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Carol Youssef-Namnoum, Benoit Hilloulin, Frederic Grondin, Ahmed Loukili. Determination of the origin of the strength regain after self-healing of binary and ternary cementitious materials including slag and metakaolin. Journal of Building Engineering, 2021, 41, pp.102739. 10.1016/j.jobbe.2021.102739 . hal-03537509

HAL Id: hal-03537509

<https://hal.science/hal-03537509>

Submitted on 20 Jan 2022

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**Determination of the origin of the strength regain after self-healing of
binary and ternary cementitious materials
including slag and metakaolin**

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Highlights

- Mechanical tests discriminate the healing performance of concretes
- XRD, TGA and SEM were employed to analyze the reaction products formed during the healing process
- Ternary formulations with slag and metakaolin show better self-healing performances
- Additional healing products are formed due to minerals additions in healed cracks
- Microstructure of the healing products explain the global self-healing performance

Abstract

A mechanical assessment of the self-healing process of complex cementitious materials with mineral additions is presented. Mortars made with binary and ternary binders (blast furnace slag, fly ash, metakaolin and silica fume) to reach 30 vol% substitution ratios were prepared, and then small cracks with a width of 10 μm were created at the age of 28 days. After a 26-day healing period, mechanical properties obtained from three point bending tests were analyzed to identify the recovery due to healing. In addition, the microstructure of self-healing products was studied using various techniques (TGA, SEM/EDS, and XRD). It was found that ternary compositions might exhibit a better self-healing performance compared to single or binary compositions. The mechanical tests indicate a better stiffness recovery for specimens prepared from the ternary mixture. This improvement of mechanical response is presumably due to the newly formed products precipitated in the cracks.

Keywords: self-healing; cementitious materials; minerals additions; mechanical properties; microstructure; ternary compositions.

1. Introduction

In the actual context of climate change and the necessity to decrease greenhouse emissions, the development of building materials with low content of cement has become more relevant to reduce the civil engineering industry's carbon footprint. The use of latent hydraulic or pozzolanic materials in place of clinker is one of the strategies discussed by cement industry leaders and scientists. Besides, the deterioration of concrete structures by time imposes enormous economic loss and environmental damage. Cracks, as a damage sign, make it easier for harmful substances to penetrate into the concrete matrix

and thus reduce the durability of concrete structures. Therefore, a better characterization of their properties and the prediction of their durability are important. In the last decade, self-healing performance of concrete structures appears as a promising technique to improve the durability and sustainability of a damaged structure by restoring its original mechanical or permeability properties [1-3].

The intrinsic ability of concrete to heal is associated with the continuous hydration of unhydrated cementitious particles and/or precipitation of calcium carbonate [4], [5]. When cracks occur in concrete structure and supplement water penetrates into the crack, further hydration reactions take place owing to the presence of unhydrated cement particles. This type of self-healing is called ‘autogenous healing’ process [6] where the presence of water is essential to initiate the chemical reaction of the unreacted particles of clinker. This healing process leads to secondary hydration products like C-S-H and portlandite. The contact occurring between water and unhydrated particles of cement induces the dissolution of Ca^{2+} and OH^- ions that start diffusing into the crack and promotes the precipitation of new products around the crack. Following this mechanism, the hydration products formed can re-establish the continuity of the material and improve the mechanical properties of damaged concrete structure.

To highlight the self-healing efficiency, some researchers have adopted the visualization (optical microscopy or X-ray microtomography technique) of crack filling as a direct test to prove the continuous hydration [7]–[12]. Some other authors choose to indirectly measure the recovery of matrix properties by means of mechanical tests [9], [10], [13]–[15], durability tests such as air or water permeability [16]–[18] or nondestructive testing [19].

It is generally considered that both stiffness and strength regains can be obtained after two weeks of continuous immersion into water for 10 μm width crack [9], [16]. Moreover,

most of studies indicate that continued or cyclic immersion into water for several weeks is needed to increase mechanical recovery. Others studies showed that healing potential is highly improved when the crack is created at early age [5], [19]. The self-healing properties vary according to the crack width, the type of binder [11], [12], [20], [21] and the amount of unreacted cement grains in the concrete matrix [9], [13], [15], [21]–[23]. Studies showed that healing process is limited to a crack width smaller than 50 μm [14], while others conclude that complete sealing (restoration of permeability) is also possible for crack widths up to 200 μm [11]. While regarding mechanical properties, healing has been reported as efficient for smaller width crack.

By now, several studies have been carried out to get more information about self-healing by further hydration [7]–[12]. Concerning mechanical properties of healed cementitious materials, experimental results reveal a possible strength recovery as well as a stiffness recovery [13].

Moreover, it was found that using mineral additions could improve the autogenous self-healing capabilities of concrete. By using mineral additions, an improvement of permeability and strength of structure was observed compared to Portland cement that has better mechanical properties at early age [11, 24–32,33]. These mineral additions lead to change an ordinary cement paste to binary and ternary cementitious materials. Recently, there is a great interest in using metakaolin as a supplementary cementitious material in concrete. It is an ultra-fine material with strong pozzolanic activity, produced by calcination of kaolin at temperatures between 700 and 900 $^{\circ}\text{C}$ [15]. Metakaolin consists of silica and alumina product that react with portlandite to produce C-S-H gel and alumina phases (C_2ASH_8 , C_4AH_{13} and C_3AH_6) [34]. Research results have shown that the use of metakaolin is quite useful in improving the strength of concrete at a young age [36, 37], or later [38, 39]. The combine use of slag and metakaolin have an influence in enhancing

mechanical properties and durability of mortar and concrete. The highly active pozzolanic reaction of metakaolin with respect to the latent hydraulic properties of slag can explain this equilibrium of functions leading to improved mechanical behaviour, where the presence of both materials have no adverse effect [38]. This enhanced performance is due to the filler effect which improve the microstructure density [39] and the diversity of hydration products formed from a ternary mixture containing metakaolin and slag, like C_2ASH_8 , C_4AH_{13} and C_3AH_6 [39]. Mohammadi et al. [40] have recently shown the interest to combine formulations and other mineral additions on the self-healing capacity regarding the variety of the self-healing products.

In spite of the benefits of using mineral additions, few tests have been performed in order to investigate their role on the mechanical properties through the self-healing process. Salama et al. [27] reported that the highest recovery in mechanical and permeability properties was obtained with cement composites incorporating 25% of slag and with the mixtures containing metakaolin, which behaves very similarly to the ordinary mixture containing 100% cement. Termkhajornkit et al. [38] reported that increasing the fly ash content leads to an increasing of the self-healing efficiency by measuring the amount of chloride ions diffused before and after self-healing. Erdoğan Özbay and Sahmaran [39] assessed the healing performance of fiber concrete ECC containing fly ash. The results show a better healing performance when the CaO content is higher.

With the increasing development of ternary formulations motivated by economic and environmental considerations in the first place, it is important to understand what happens during the self-healing phenomenon. The development of ternary formulations favorable to healing could be useful for on-site industrial applications. Research works have mainly focused on characterizing self-healing properties for binary blends of concrete materials regarding permeability regains, and very little work has been carried out on the

microstructure and durability of concrete incorporating various mineral admixtures. In particular, the effect of using both slag and metakaolin on the mechanical performance of healing process has never been reported in the literature to our knowledge. This paper presents an experimental study on the chemo-mechanical characterization of the self-healing phenomenon of cementitious materials with low content of cement including supplementary cementitious materials. Therefore, a complete study has been performed to highlight the best binder mixture regarding the self-healing capacity. The mineralogy of the self-healing products in cracks of various cement pastes including SCMs was investigated with scanning electron microscope equipped with an energy dispersive spectroscopy (EDS), thermogravimetric analysis (TGA) and X-ray diffraction test (XRD). Artificial gaps were designed to obtain the powders of healing products in order to distinguish the newly formed reaction products from the bulk paste [10]. In addition, the influence of the mix design on the potential of self-healing was studied. 2D microscope measurements were performed before and after healing to indicate the processing of self-healing phenomenon. The mechanical behaviour of pre-cracked mortars containing SCM subjected to healing was assessed by means of three points bending tests to quantify the regains of mechanical properties.

2. Materials and methods

2.1 Materials

In this study, mortars were prepared with materials used to have beneficial effects on healing potential. All mortars mixtures were prepared with ordinary Portland cement (CEM I 52.5 N), SAREMER sea sand 0/4, the same paste volume 530 l/m^3 and the same

water-to-binder ratio of 0,4. Different supplementary cementitious materials (SCM) like Metakaolin (MK), Slag (S), Fly Ash (FA) and Silica Fume (SF) were used as partial volume substitution of cement up to 30%. Chemical compositions and physical properties are detailed in **Erreur ! Source du renvoi introuvable..** C₁₀₀ was considered as the ordinary mixture made with only Portland cement (100% of cement). Binary (C_xA_y), ternary (C_xA_yB_z), mixtures were made with x% of cement (C_x) and y% of SCM, respectively y% and z% of SCM = {MK, S, FA, SF}. The mixture design of all mortars prepared for this study is summarized in Table 2.

