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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

Carol Youssef-Namnoum, Benoit Hilloulin, Frederic Grondin, Ahmed Loukili

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

4 Carol Youssef Namnoum, Benoit Hilloulin, Frederic Grondin\*, Ahmed Loukili

5 *Institut de Recherche en Génie Civil et Mécanique (GeM), UMR 6183, Centrale Nantes –*  
6 *Université de Nantes – CNRS, 1 rue de la Noë, 44321 Nantes, France*

7 e-mail: [carol.youssef-namnoum@ec-nantes.fr](mailto:carol.youssef-namnoum@ec-nantes.fr); [benoit.hilloulin@ec-nantes.fr](mailto:benoit.hilloulin@ec-nantes.fr);  
8 [frederic.grondin@ec-nantes.fr](mailto:frederic.grondin@ec-nantes.fr); [ahmed.loukili@ec-nantes.fr](mailto:ahmed.loukili@ec-nantes.fr)

9 \* Corresponding author: Tel.: + 33 (0) 2 40 37 68 47

10  
11  
12 **Highlights**

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

25 **Abstract**

26 A mechanical assessment of the self-healing process of complex cementitious materials  
27 with mineral additions is presented. Mortars made with binary and ternary binders (blast  
28 furnace slag, fly ash, metakaolin and silica fume) to reach 30 vol% substitution ratios  
29 were prepared, and then small cracks with a width of 10  $\mu\text{m}$  were created at the age of 2  
30 days. After a 26-day healing period, mechanical properties obtained from three point  
31 bending tests were analyzed to identify the recovery due to healing. In addition, the  
32 microstructure of self-healing products was studied using various techniques (TGA,  
33 SEM/EDS, and XRD). It was found that ternary compositions might exhibit a better self-  
34 healing performance compared to single or binary compositions. The mechanical tests  
35 indicate a better stiffness recovery for specimens prepared from the ternary mixture. This  
36 improvement of mechanical response is presumably due to the newly formed products  
37 precipitated in the cracks.

38  
39 **Keywords:** self-healing; cementitious materials; minerals additions; mechanical  
40 properties; microstructure; ternary compositions.

41  
42 **1. Introduction**

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

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

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

67 To highlight the self-healing efficiency, some researchers have adopted the visualization  
68 (optical microscopy or X-ray microtomography technique) of crack filling as a direct test  
69 to prove the continuous hydration [7]–[12]. Some other authors choose to indirectly  
70 measure the recovery of matrix properties by means of mechanical tests [9], [10], [13]–  
71 [15], durability tests such as air or water permeability [16]–[18] or nondestructive testing  
72 [19].

73 It is generally considered that both stiffness and strength gains can be obtained after  
74 two weeks of continuous immersion into water for 10  $\mu\text{m}$  width crack [9], [16]. Moreover,

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

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

88 Moreover, it was found that using mineral additions could improve the autogenous self-  
89 healing capabilities of concrete. By using mineral additions, an improvement of  
90 permeability and strength of structure was observed compared to Portland cement that  
91 has better mechanical properties at early age [11, 24–32,33]. These mineral additions lead  
92 to change an ordinary cement paste to binary and ternary cementitious materials.

93 Recently, there is a great interest in using metakaolin as a supplementary cementitious  
94 material in concrete. It is an ultra-fine material with strong pozzolanic activity, produced  
95 by calcination of kaolin at temperatures between 700 and 900  $^{\circ}\text{C}$  [15]. Metakaolin consists  
96 of silica and alumina product that react with portlandite to produce C-S-H gel and alumina  
97 phases ( $\text{C}_2\text{ASH}_8$ ,  $\text{C}_4\text{AH}_{13}$  and  $\text{C}_3\text{AH}_6$ ) [34]. Research results have shown that the use of  
98 metakaolin is quite useful in improving the strength of concrete at a young age [36, 37],  
99 or later [38, 39]. The combine use of slag and metakaolin have an influence in enhancing

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

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

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

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

142

143 .

