properties. Self-healing may limit these phenomena. In order to study and quantify self-healing kinetics, X-ray tomography tests for mortars with different GGBFS contents are performed. Results show that X-ray tomography provides valuable information inside the specimens: crack openings and healing products distribution. It is also shown that self-healing evolves rapidly during the first weeks of water curing and it is more important for cementitious materials containing GGBFS. This is due to their lower early age hydration degree allowing an ongoing hydration after cracking and the formation of supplementary C-S-H along the crack.

1. Introduction

Concrete containing Ground Granulated Blast-Furnace Slag (GGBFS) cement is often used in civil-engineering structures. It offers many advantages such as re-use of industrial wastes, decreased CO₂ emissions during clinkerization (by limiting the clinker content in the cementitious material) and enhanced material properties such as workability and long-term compressive strength (Dubovoy et al. 1986; Itim et al. 2011). It is recommended for massive structures such as dams and bridges and for structures in aggressive environments (farm silos, water-treatment plants, mining) because of its low heat release, its high resistance to sulfate attack and chloride diffusion resulting from its low long-term porosity (Darquennes et al. 2012).

Nevertheless, civil-engineering structures made with GGBFS cement present sometimes cracking at early age due to restrained shrinkage (Darquennes et al. 2011; Brillfaut et al. 2016) that reduces the concrete mechanical properties and can increase the penetration risk of aggressive agents such as CO₂ and chlorides. Structures made with GGBFS cement present however a self-healing capacity. Under autogenous conditions, self-healing is related to the ongoing hydration (Hearn 1998; Neville 2002) and/or the calcium carbonate formation due to portlandite carbonation (Clear 1985; Van Tittelboom et al. 2012). The formation of hydrates or calcium carbonate is linked with the self-healing curing conditions and the sample characteristics (Neville 2002). Indeed, a cracked sample with an important quantity of anhydrous particles stored in water (saturated conditions) forms new hydrates (Hearn 1998; Jacobsen et al. 1995), while a cracked sample in humid conditions (water+CO₂) forms principally calcium carbonates (Edvardsen 1999; Gagné et al. 2012). These new products can partially or completely fill the cracks.

Nowadays, it is not yet thoroughly understood how GGBFS is involved in the self-healing phenomenon. Few experimental results can be found in the literature (Van Tittelboom et al. 2012; Qian et al. 2009; Sahmaran et al. 2013; Huang et al. 2014) for mixtures containing blast-furnace slag at long term (> 28 days), reporting sometimes contradictory results. Van Tittelboom et al. (2012) and Huang et al. (2014) indicate that the addition of ground granulated blast-furnace slag positively influences self-healing, whereas Qian et al. (2009) claim the opposite. As for the self-healing capacity of these materials at early age (< 28 days), few results exist in the literature and concern mainly the evolution of the mechanical properties of cracked specimens under three-point-bending tests (ter Heide et al. 2007). The main objective of the present study is to quantify the ability of GGBFS to heal cracks at early age (< 28 days) by means of an original experimental technique limiting the measurement mistakes and giving 3D information: the X-ray tomography.

The X-ray tomography (X-ray CT) presents several
advantages over conventional analysis methods such as permeability tests, mechanical tests, 2-D optical microscopy measurements and scanning electronic microscopy (SEM) (Jacobsen et al. 1995; Granger et al. 2007; Van Tittelboom et al. 2011): it is nondestructive, does not require a sample pretreatment and can assess the spatial and temporal evolutions of micro- and meso-structures inside the same cementitious material sample (Landis et al. 2013). X-ray tomography is often used to produce 3D images of cementitious materials with or without mechanical loadings, to capture damage and strain localization. Few experimental results exist however related to self-healing (Van Tittelboom et al. 2011; Henry et al. 2013; Fan et al. 2013; Fukuda et al. 2012). Van Tittelboom et al. (2011) adopted this technique to visually observe the crack and healing agent (polyurethane) distribution. Henry et al. (2013), Fan et al. (2013), Fukuda et al. (2012) performed calculations using image analysis techniques to determine the crack width before and after the healing process in specific areas of the cracked cementitious materials. Their samples were characterized by a low water-cement ratio (≤ 0.3), a parameter favorable to healing by the ongoing hydration due to the presence of numerous anhydrous cement particles. Their studies differ by the adopted method to crack the specimen and the curing type after cracking: heating and water curing (Henry et al. 2013); bending test and wet-dry cycles curing (Fan et al. 2013); splitting test and sea water curing (Fukuda et al. 2012). To the best of our knowledge, only the authors of the last study performed measurements during the healing process to characterize the evolution of the healing products distribution. These studies confirm the ability of the X-ray tomography to visually observe and quantify the healing process.