Table 1. Chemical composition and properties of Portland cement and additions used in this study.

| | | Cement | Metakaolin | Slag | Fly ash |
|---------------------------------|--|--------|------------|------|---------|
| Chemical composition (%) | SiO₂ | 19,6 | 93,16 | 37,7 | 50 |
| | Al₂O₃ | 4,5 | | 10,2 | 8,5 |
| | Fe₂O₃ | 2,3 | - | 0,6 | 29 |
| | CaO | 63,7 | 0,36 | 43,8 | 2,15 |
| | MgO | 3,9 | 0,04 | 6,4 | - |
| | SO₃ | 2,6 | - | 0,1 | 0,37 |
| Physical properties | Specific gravity (Kg / m³) | 3130 | 2500 | 2900 | 2100 |
| | Specific area (m²/g) | 0,39 | 16 | 0,45 | 0,23 |

Table 2. Mortars mixtures

| | w/b | Sea Sand 0/4 (kg/m ³) | Binders content (vol%) |
|--|-----|-----------------------------------|------------------------|
| C ₁₀₀ | 0,4 | 1231 | 0 |
| C ₇₀ MK ₃₀ | 0,4 | 1231 | 30% MK |
| C ₇₀ S ₃₀ | 0,4 | 1231 | 30% S |
| C ₇₀ SF ₃₀ | 0,4 | 1231 | 30% SF |
| C ₇₀ FA ₃₀ | 0,4 | 1231 | 30% FA |
| C ₇₀ MK ₁₅ S ₁₅ | 0,4 | 1231 | 15% MK + 15% S |

2.2 Samples preparation for the assessment of mechanical regains due to self-healing

For the determination of the compressive strength of mortars mixtures, three $4 \times 4 \times 16 \text{ cm}^3$ specimens of each mixture were tested at 2, 7 and 28 days, according to European standard protocol EN 12 390-3. For binary and ternary mixtures, activity index R was presented as the ratio between the compressive strength of the mortar with mineral addition (f_i) and the compressive strength of the ordinary mixture mortar C₁₀₀ (f_0) : $R = f_i / f_0$.

In order to study the effect of healing process on mechanical properties of these different mixtures, mortar prisms of dimensions $7 \times 7 \times 28 \text{ cm}^3$ and $4 \times 4 \times 16 \text{ cm}^3$ were prepared. Specimens were vibrated into two layers on a horizontal vibrating table in order to minimize the amount of occluded air. After 24 hours of curing under sealed conditions in a room at 20 °C and 85-95% relative humidity, the specimens were demolded. A notch was cut at the middle of $7 \times 7 \times 28 \text{ cm}^3$ specimens with a depth of 7 mm and thickness of 5 mm by means of precision saw machine, in order to initiate cracking at a specific location using three-point bending test. Following that, specimens were stored in tap water at 20 °C before cracking and during the healing period. Two prepared samples of each mixture were pre-cracked at the age of 48 hours by three-point bending test whereas the crack mouth opening displacement (CMOD) was controlled with a constant rate of 0,2 $\mu\text{m/s}$, following ASTM C78 norm. The aim of this step was to obtain a residual crack width equal to 10 μm , which permits to get a fast healing process. The choice of an initial width-crack of 10 μm created at the age of 48 hrs is related to better mechanical regains obtained for specimens cracked at a young age as revealed by [41]. The real crack width was measured using a 2D microscope. Then, the specimens were further cured in tap water 20 °C under unsealed condition.

. After healing for 26 days, the healed and the reference specimens were reloaded after 1-h exposure to room temperature necessary for the Crack Mouth Opening Displacement

(CMOD) dispositive preparation. The drying time is chosen to be as short as possible to avoid alteration of the healing products. The healing phenomenon was verified by 2D microscopic observations that show the precipitations of newly formed healing products. By employing three-point bending test, three prisms specimens from each mixture were reloaded in order to characterize the residual mechanical properties after healing process. These three specimens consist of two samples pre-cracked and healed while the third one represents the reference sample (un-cracked before curing). At this step, a flexural stress-deflection curve obtained when the healed samples were mechanically reloaded is compared to the loading curves of the reference sample having undergone the same curing conditions [31], [41].

The performance of healing was quantified by using two equations 'format of mechanical regains related to strength and stiffness recovery respectively [31]:

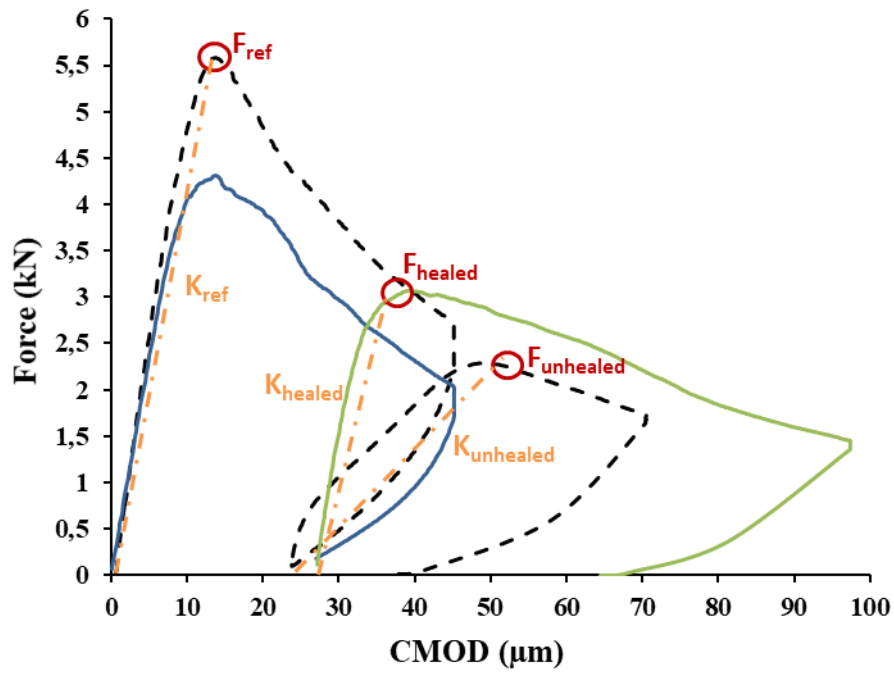
$$IR.strength = \frac{F_{healed} - F_{unhealed}}{F_{ref} - F_{unhealed}} \quad (1)$$

$$IR.stiffness = \frac{K_{healed} - K_{unhealed}}{K_{ref} - K_{unhealed}} \quad (2)$$

where F_{healed} represents the maximum strength of the healed samples during reloading, F_{ref} the maximum strength of reference sample loaded at 28 days, $F_{unhealed}$ the reloaded-maximum strength of reference sample, K_{healed} the maximum stiffness of the healed samples during reloading, K_{ref} the maximum stiffness of reference sample and $K_{unhealed}$ the reloaded-maximum stiffness of reference sample. K values were calculated by drawing a tangent on the loaded and reloaded curve. These two indexes vary between 0 (no healing) and 1 (total healing). The different elements of indexes are represented in Fig.1. The overall program for three point bending test after 4 weeks of age is presented in Fig.2.

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216 **Fig.1** Example of Load vs. CMOD curves for specimens submitted to healing and
 217 reference specimens; representation of quantities for calculation of self-healing indexes.