144

## 145 **2. Materials and methods**

### 146 **2.1 Materials**

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

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

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

		Cement	Metakaolin	Slag	Fly ash
<b>Chemical composition (%)</b>	<b>SiO<sub>2</sub></b>	19,6	93,16	37,7	50
	<b>Al<sub>2</sub>O<sub>3</sub></b>	4,5		10,2	8,5
	<b>Fe<sub>2</sub>O<sub>3</sub></b>	2,3	-	0,6	29
	<b>CaO</b>	63,7	0,36	43,8	2,15
	<b>MgO</b>	3,9	0,04	6,4	-
	<b>SO<sub>3</sub></b>	2,6	-	0,1	0,37
<b>Physical properties</b>	<b>Specific gravity (Kg / m<sup>3</sup>)</b>	3130	2500	2900	2100
	<b>Specific area (m<sup>2</sup>/g)</b>	0,39	16	0,45	0,23

160

161 **Table 2.** Mortars mixtures

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

162

163 **2.2 Samples preparation for the assessment of mechanical regains due to self-healing**



164 For the determination of the compressive strength of mortars mixtures, three  $4 \times 4 \times 16 \text{ cm}^3$   
165 specimens of each mixture were tested at 2, 7 and 28 days, according to European  
166 standard protocol EN 12 390-3. For binary and ternary mixtures, activity index R was  
167 presented as the ratio between the compressive strength of the mortar with mineral  
168 addition ( $f_i$ ) and the compressive strength of the ordinary mixture mortar  $C_{100}$  ( $f_0$ ) :  $R = f_i$   
169 /  $f_0$ .

170 In order to study the effect of healing process on mechanical properties of these different  
171 mixtures, mortar prisms of dimensions  $7 \times 7 \times 28 \text{ cm}^3$  and  $4 \times 4 \times 16 \text{ cm}^3$  were prepared.  
172 Specimens were vibrated into two layers on a horizontal vibrating table in order to  
173 minimize the amount of occluded air. After 24 hours of curing under sealed conditions in  
174 a room at  $20 \text{ }^\circ\text{C}$  and 85-95% relative humidity, the specimens were demolded. A notch  
175 was cut at the middle of  $7 \times 7 \times 28 \text{ cm}^3$  specimens with a depth of 7 mm and thickness of  
176 5 mm by means of precision saw machine, in order to initiate cracking at a specific  
177 location using three-point bending test. Following that, specimens were stored in tap  
178 water at  $20 \text{ }^\circ\text{C}$  before cracking and during the healing period. Two prepared samples of  
179 each mixture were pre-cracked at the age of 48 hours by three-point bending test whereas  
180 the crack mouth opening displacement (CMOD) was controlled with a constant rate of  
181  $0,2 \text{ }\mu\text{m/s}$ , following ASTM C78 norm. The aim of this step was to obtain a residual crack  
182 width equal to  $10 \text{ }\mu\text{m}$ , which permits to get a fast healing process. The choice of an initial  
183 width-crack of  $10 \text{ }\mu\text{m}$  created at the age of 48 hrs is related to better mechanical regains  
184 obtained for specimens cracked at a young age as revealed by [41]. The real crack width  
185 was measured using a 2D microscope. Then, the specimens were further cured in tap  
186 water  $20 \text{ }^\circ\text{C}$  under unsealed condition.