The present study aims to quantify the ability of GGBFS to heal cracks at early age. The experimental research program presented hereafter is innovative in many aspects:

- the X-ray tomography is used to monitor the self-healing evolution as well as the healing products distribution along the specimen height using a much denser spatial and time discretisation than the previous studies;
- the repeatability of the adopted experimental procedure (measurement and post-treatment) is validated for the studied composition;
- to the authors’ knowledge, this experimental technique is for the first applied to study the self-healing of cementitious materials containing ground granulated blast-furnace slag;

- finally, the measurements at meso-scale are combined by analyses at micro-scale using SEM (Scanning Electron Microscopy), EDS (Energy Dispersion Spectroscopy) and TGA (Thermogravimetry Analysis) to gain a better insight on the phenomena responsible to crack healing.

### Table 1: Mortar compositions [kg/m³]

<table>
<thead>
<tr>
<th></th>
<th>Cement</th>
<th>Water</th>
<th>Sand</th>
<th>GGBFS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>563</td>
<td>281</td>
<td>1409</td>
<td>258</td>
</tr>
<tr>
<td>Slag</td>
<td>281</td>
<td>281</td>
<td>1409</td>
<td>258</td>
</tr>
</tbody>
</table>

### Table 2: Chemical compositions of CEMI and GGBFS.

<table>
<thead>
<tr>
<th>Oxides [%]</th>
<th>CEMI</th>
<th>GGBFS</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>64.85</td>
<td>43.21</td>
</tr>
<tr>
<td>SiO₂</td>
<td>18.60</td>
<td>33.08</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.92</td>
<td>9.50</td>
</tr>
<tr>
<td>MgO</td>
<td>1.15</td>
<td>5.77</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.90</td>
<td>2.35</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.46</td>
<td>0.43</td>
</tr>
</tbody>
</table>

### Table 3: Laser particle-size distribution of CEMI and GGBFS.

<table>
<thead>
<tr>
<th>% &lt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 µm</td>
</tr>
<tr>
<td>10 µm</td>
</tr>
<tr>
<td>100 µm</td>
</tr>
</tbody>
</table>

### 2. Materials and Experimental Techniques

#### 2.1 Materials

The two studied mortar compositions are (1) a mortar with 100% Portland cement (CEMI 52.5 N CP2 NF) and (2) a mortar with 50% Portland cement (CEMI 52.5 N CP2 NF) and 50% ground granulated blast-furnace slag (GGBFS) (Table 1). These mixtures are referred hereafter as “control mortar” and “slag mortar” respectively. Their water/binder (W/B) ratios are equal to 0.50 and 0.52 and their binder contents 563 kg/m³ and 539 kg/m³ respectively. A volume substitution is chosen in order to keep the same absolute volume of the two compositions (Darquennes et al. 2012; Bessa-Badreddine 2004): the cement paste content, a parameter strongly affecting the shrinkage amplitude, is kept constant for both mixes and the same normalized siliceous sand is used (EN 196-1).

X-ray diffraction and X-ray fluorescence were performed to characterize the cement and GGBFS mineralogy. X-ray diffraction shows that the Portland cement is principally composed of C₃S, C₂S, C₃A, and C₄AF. The presence of gypsum, periclase and calcite is also noted. The GGBFS shows amorphous behavior with some crystalline peaks of akermanite, melilite, and merwinite. Table 2 provides the chemical compositions of the CEMI and the GGBFS, as measured by X-ray fluorescence. The CEMI is mainly composed of CaO (64.85%). The GGBFS contains a smaller proportion of CaO (43.21%), but greater amounts of SiO₂ (33.08%), Al₂O₃ (9.50%), and MgO (5.77%). The Hydralic Factor (HF) calculation (Eq. 1) is up to 1 (1.76), indicating good reactivity for the GGBFS. Table 3 presents the results of the Laser Particle-Size Distribution (PSD) testing showing that the GGBFS is finer than the CEMI with 52.30% of its particles below 10 µm (compared to 16.73% for the CEMI), which improves blast-furnace slag reactivity.