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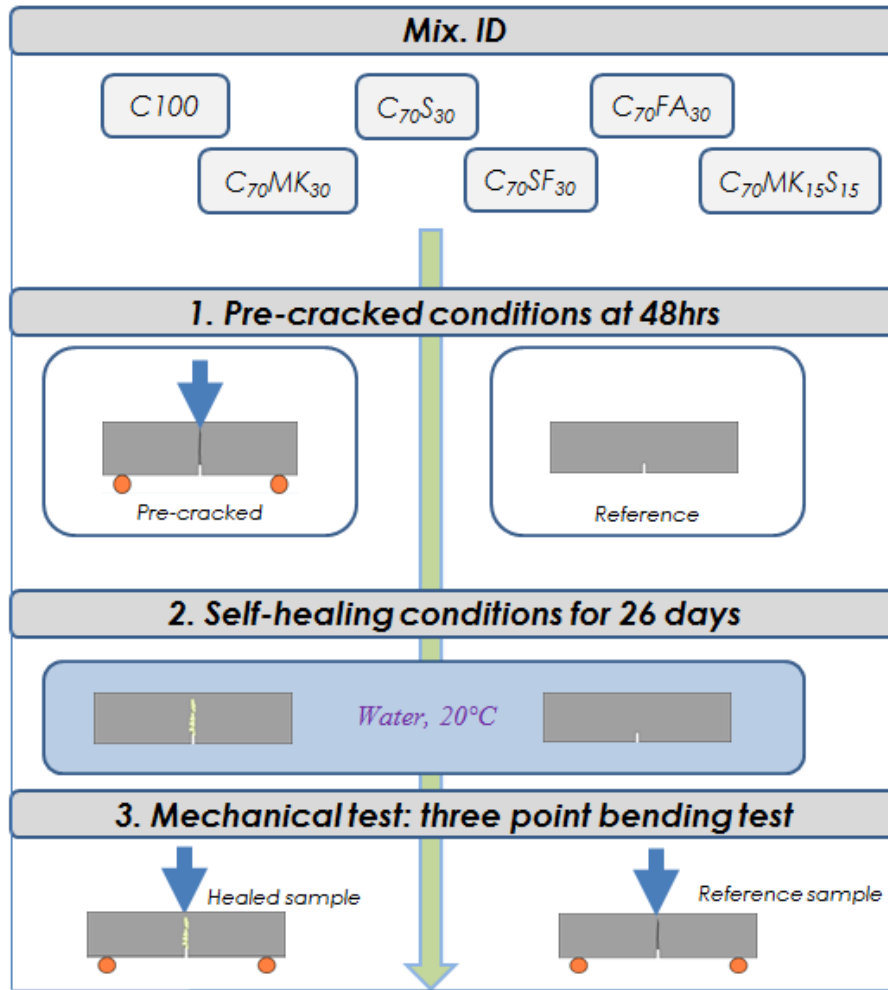


Fig.2 The experimental program flowchart adapted to identify the performance of self-healing.

2.3 Morphology of self-healing products: testing procedures

The characterization of reaction products formed in healing process has been performed by using different tests 'SEM/EDS, TGA, XRD analyses. A special procedure consisted of the creation of artificial cracks was followed [10]. First, $4 \times 4 \times 16 \text{ cm}^3$ cement paste samples were prepared from the different mortars formulations mentioned before. Then, the samples were demolded after 24 hours of curing in room at 20°C and $90 \pm 5\%$ relative humidity.

At 48 hours, the specimens were sliced into dimensions of 4 cm height, 4 cm length and 1 cm thickness. A total of 16 slices was obtained per 1 specimen. Following that, the 16

slices were pressed together by using a plastic clamp and immersed in tap water for 4 weeks (Fig.3 **Erreur ! Source du renvoi introuvable.**). The gap width between the slices does not exceed the 30 μm . It was measured by a microscope. During the healing process, new reaction products were precipitated inside the artificial planar gaps between two slices. After the self-healing period, the cement paste slices were separated and vacuum-dried during 2h. The slices have been observed by SEM equipped with EDS to determine the morphology of healing products formed between each two flat slices and their chemical structures.

In addition, the healing products were scratched off easily from the slice surfaces by using an aluminum spatula then powders obtained were tested. Besides, the internal part of cement paste matrix were grounded into powder and tested in order to differentiate the primary hydrate phases from the healed products formed between the slices. Analysis of mineralogy was performed on these fine powders using TGA and XRD tests. As mentioned in [10], the planar gaps have no influence on the chemical natures of the healing products formed by further hydration.

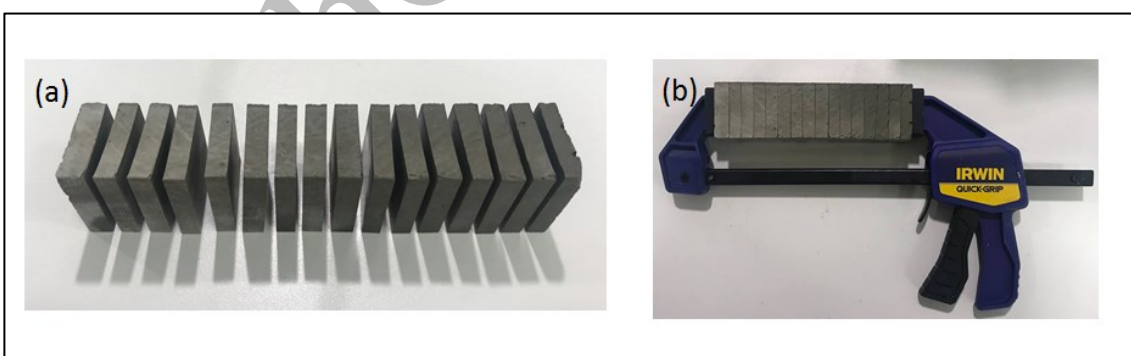


Fig.3 Slices cut from 40x40x160 mm cement paste specimen (a), slices pressed together using a clamp (b).

2.3.1 SEM / EDX

The microstructure of products formed in planar gaps was observed via scanning electronic microscopy (SEM) coupled with EDS in order to get more information on

chemical elements of the reaction products. The microscopic analysis technic used was a scanning electron microscope JEOL JSM-6060LA, used at a distance of 9-11mm for pictures, and an acceleration voltage of 20kV to acquire high contrast images. It was equipped by an EDS detector. The slices observed were placed into vacuum under a pressure of 60Pa into the SEM.

2.3.2 TGA

Thermogravimetric measurements (TGA) were performed in nitrogen atmosphere at 0.6 bars by using a Netzsch STA 449 F3 Perseus device. The studied materials were crushed to obtain 50 mg samples. The heating rate was 20 °C/min and the highest temperature applied was 1400°C.

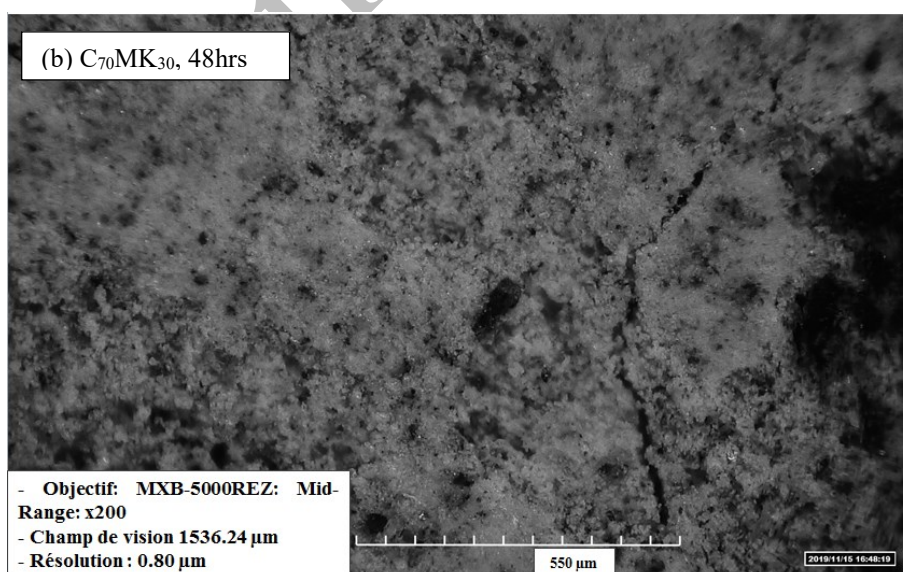
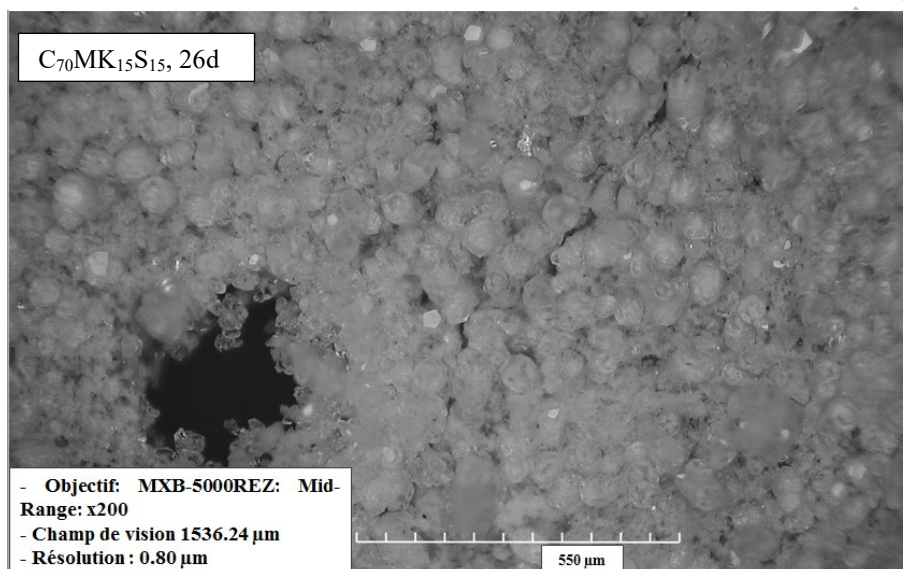
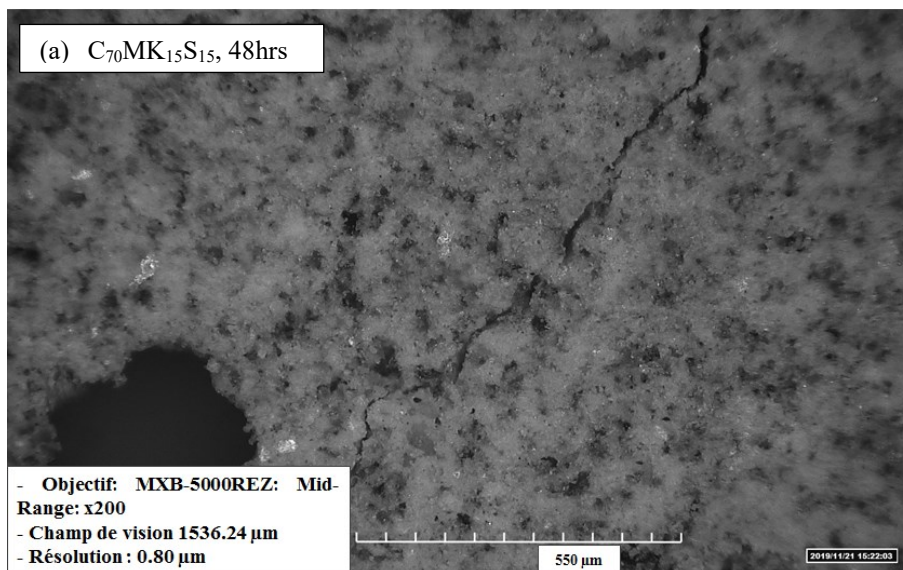
2.3.3 XRD