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

189 (CMOD) dispositive preparation. The drying time is chosen to be as short as possible to  
 190 avoid alteration of the healing products. The healing phenomenon was verified by 2D  
 191 microscopic observations that show the precipitations of newly formed healing products.  
 192 By employing three-point bending test, three prisms specimens from each mixture were  
 193 reloaded in order to characterize the residual mechanical properties after healing process.  
 194 These three specimens consist of two samples pre-cracked and healed while the third one  
 195 represents the reference sample (un-cracked before curing). At this step, a flexural stress-  
 196 deflection curve obtained when the healed samples were mechanically reloaded is  
 197 compared to the loading curves of the reference sample having undergone the same curing  
 198 conditions [31], [41].  
 199 The performance of healing was quantified by using two equations 'format of mechanical  
 200 regains related to strength and stiffness recovery respectively [31]:

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

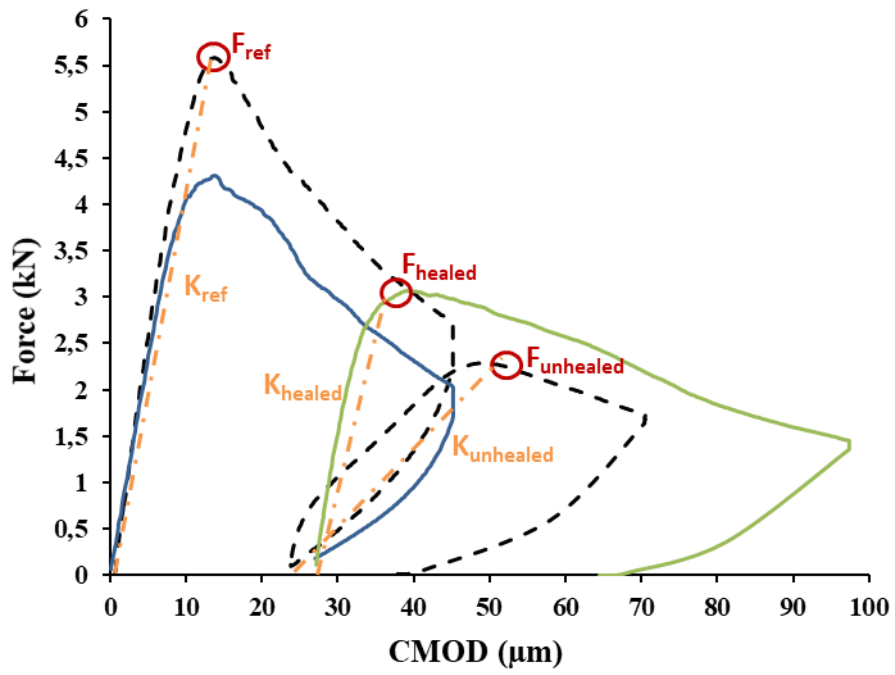
$$IR.stiffness = \frac{K_{healed} - K_{unhealed}}{K_{ref} - K_{unhealed}} \quad (2)$$

201  
 202 where  $F_{healed}$  represents the maximum strength of the healed samples during reloading,  
 203  $F_{ref}$  the maximum strength of reference sample loaded at 28 days,  $F_{unhealed}$  the reloaded-  
 204 maximum strength of reference sample,  $K_{healed}$  the maximum stiffness of the healed  
 205 samples during reloading,  $K_{ref}$  the maximum stiffness of reference sample and  $K_{unhealed}$   
 206 the reloaded-maximum stiffness of reference sample. K values were calculated by  
 207 drawing a tangent on the loaded and reloaded curve. These two indexes vary between 0  
 208 (no healing) and 1 (total healing). The different elements of indexes are represented in  
 209 Fig.1. The overall program for three point bending test after 4 weeks of age is presented  
 210 in Fig.2.