\[
\text{HF} = \frac{\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3}{\text{SiO}_2}
\]  

(1)

2.2 Experimental Techniques

2.2.1 X-ray Computed Tomography

During a X-ray CT test, the specimen is crossed by X-ray beams in order to obtain a 3-D image (a set of 2-D radiographies around a rotation axis is used) (Fig. 1). The achieved X-ray CT picture resolution depends on the specimen dimensions. A thinner specimen facilitates crossing, leading to a smaller voxel size and better resolution. To achieve a reasonable voxel size (20 µm, see thereafter), cylindrical specimens with a 4 cm diameter (height \( h = 2 \) cm) were tested. In this way, the formation of products for a crack size up to 20 µm is studied. This size limit is adequate to determine the durability benefits of self-healing (Darquennes et al. 2016).

After mixing, the specimens (diameter \( \Theta = 4 \) cm, \( h = 10 \) cm) were kept in a room at 23°C ± 1°C and 45% ± 5% of Relative Humidity (RH). The molds were removed after 2 days and the specimens were stored underwater at 23°C ± 1°C. At 6 days, they were confined with a two-component resin reinforced with glass fibers (Fig. 2a) to prevent complete separation of the sample fragments during the splitting tests (performed at 7 days). Then, the samples were sawn into 2 cm thick disks. As sawing is made under water to limit heating, some leaching of the chemical phases (anhydrous and hydrated products) on the sample surfaces can take place. However, its effect on the healing process is limited as shown by the distribution of the healing products along the crack (§3.2). The samples were put on a support keeping their upper and lower faces free (Fig. 2b) and scanned using X-ray CT to determine their initial state. Then they are stored in individual containers inside tap water at 23°C ± 1°C. The main mineral compounds of the used tap water determined by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) are: 101 mg/L Ca, 13 mg/L Na, 4 mg/L Mg, 13 mg/L K. The specimens were regularly analyzed with X-ray CT (during a full month period) to monitor the self-healing evolution.

During the X-ray CT tests, each sample was placed on a rotating support between the X-ray tube and the detector (Fig. 1). Three scans were performed for each table position (600 positions) and the average of the signal intensity was used for the 3-D image reconstruction. Figure 3 presents the different steps: the first step consists in taking radiographies for each specimen position (Fig. 3 - 1st step). A 3-D image of the specimen is then reconstructed (using the eX-CT software). In these 3-D images, the material volumes characterized by lower density (e.g. air) show a darker grey level (Fig. 3 - 2nd step). The specimen can then be isolated through a gray-level selection (Fig. 3 - 3rd step). Artifacts around the specimen can be seen on the resulting picture (Fig. 3 - 3rd step). To limit the effect of these artifacts, a sub-volume around the crack is defined inside the specimen (Fig. 4). The chosen test parameters are: position number for one test, high-voltage, target power, and frames per second equal to 600, 160 kV, 5.5 W, and 0.4, respectively. These parameters provide a resolution of 20 µm per voxel.

![Fig. 1 Principle of X-ray tomography.](image1)

![Fig. 2 Specimen confined and reinforced with resin and glass fibers (a) – Support and specimen (b).](image2)