After healing for 26 days, X-ray diffraction (XRD) measurements were performed on a Bruker D8 phaser instrument. Scans were conducted with a step size of 2.5°, for 0.1 s per step while 2θ range between 5° and 60°. Analysis was carried out by using Eva software.

3. Results and discussion

3.1 2D microscope measurements and SEM/EDX analysis

For the cracked specimens, 2D microscope observations were performed at 48 hours following the three-point-bending tests. After 26 days of healing in water, observations of the precipitation of healing products were done. Fig.4 shows that after self-healing, newly formed reaction products were precipitated in crack, which re-establish the link between the two surfaces of crack. The reaction products are white crystals.



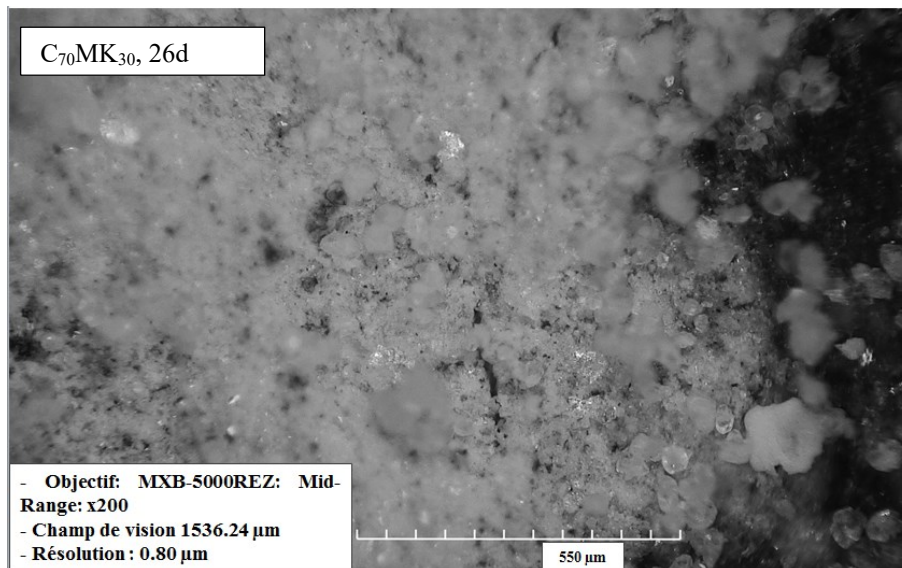


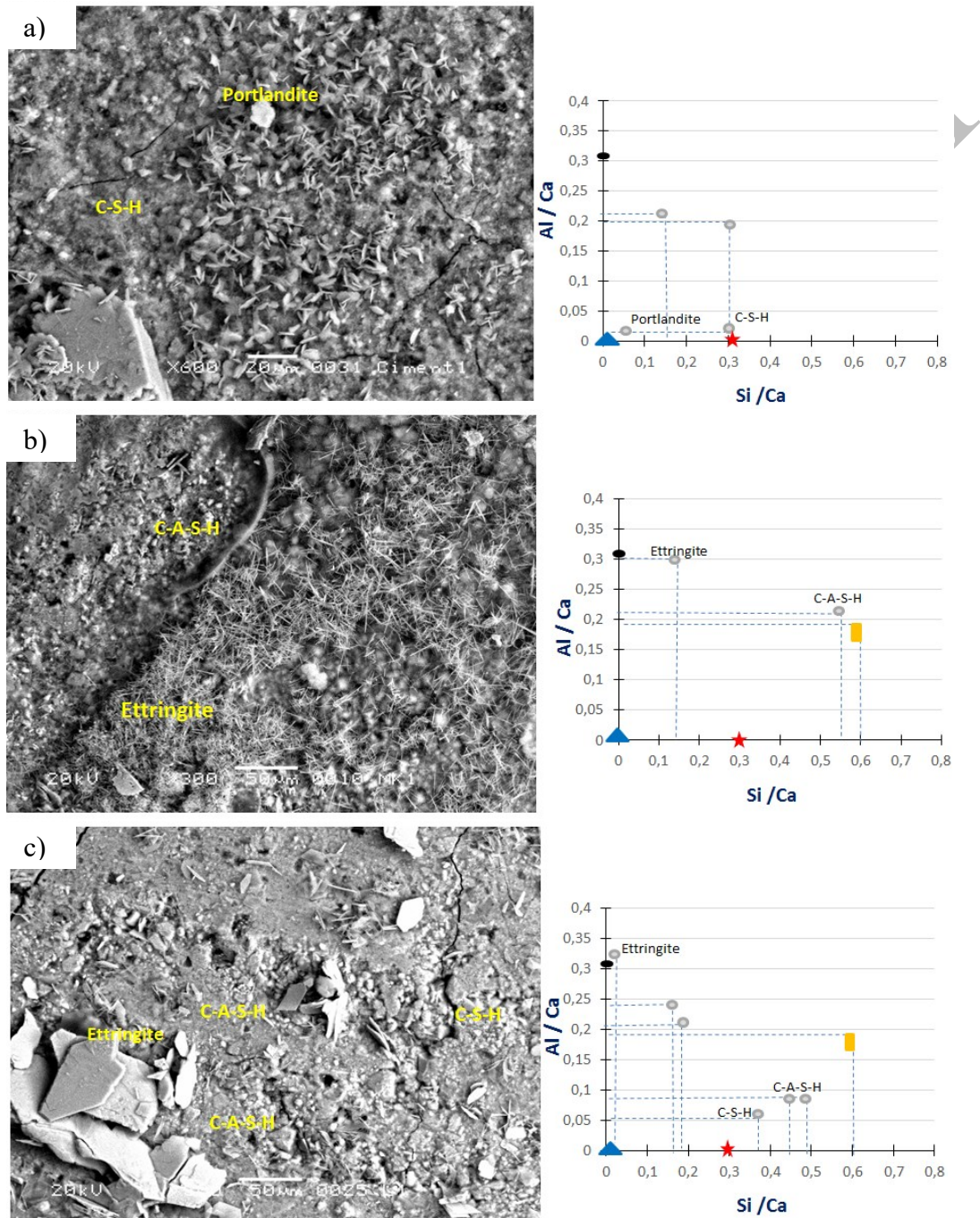
Fig.4 2D microscopic image of specimen with minerals additions before healing (48 hours) and after healing (26 days of immersion in water), (a) for ternary binders containing 15% of metakaolin and 15% of slag, (b) for binary binders containing 30% of metakaolin.

Fig.5 illustrates the surface of artificial cracks after self-healing for 26 days. The presence of ettringite as healing products was commonly found for C_{100} , $C_{70}MK_{30}$ and $C_{70}S_{30}$. This product appears due to continuous hydration of unreacted particles of cement.