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 212

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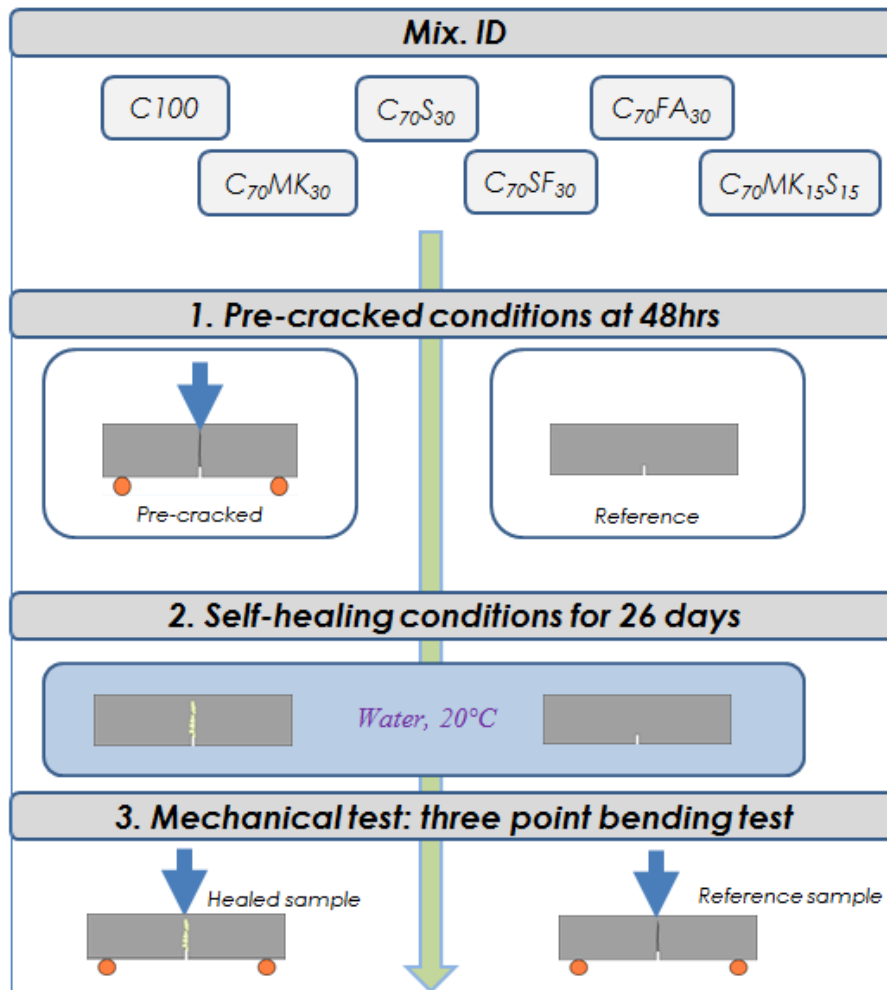


215

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.

218

Authors



219

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

222

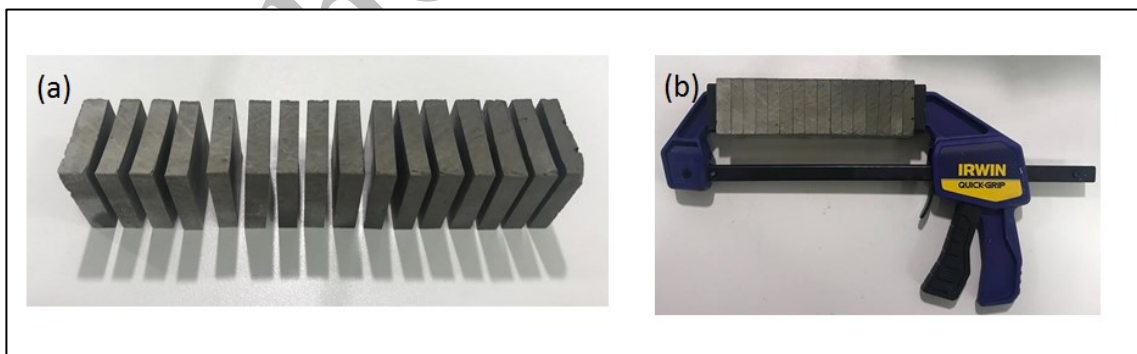
### 223 2.3 Morphology of self-healing products: testing procedures

224 The characterization of reaction products formed in healing process has been performed  
 225 by using different tests 'SEM/EDS, TGA, XRD analyses. A special procedure consisted  
 226 of the creation of artificial cracks was followed [10]. First, 4×4×16 cm<sup>3</sup> cement paste  
 227 samples were prepared from the different mortars formulations mentioned before. Then,  
 228 the samples were demolded after 24 hours of curing in room at 20°C and 90± 5% relative  
 229 humidity.