![Fig. 3 The different steps for the 3-D reconstruction of the specimen.](image3)
To assess the evolution of the crack volume, the 3-D X-ray tomography images (1300 x 300 x 600 voxels, with 256 gray levels) undergo a specific post-processing. First, the 3-D image is transformed into a set of pictures along the Z-axis (Fig. 4) containing 600 pictures with a size of 1300 by 300 pixels (Fig. 5). A segmentation algorithm is applied on each picture to determine the gray-level threshold corresponding to the internal porosity (voids, cracks) in the mortar samples (Landis 2013) based on the method developed by Ridler et al. (1978). In a typical segmented image, white voxels correspond to cracks and porosity and black voxels to the cementitious matrix (Fig. 6). To isolate the cracked volume (created by the splitting test), a connected-component analysis algorithm (Fig. 7) is used maintaining only the largest domain of the connected void voxels (Ridler et al. 1978) (Figs. 6 and 8). The algorithm considers several connections types between voxels: faces (6 connections), edges (18 connections), and corners (26 connections). Face connections were used instead of corner connections because that approach allows a 42% ± 11% gain in calculation time for a difference of 0.004‰ ± 0.002‰ in crack volume estimation. Figure 8 presents a
typical result in which the isolated groups of white voxels in the matrix (for example porosity, air void) are mainly discarded. The crack volume is then easily calculated. Note that this method accounts for some pores intersected by cracks (Fig. 8). This is not a problem in this case, since only the evolution of the crack volume is of interest. Figure 9 presents the crack evolution of a slice (n°300) for the control mortar as a function of the sample age. One can observe the decrease of the crack width with the curing time under water. During the experimental campaign, two specimens were tested for the slag mortar (named hereafter slag mortar_1 and slag mortar_2) and one for the control mortar (named hereafter control mortar).

2.2.2 SEM-EDS
At the end of the X-ray CT tests, Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDS) analysis was performed to determine the nature of the products formed in the healed cracks. Observation at the top of the specimens revealed a carbonated surface (crack and matrix). To visualize the self-healed products in the crack, the specimens were sawn in half in the lengthwise direction (Fig. 10). The coarse surfaces and the products located in the healed crack were analyzed by means of EDS.

2.2.3 Thermogravimetric Analysis (TGA-DTA)
ThermoGravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were performed on the mortar specimens to determine their hydration kinetics and hydration capacity after cracking. The weight-loss evolution of the specimens is monitored between 50°C and 1,000°C with a heat rate of 10°C/min in an argon environment (inert gas). The samples (60 mg) placed in an alumina crucible were tested at 2, 3, 7, 14, 28, and 90 days. Three measurements were performed for each age. The chemically bound water is quantified by the mass-loss difference from 105°C to 1,000°C and from 600°C to 880°C (decarbonation of CaCO₃). The temperature of 105°C corresponds to free-water evaporation. Equation 2 summarizes the method (Popic 2010):

\[
\text{w}(t) = \frac{\Delta m_{\text{bound}}(t) - \Delta m_{\text{bound}}(t_0) - m_{\text{LOI}} \sum m_k \times \text{LOI}_k}{m_s}
\]

where \( w(t) \) is the chemically bound water (g/g binder) at time \( t \), \( \Delta m_{\text{bound}}(t) \) the mass loss between temperatures \( i \) to \( j \) (g), \( m_{\text{LOI}} \) the mass of the sand in the sample (g), \( m_k \) the mass of cement or blast-furnace slag (g), \( \text{LOI}_k \) the loss on ignition (%), \( m_s \) the mass of cement or blast-furnace slag (g), \( \text{LOI}_s \) the loss on ignition of the sand.

Fig. 8 Typical segmented image (2-D slice) for the cracked control mortar at the day of cracking after the application of the connected-component analysis algorithm.

Fig. 9 Evolution of the crack located on the slice n°300 (height = 6 mm) as a function of the sample age for the control mortar.

Fig. 10 Preparing the specimen for SEM observations.
cement or of the blast-furnace slag (%) and \(m_b\) the mass of the binder (g).

To determine the hydration degree evolution, it is necessary to quantify the ultimate chemically bound water \(w_{\infty}\). Several methods are proposed in the literature: an equation based on the Bogue calculation, in which \(w_{\infty}\) is computed using the clinker composition (Mounanga et al. 2004); adopting \(w_{\infty}\) equal to \(w_{\text{max}}\), the maximal value of the chemically bound water at long term (Darquennes 2009); extrapolating \(w_{\infty}\) from the experimental results (Darquennes et al. 2013). In this article, the experimental approach proposed by Bentz was adopted (Bentz 1995; Popic 2010). It consists in mixing a cementitious material characterized by water/binder ratio equal to 3.0 with steel balls in a hermetic bottle during 56 days. The method allows optimizing and accelerating the hydration of the binder particles, not limited by the free space needed for the development of the hydration products and the water diffusion through the hydrates shell around the unhydrated binder particles. TGA is then performed to determine the chemically bound water necessary to hydrate whole grains of cement and blast-furnace slag.