Fig.5 shows also the EDS analysis plotted as Al/Ca ratio against of Si/Ca (atomic %). For binary mixture $C_{70}MK_{30}$ (Fig.5b), C-A-S-H sheets were detected in addition to the ettringite as healing products. Metakaolin contains silica and alumina in an active form, which was assumed to react with portlandite to form C-A-S-H gel [42].

As presented in Fig.5d ($C_{70}MK_{15}S_{15}$), the healing products are most like C-A-S-H. It can be explained by the pozzolanic reaction of metakaolin and the hydration reaction of slag. From EDX analysis, it was difficult to determine the composition of products due to high level intermixing with metakaolin, slag, ettringite and C-A-S-H. However, we do not notice the presence of stralingite, which is also considered as one of the hydration products of metakaolin [39].

Moreover, the healing products as can be seen in Fig.5 c) (C_7S_{30}) are most like C-S-H, ettringite and C-A-S-H. Whenever slag particles are present into contact with portlandite, their reaction can directly appear by the presence of C-S-H [43]. Therefore, this can lead to a better self-healing process than that of ordinary mortar mixture.



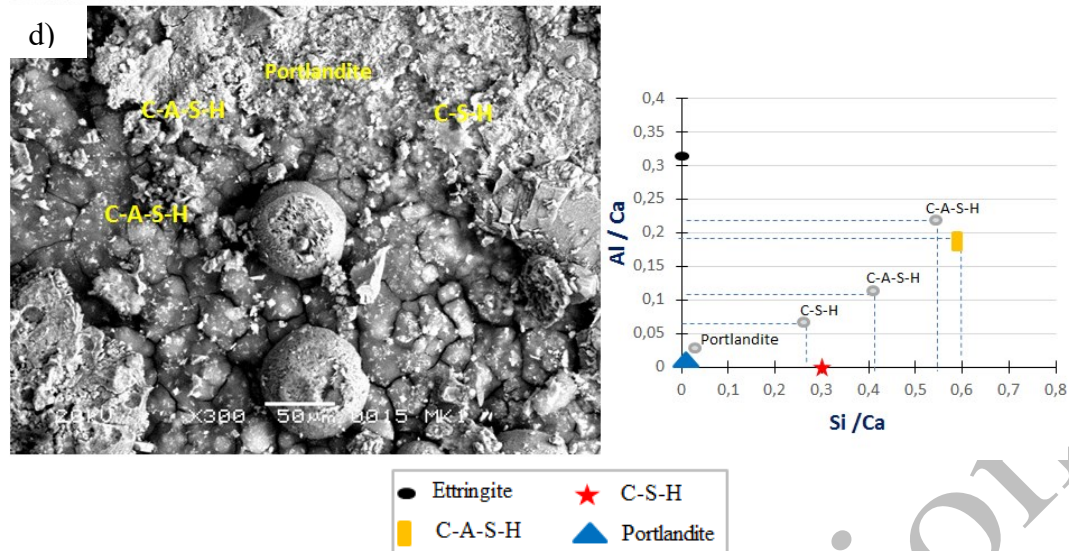


Fig.5 SEM/EDS analysis of an artificial cracks after 26 days of healing: (a) C₁₀₀, (b) C₇₀MK₃₀, (c) C₇₀S₃₀, (d) C₇₀MK₁₅S₁₅. Scale bar of BSE images corresponds to 50 μm. Graphical treatment of EDX points analysis obtained for healed products, AL/Ca ratio is plotted as a function of Si/Ca ratio (in atomic percentage).

3.2 TGA analysis

Fig.6 illustrates the DTA/DTG profiles of bulk cement paste and healing products formed in cracks after curing up in water to 26 days. Overall TGA graphs show common hydration products peaks around 110 °C to 200 °C for hydrates like ettringite, C-S-H gel [42], [44], around 410 °C to 550 °C for portlandite [45], and the peaks between 660 °C and 840 °C is mainly due to the decomposition of calcite [46].

For DTG profiles of the healing products for binary and ternary blends (C₇₀MK₃₀, C₇₀S₃₀ and C₇₀MK₁₅S₁₅), small peaks are observed at about 190-280 °C. They represent the decomposition of crystalline part of C-A-H, C-A-S-H and the presence of monocarboaluminate and gehlenite hydrates [42]. Thus, they participate in the diversification of healing products [47].

These phases are formed as results of the pozzolanic reaction of metakaolin with portlandite that enhances the hydration process. Indeed, a carbonation reaction products located in cracks evolved rapidly due to the air exposition with a 51% and 70% RH [15],

[38]. Moreover, the ingress of CO₂ between each two slices is accelerated by the porous structure of reaction products present between the gaps [15].

As shown in Fig.6b and Fig.6c, in the DTG profile of healing products in cracks, the endothermic peak located at 350 °C represents the decomposition of brucite. The presence of brucite as reaction products could be attributed to the presence of Mg in slag composition.

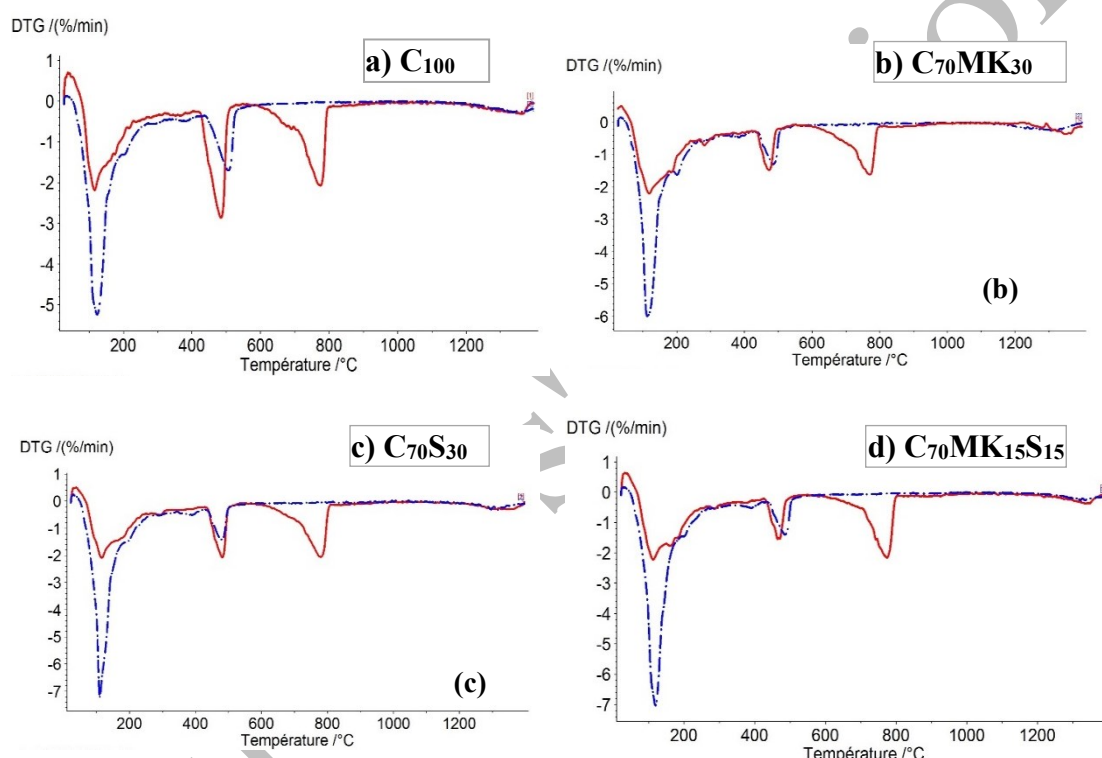


Fig.6 DTG profiles of cement paste (dashed line) and healing products (continuous line) for the different mixtures.

3.3 XRD analysis

XRD tests were performed to obtain more detailed information about the components of healed products of mixtures containing minerals additions.

Fig.7 shows the XRD patterns of the reaction products of self-healing in the specimens continuously immersed in tap water for 26 days. As shown in Fig.7, the reaction products

mainly consisted of portlandite and calcite. These products are observed in common for the four different mixtures. In contrast, C-S-H sheets are hardly noticeable by XRD analysis due to their low degree of crystallization. The microstructure of the healing products varies with the chemical composition of minerals additions used. For ordinary C₁₀₀ mixture, the C₂S remains visible after 28 days of aging.

In the case where a part of the cement was replaced by metakaolin and slag, XRD patterns indicate that gehlenite, hemicarboaluminate, monocarboaluminate and calcite are formed as reaction products of this combination. Metakaolin hold actively amorphous dioxide and aluminum oxide, they can react with portlandite to form C-S-H, sulfoaluminate and gehlenite [38]. In addition, slag is considered as a pozzolanic material and can react with hydrates of cement (portlandite) to form C-S-H and hydrotalcite [35].