The portlandite (Ca(OH)_2) content \((g/g\text{ binder})\) is determined to assess the evolution of the blast-furnace slag reaction according to Eq. (3) (Popic 2010).

\[
\text{Ca(OH)}_2 = \frac{\Delta m_{\text{400-600°C}}(t)}{m_b} \cdot \frac{M_{\text{Ca(OH)}_2}}{M_{H_2O}} \tag{3}
\]

where \(\Delta m_{\text{400-600°C}}\) is the mass loss from 400°C to 600°C (g), \(m_b\) the mass of the binder (g), and \(M_{\text{Ca(OH)}_2}\) and \(M_{H_2O}\) the molar mass of portlandite and water (g/mol) respectively.

3. Results and Discussion

X-ray CT tests allow determining the self-healing kinetics by monitoring the cracks dimensions and indirectly the volume of the healing products, their distribution along the crack and the influence of the ground granulated blast-furnace slag.

3.1 Volume of healing products

Figure 11 shows that the volume of healing products increases with the duration of water storage in both mortar compositions. For all compositions, the change increases with the duration of water storage in both compositions, and characterized by different crack widths.

At 7 and 14 days after cracking, the average volumes of the self-healing products are (1) 5.8 mm³ ± 0.6 mm³ and 18.9 mm³ ± 0.4 mm³ for the slag mortars, and (2) 4.3 mm³ and 8.3 mm³ for the control mortar. The formation of new products is therefore doubled for the slag mortars after the first two weeks of water curing.

Fig. 11 Healing products volume evolution.
by the healing products at the top of the control mortar specimen. Indeed, the crack volume filled by the healing products close to the top surface of the specimen (2 mm depth) is comparable after a week of water curing: 9.8% for the slag mortar_1 and 5.2% for the control mortar.

3.3 Influence of blast-furnace slag
Comparison of the tomography tests for the slag mortar_1, the slag mortar_2 and the control mortar, confirm that blast-furnace slag has a positive effect on self-healing at early age cracking (7 days). Figures 11, 12 and 13 show that mortars containing GGBFS present a faster initial self-healing evolution rate (approximately 2 times faster) and a higher content of healing products than the control mortar. Two factors, the initial crack opening and the hydration kinetics can explain this difference:

3.3.1 Initial crack opening
The initial crack opening determines the final crack size (after self-healing). Finer cracks tend to heal (almost) completely because of the smaller initial volume that has to be filled (Edvardsen 1999; Gagné et al. 2012). The initial crack opening affects also the self-healing rate. Results reported in the literature are however contradictory. Gagné et al. (2012) found that the self-healing rate is faster for a larger crack (≥ 200 µm) than for finer crack (< 50 µm). Reinhardt et al. (2003) showed that cracks characterized by a width between 50 and 150 µm heal faster.

In order to take into account the effect of the initial crack opening, the volume of the self-healing products is divided by the initial crack volume in Fig. 14. For the slag mortars, the initial crack openings are different: 71 µm for the slag mortar_1 and 116 µm for the slag mortar_2, while for the control mortar it is equal to 114 µm. At 35 days, 41% ± 0.7% of the initial crack of the slag mortars is filled, while only 12% for the control mortar. The crack filling rate during the first week of water curing is equal to 1.5 %/day for the slag mortar_1, 1.2 %/day for the slag mortar_2 and only 0.7%/day for the control mortar.

Results confirm also that slag mortars have a higher capacity to form healing products and present a faster kinetics than the control mortar. Finally and despite a different initial crack opening, the two slag mortars show a similar behavior (healing kinetics and healing products volume). The initial crack opening is therefore not the cause for the difference on the behavior of slag and control mortars.

3.3.2 Hydration kinetics
Figure 15 presents the average degree of hydration as function of time. The hydration degree is calculated with Eq. 4.

\[
\alpha(t) = \frac{w(t)}{w_\infty} \cdot \alpha_\infty
\] (4)

Fig. 12 Crack volume distribution for each 2 mm height of the analyzed subvolume at the cracking day (at 7 days), after a week of water curing (at 14 days) and at the end of the water curing (at 35 days) for the slag mortar_1.