It is well known that the lower hydration reaction of slag in comparison to that of cement clinker makes it possible to find, even after years of casting, a large amount of unreacted particles in slag cement paste [15]. Therefore, further reactions of slag particles explain their significant role in self-healing phenomenon [48]. It was confirmed that the self-healing performance was improved when slag that can supply Al ions was incorporated [23], [45]. As reported by many researchers, the complex mechanism reaction of slag leads to a complex mineralogy of healing products in slag cement paste compared to self-healing in Portland cement paste [23]. Moreover, the space factor may also influence the morphology of the reaction products. There is a difference in mineralogy structure of reaction products formed in cracks compared to the hydration products in bulk matrix [10].

As indicated in Fig.7, hydrotalcite is not detected as labeled by TGA analyzes for binary mixture that contained slag as a supplementary addition (C₇₀S₃₀). It should be noticed that since the XRD pattern of hydrotalcite is closed to monocarboaluminate, it is possible that

monocarboaluminate includes some hydrotalcite that is also considered as reaction products. In $C_{70}MK_{30}$ blend, which contains 30% of MK, there is no trace of stralingite, but the appearance of hydrated calcium aluminate was detected at lines 12° , 26° , 36° and $44^{\circ} 2\theta$. An increasing value of CH / MK ratio was found more favorable for the production of hydrated calcium aluminates to the detriment of stralingite (C_2ASH_8), which explains the absence of stralingite [49]. The appearance of hydrated calcium aluminates is caused by super saturation of the aqueous phase with respect to CH. High concentrations of Ca^{2+} and OH^{-} in the pore solution maintained a pore fluid composition that allowed hydrated calcium aluminates to precipitate. XRD data of $C_{70}MK_{30}$ also shows the development of brucite, which is already observed by the DTG analysis of this mixture.

By looking at the process of scratching and collecting of healing products, the carbonation of reaction products can take place [35]. Moreover, hemicarboaluminate and monocarboaluminate can be detected when the carbonation of C-A-H takes place especially when reaction products are exposed to air [35], [50]. As discussed above, XRD results of healing products are in agreement with TGA elements detection.

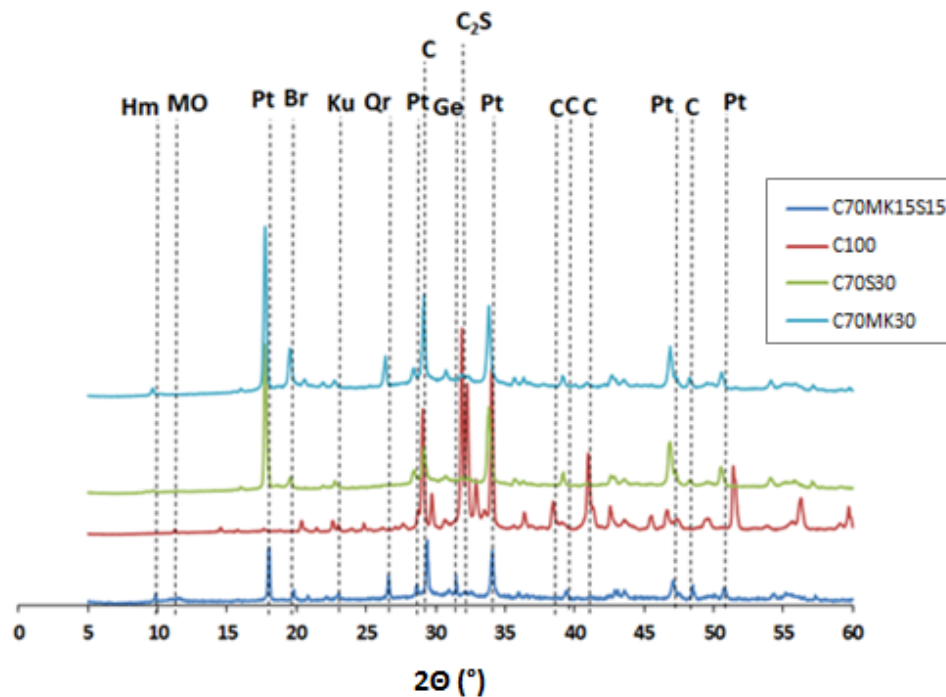


Fig.7 XRD patterns of healing products formed in cracks created at 2 days and healed for 26 days from single, binary and ternary compositions including slag and metakaolin. HM (hemicarboaluminate), MO (monocarboaluminate), Pt (portlandite), Br (Brucite), Ku (kuzelite), Qr (quartz), C (calcite), Ge (gehlenite).

3.4 Quantification of mechanical regains due to self-healing

In Fig.8 the activity index of SCM mixtures is plotted at different ages: 2, 7 and 28 days. It can be observed that the relative compressive strength significantly varied depending on the type of SCM.

At 2 days, the compressive strength of mortar mixture containing silica fume was higher than that of ternary composition. At early age, the increase of compressive strength during the first stage of hydration is attributed to the filler effect. According to the fineness of silica fume, these results are explained by the filler effect that consists in filling the pore and thus leading to a denser structure. The lowest rate of compressive strength was obtained for the mortar sample containing fly ash. Using fly ash shows a reduction in compressive strength due to low reactivity under ambient conditions [31].

Indeed, fly ash is a pozzolanic material that reacts with portlandite of cement matrix and produces C-S-H gel, which contributes in filling the space into cracks. In addition, the benefits added to self-healing ability of cement composites containing fly ash was limited according to CaO content of fly ash [51]. Samson et al. [51] showed that the autogenous healing efficiency was increased when CaO content was high. Otherwise, Hu et al. [29] proved the benefits of combining slag and fly ash on healing properties. The lower reactivity of these two materials compared to cement increases the quantity of unreacted grains and improves the autogenous healing performance.

For ternary binder's mixture ($C_{70}MK_{15}S_{15}$), mortar sample developed higher compressive strength than binary mixture containing pure metakaolin or slag ($C_{70}MK_{30}$, $C_{70}S_{30}$) whatever their age. At 28 days, their compressive strength rate was close to sample (C_{100}), confirming that the partial replacement of Portland cement with slag and metakaolin can allow reaching the same compressive strength as ordinary mortar. The highly active pozzolanic reaction of metakaolin with respect to the latent hydraulic properties of slag can explain this balance of functions, which improves compression strength at young age. At early stage of hydration, metakaolin reacts with free lime which leads to reducing the Ca/Si ratio and the pH of internal solution, thus reducing the concentration of hydroxyl ions which are necessary for the hydration phase of slag [43], [52].

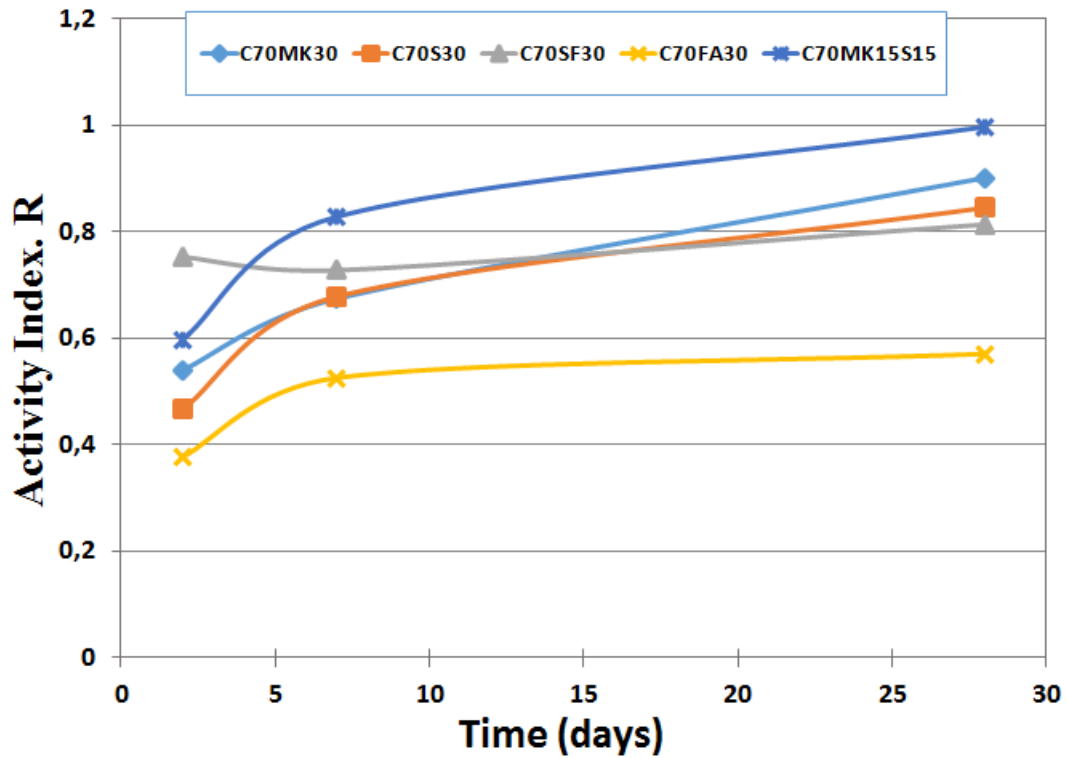


Fig.8 Activity index for different mixtures (w/b = 0.4)

Fig.9 shows the average force – CMOD curves obtained for beam specimens prepared with different mixtures and subjected to same exposure regime. In this figure, two types of mechanical results are represented:

- The curves for a cracked specimen and immediately reloaded (test applied on specimen to characterize the mechanical behaviour of specimen without healing process) are included.
- The reloading curves for healed samples aged 4 weeks in water are also drawn.