Fig. 13 Crack volume distribution for each 2 mm height of the analyzed sub-volume at the cracking day (at 7 days), after a week of water curing (at 14 days) and at the end of the water curing (at 42 days) for the control mortar.

Fig. 14 Healing products and initial crack volumes ratio evolution.
Two parameters are needed:

1) The final chemically bound water \( w_\infty \) determined experimentally following the approach developed by Bentz (1995) (see § 2.2.3). The values of the final chemically bound water \( w_\infty \) for the slag and control mortar are \( 20.45 \times 10^{-2} \pm 0.37 \times 10^{-2} \, g/g_{\text{binder}} \) and \( 22.90 \times 10^{-2} \pm 0.06 \times 10^{-2} \, g/g_{\text{binder}} \), respectively. These values are in agreement with (Popic 2010) where mortars containing mineral additions were tested.

2) The ultimate hydration degree \( \alpha_u \). The binder hydration often stops before the total consumption of the binder. Several parameters can limit its final hydration degree: available water (Hansen 1986), available space in the matrix for the development of new hydrates (Oh et al. 2003), presence of supplementary cementitious materials (Schindler et al. 2005), etc. In order to take into account these effects, several authors (Mills 1966; Schindler et al. 2005) introduce a parameter to characterize the ultimate extent of the hydration reaction: the ultimate hydration degree. Based on chemically bound water measurements of Portland cement, Mills (1966) proposed a relation to compute the ultimate hydration degree that takes into account the water-cement ratio effects - the first term in equation 5. In presence of mineral additions, the ultimate hydration degree increases. For this reason, Schindler et al. (2005) added in the Mills’ relation two terms \( (p_{FA}, p_{slag}) \) related to the fly ash and blast-furnace slag contents (the second and third terms in equation 5). Their coefficients were determined from experiments performed on mixtures with maximal content of mineral additions equal to 50%. According to Schindler et al. (2005), this improved relation is however not suitable for all combinations of cementitious materials due to the high number of interactions. Nevertheless, this relation (Eq. 5) is adopted in the present study as the binders are similar to those used by Schindler et al. (2005): a Portland cement and a blast-furnace slag content equal to 50%.

\[
\alpha_u = \frac{1.031 \times W/C}{0.194 + \frac{W/C}{C} + 0.50 \times p_{FA} + 0.30 \times p_{slag}}
\]  

(5)

where \( W/C \) is the water–cement ratio, \( p_{FA} \) and \( p_{slag} \) the fly ash and slag content (as percentages). \( \alpha_u \) for the slag and control mortar is equal to 0.90 and 0.74 respectively. Notice that the hydration degree value presents a (average) standard deviation of 0.02.

During the first week, the slag mortar shows a lower degree of hydration than the control mortar. This can be explained by the blast-furnace slag hydration kinetics related to two phenomena (Moranville-Regourd 2004; Taylor 1997): (1) initiation of the GGBFS dissolution requiring high pH in the interstitial water, directly related to its alkali content; and (2) formation of supplementary C-S-H from GGBFS and portlandite (a product of the Portland cement hydration). The increase of the portlandite content of the slag mortar is smaller than for the control mortar. More specifically between 2 and 90 days, the portlandite content increases only \( +3.96 \times 10^{-2} \, g/g_{\text{binder}} \) in the slag mortar and \( +9.45 \times 10^{-2} \, g/g_{\text{binder}} \) in the control mortar. This is explained by (1) the smaller amount of clinker in the slag mortar, and (2) the consumption of portlandite \( \text{Ca(OH)}_2 \) for the reaction with GGBFS particles to produce supplementary C-S-H. The formation of C-S-H can be indirectly estimated by the mass loss between 105-400°C (\( \Delta m_{105-400°C} \)) corresponding to C-S-H dehydration - if the other hydrates (e.g. ettringite, monosulphate) present to a less extent are neglected. The mass loss between 400-600°C (\( \Delta m_{400-600°C} \)) corresponds to portlandite dehydroxylation. The mass losses ratio \( \Delta m_{105-400°C}/\Delta m_{400-600°C} \) allows characterizing the pozzolanic reaction of the blast-furnace slag and thus, the formation of supplementary C-S-H. This ratio is equal to (about) 5.5 and 2.8 for the slag and control mortars respectively at 90 days (Fig. 16) confirming the more important content of C-S-H for the GGBFS composition and its lower content in portlandite.