CMOD of reloading curves are set to 0 in order to have the same initial state, in order to show the effect of mineral additions on mechanical properties after healing process. The recovery in material stiffness is more evident for specimens prepared with the following mixtures: C₇₀MK₁₅S₁₅, C₇₀MK₃₀ and C₇₀S₃₀. We can notice that reloading stiffness tends to be the same as for reference sample. These results indicate that new healing products,

with stiffness close to that of primary hydration products, have precipitated in cracks and re-build the link between crack faces.

By considering that the reloading part corresponds to the re-opening of the existing crack until the peak load, it is noticeable that there is a brittle damage observed as sharp peak on the graph of $C_{70}SF_{30}$ mixture. We can also notice a variation of stiffness value for the healed specimens of $C_{70}SF_{30}$ (Fig.9 d red curve vs blue curve) caused by the variability of healing, that explain the huge error bar showed in Fig.10. For $C_{70}FA_{30}$, the maximum load obtained was found lower compared to the maximum load for all prepared mortars. It is explained by the reducing of workability of mortar mixture because $C_{70}FA_{30}$ mixture was prepared without adding superplasticizer. The bubbles air of the specimens for this mixture had been observed at the surface of sample. The efficiency of autogenous healing increases with high CaO content [51] [53]. In our work, the fly ash used is Class F (i.e. low calcium content), therefore, it has a very low reactivity. This may explain the limited increase in rigidity of specimens of mortars containing fly ash.

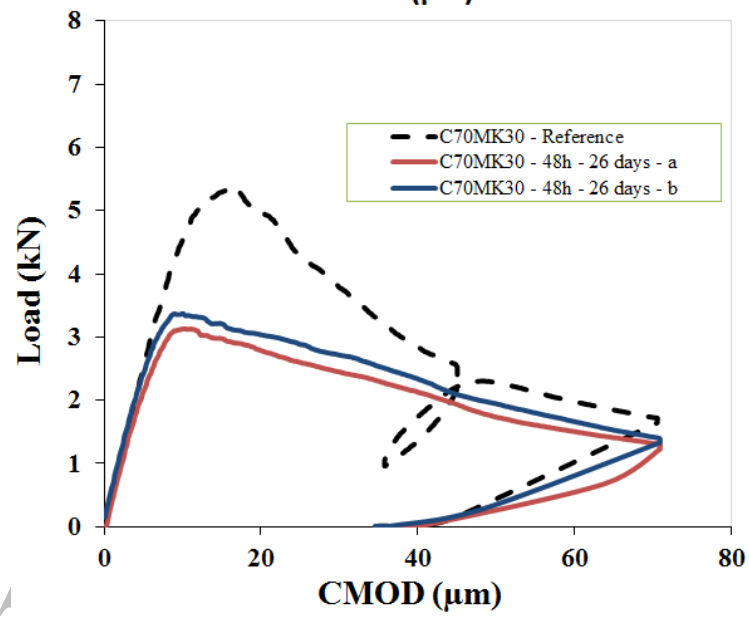
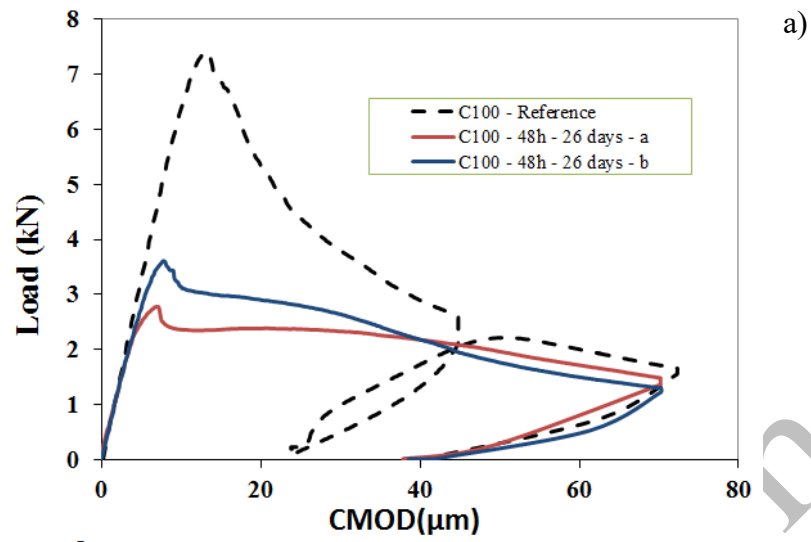
The index regains of each mixture test are shown in Fig.10. The strength regains are limited compared to the stiffness regains for all prepared mortars. Likewise, these results have been reported by [13] where a fast recovery of stiffness is noted for specimens cracked at 2 days with a residual crack width of 10 μm . While for the C_{100} samples the amount of stiffness regain is lower than 70%, the other two samples ($C_{70}MK_{30}$ and $C_{70}MK_{15}S_{15}$) containing metakaolin as partial replacement of cement show a higher average stiffness regain ratio (Fig.10). There is a fast recovery by self-healing for samples incorporating 30 vol% metakaolin ($C_{70}MK_{30}$). It can be explained by the highly active pozzolanic reaction of metakaolin with portlandite. Metakaolin reacts with portlandite derived from cement hydration to form additional C-S-H and crystalline products, which

contain C_2ASH_8 , C_4AH_{13} and C_3AH_6 . The crystalline products depend mainly on the MK/CH ratio [44], [49].

Also Fig.10 highlights that the amount of stiffness regain is much greater compared to others samples due to the presence of slag content with metakaolin. These results can be explained by the fact that both metakaolin and slag are described as active mineral admixtures. They can enhance the mechanical properties and the structure density of cement sample. Generally, the physical effect of these two admixtures is observed when the ultra-fine particles fill the voids and makes the structure denser. The chemical reaction of metakaolin and slag with portlandite produce a dense structure hydration, especially secondary C-S-H phases, which increase the combination force inside the paste matrix, and lead to a higher strength of cement.

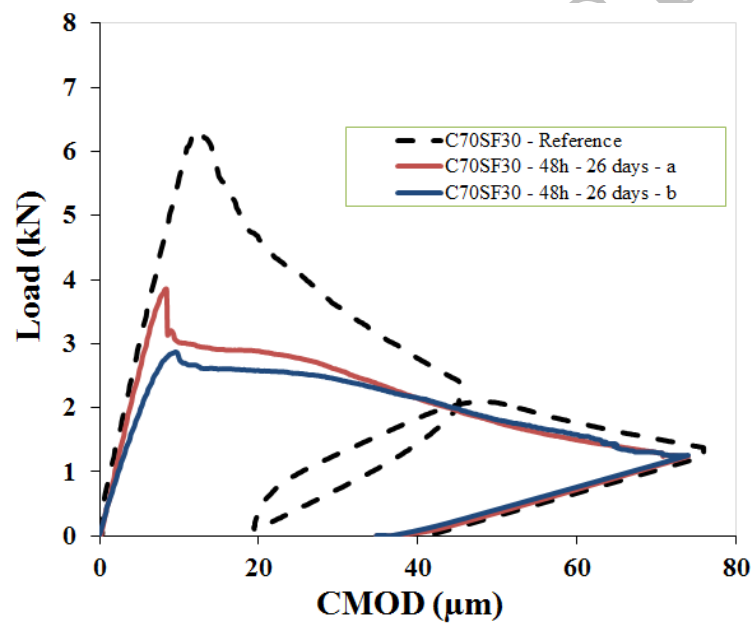
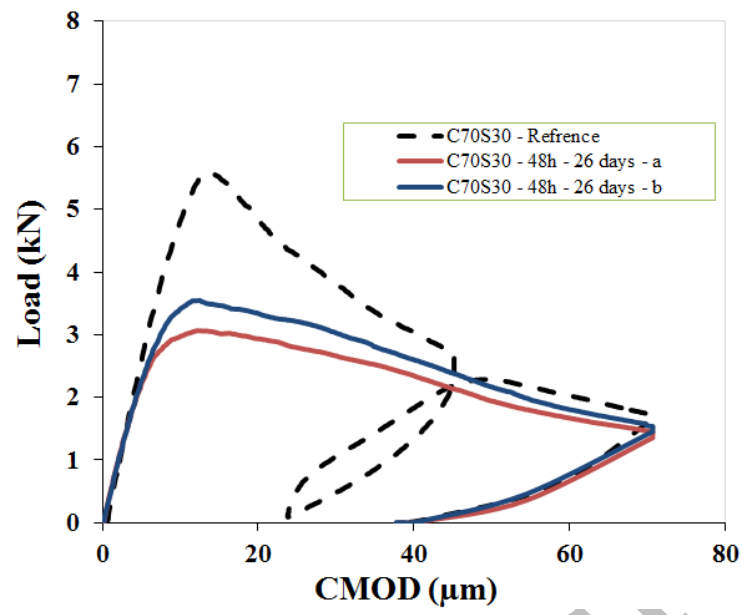
It should be noticed that hydration products fill the pore volume because their volume is twice greater than that of anhydrous cement phases, which lead to an increase in bulk density of cement matrix [35]. We can also conclude that the stiffness recovery due to healing by newly formed products is clearly more significant than the strength recovery. It shows that self-healing provides an improvement of rigidity compared to the resistance of healed samples. This can be explained by the fact that the products precipitated re-establish the bond between the two lips of the crack, but do not restore the complex structure that gives its resistance to concrete.

When both metakaolin and slag were used at the same time, the chemical phenomenon was called compounding effect [43]. Self-healing with ternary binder provides an improvement of stiffness as compared to cement mortar.



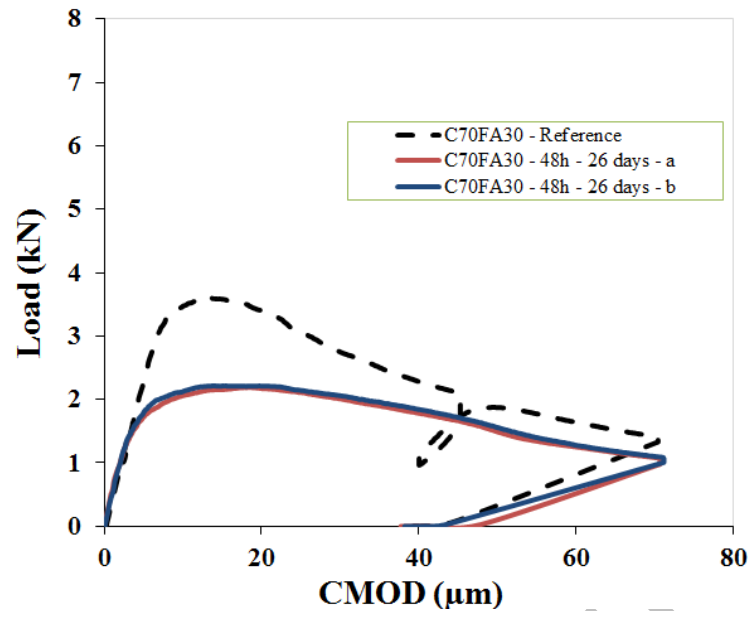
b)

c)



d)

e)



f)

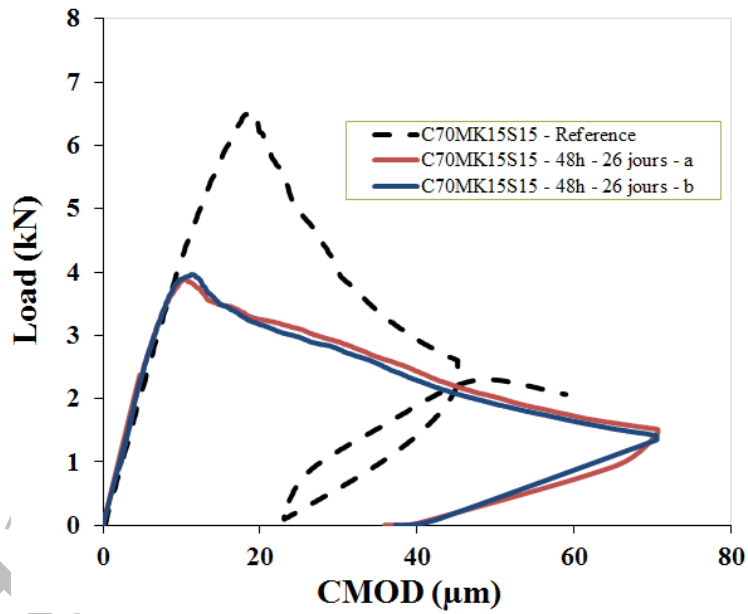


Fig.9 Mechanical behaviour of aged mortar specimens for different SCM's mixtures (load applied vs. $CMOD$): (a) C_{100} , (b) $C_{70}MK_{30}$, (c) $C_{70}S_{30}$, (d) $C_{70}SF_{30}$, (e) $C_{70}FA_{30}$ and (f) $C_{70}MK_{15}S_{15}$ (reloading of healed specimens is represented by continuous red/blue curve while the reference one is represented by a dotted black curve).

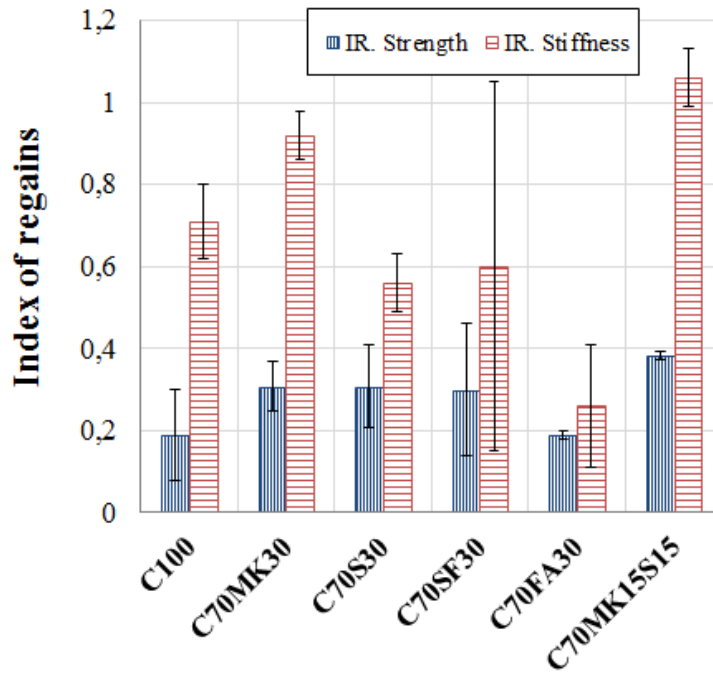


Fig.10 Effect of different minerals additions on mechanical properties: index of stiffness and index of strength for healed mortars (10 μ m crack and 26 days of healing). The error bars indicates the range of standard deviation.

4. Conclusion and perspectives

In this study, the extent of self-healing and the chemical composition of self-healing products of binary and ternary cementitious materials were investigated. Mortar samples were prepared with a crack width of 10 μ m and healed by water immersion. The mechanical behaviour of the healed samples was assessed by means of three-point-bending tests. Besides, artificial cracks were formed in order to characterize the correspondent self-healing products. SEM/EDS, TGA and XRD tests were carried out to gain insights into the mineralogical structure of the self-healing products. Based on the experimental results obtained, conclusions can be drawn as follows:

- In the case of ternary blends, the self-healing products formed between planar gaps by continuous hydration were found to be numerous. TGA and XRD results show newly hydration products precipitates in cracks compared to primary hydration products (products of bulk paste). The healing products consist of

monocarboaluminate, hydrotalcite and hemicarboaluminate besides previously reported C-S-H, portlandite and calcite.

- SEM observations are in agreement with TGA and XRD results as the self-healing products of ternary binders were found very various.
- The compressive strength of the ternary composition $C_{70}MK_{15}S_{15}$ tends to increase progressively to reach approximately the compressive strength of Portland cement-based composition after 28 days of casting.
- The partial replacement of cement by metakaolin and slag improves the self-healing efficiency of ternary binders as compared to ordinary formulations. This tendency was shown to be more significant for stiffness than strength probably due to the formation of various products like C-A-S-H phases as well as portlandite and C-S-H gel that make the structure denser.

Acknowledgments

The authors would like to acknowledge Vincent Wisniewski (GeM, Centrale Nantes) for his assistance while performing the experimental tests and Yannick Benoit (GeM, Centrale Nantes) for his technical assistance during SEM/EDX observations. Special thanks are due to Johan Vandenberg for his help in accomplishing XRD tests at Subatech laboratory, IMT Atlantique.

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