At 7 days, the evolution of the slag mortar hydration degree (0.53) is lower than for the control mortar (0.64) (Fig. 15), in agreement with (Van Tittelboom et al. 2012; Darquennes et al. 2013). It results that slag mortar shows a higher hydration potential capacity at the cracking day (at 7 days). Moreover, the ratios of C-S-H and

![Fig. 15 Hydration degree evolution for the studied mortars.](image)

![Fig. 16 The evolution of the mass loss ratio C-S-H (\( \Delta m_{105-400°C}/\Delta m_{400-600°C} \)) contents for the studied mortars.](image)
Ca(OH)$_2$ contents (Fig. 16) begin to strongly increase only after this age confirming a greater amount of anhydrous elements at 7 days. After this period, the slag mortar’s hydration degree increases and surpasses that of the control mortar (0.88 for the slag mortar and 0.70 for the control mortar at 28 days). A fast evolution of the ratio of C-S-H and Ca(OH)$_2$ contents is also observed confirming that the formation of supplementary C-S-H is important after 7 days thanks to the ongoing hydration.

Results also confirm the slower hydration rate and therefore the higher number of anhydrous particles in the slag mortar at early age. Its larger hydration potential after 7 days leads to a higher self-healing potential at early age for compositions containing GGBFS. In this case, the main self-healing process is the ongoing hydration. This observation is also validated hereafter with further experimental studies on the microstructure of the self-healing products.

3.4 Microstructure of self-healing products

Figures 17 and 18 illustrate self-healed cracks in the heart of the slag and control mortar samples. While sawing may have slightly damaged the new products, the bridging between the two crack faces is clearly visible. EDS analysis shows the predominance of Ca and Si (Fig. 19) for both specimens revealing that the new products are mainly C-S-H (Figs. 17 and 18). Moreover, the presence of alumina and magnesium ions from GGBFS is also detected in the new products for the slag mortar (Fig. 19). The C/S ratio of the new products is lower for the slag mortar (1.21) than for the control mortar (1.26). These ratios are inferior to those for the C-S-H from sound materials (1.39 for slag mortar and 1.47 for control mortar). Notice that the difference between C/S ratio for C-S-H from compositions with and without GGBFS is also reported in the literature (Taylor et al. 2010). The C-S-H formation confirms that the self-healing of early-age cracks corresponds to ongoing hydration. As suggested by Neville (2002), this process appears if two conditions are achieved: a water storage during self-healing conditions and a low hydration degree at cracking day. C-S-H as the main self-healing products is also mentioned by Hearn (1998) and Jacobsen et al. (1995).

4. Conclusions

The early age self-healing capacity of cementitious materials with various GGBFS contents was studied in this article using a modern (X-ray Tomography) experimental technique, able to quantify the self-healing kinetics and the distribution of the healing products inside the specimens. The main results of the study are summarized hereafter:

- X-ray tomography is an effective nondestructive modern experimental technique, presenting a good repeatability, for observing the spatial and temporal...
The evolution of the 3D self-healing phenomenon as well as to assess the crack development and the formation of the healing products.

- The X-ray tomography results show that self-healing at early age occurs inside the specimen (at a certain depth) and presents a double kinetic: faster during the first two weeks after cracking and then slowing down. The mortar with ground granulated blast-furnace slag has a higher self-healing capacity than a Portland cement mortar: its healing kinetics is faster, the quantity of healing products is more important and presents a more homogeneous distribution inside the specimen.

- The higher early age self-healing capacity of the ground granulated blast-furnace slag specimen can be explained by the slow hydration kinetics at early age, leading to a significant quantity of unhydrated GGBFS particles at cracking and by the important capacity of ongoing hydration after cracking.

- For cracking at early age (< 28 days) and water curing, the main healing products are C-S-H characterized by a C/S ratio slightly lower than that of the sound binder matrix.

Acknowledgment

This work has benefited from the support of the French “Agence Nationale de la Recherche”, through the “Investissements d’avenir” program under the reference “ANR-10-EQPX-37 MATMECA.”

References