230 At 48 hours, the specimens were sliced into dimensions of 4 cm height, 4 cm length and  
 231 1 cm thickness. A total of 16 slices was obtained per 1 specimen. Following that, the 16

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

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



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

### 247 **2.3.1 SEM / EDX**

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

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

255

### 256 **2.3.2 TGA**

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

261

### 262 **2.3.3 XRD**

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

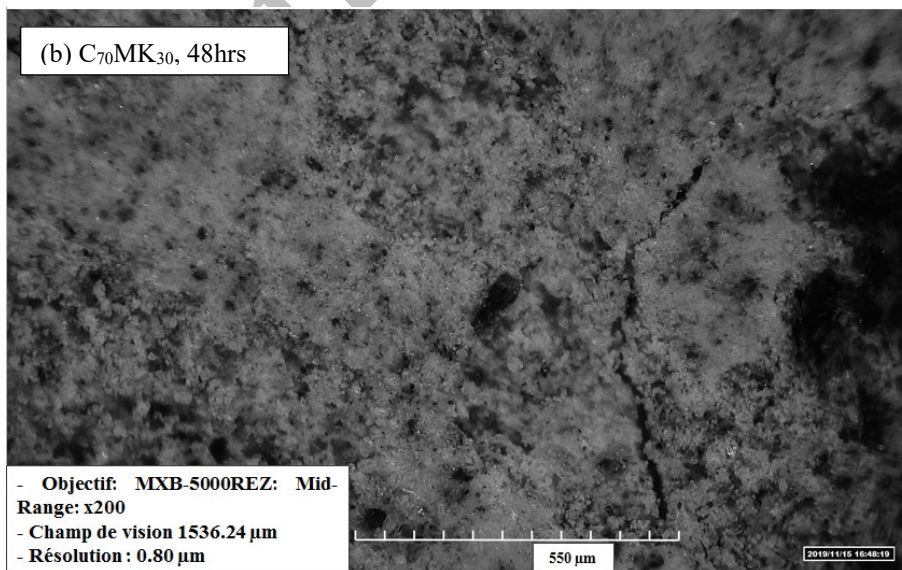
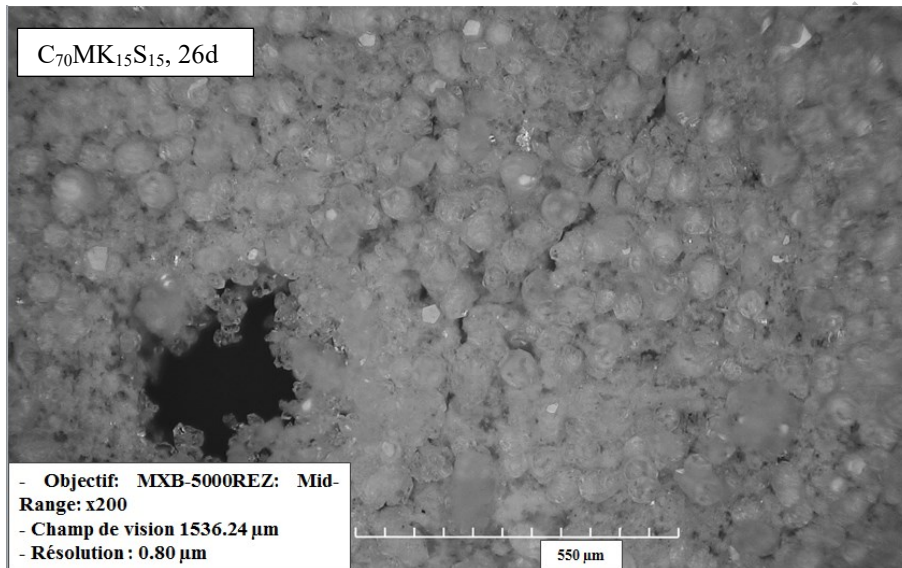
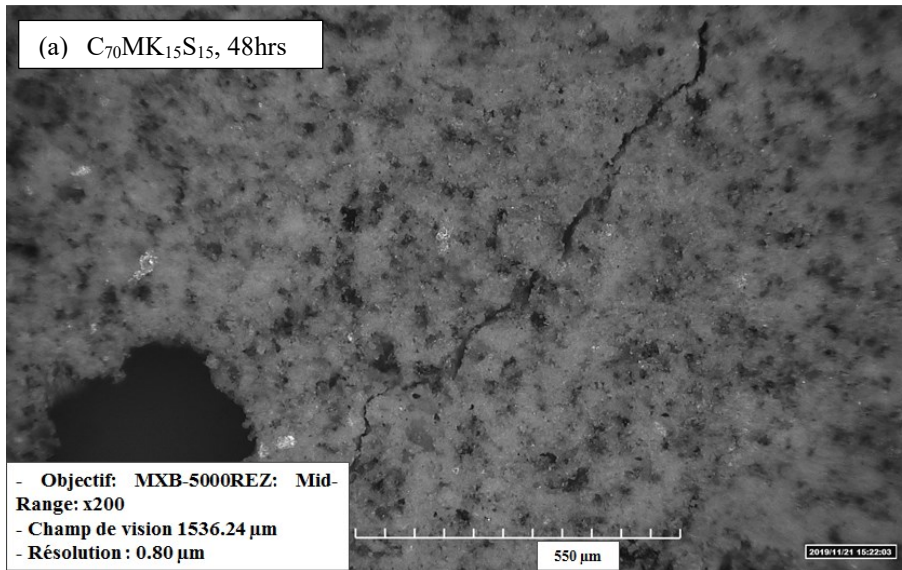
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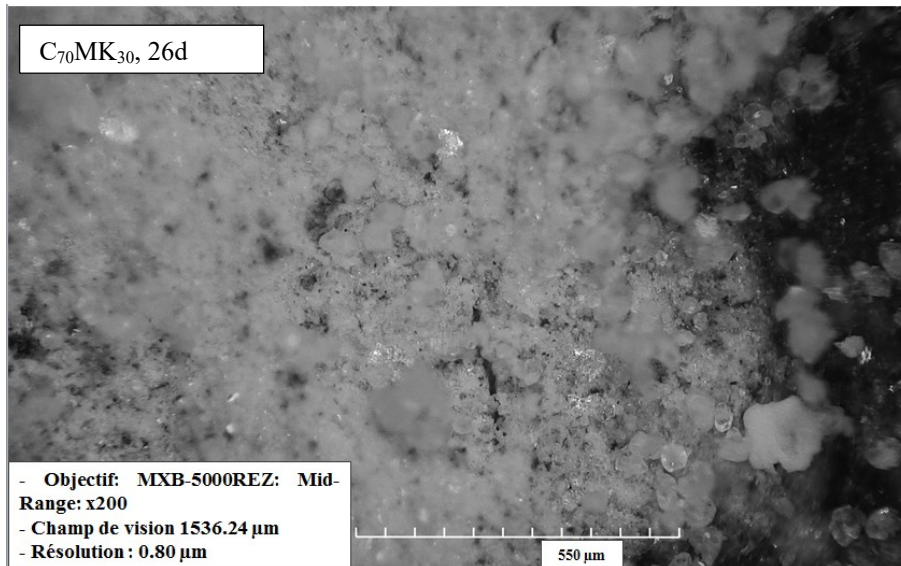
## 267 **3. Results and discussion**

### 268 **3.1 2D microscope measurements and SEM/EDX analysis**

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

274





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

279

280 Fig.5 illustrates the surface of artificial cracks after self-healing for 26 days. The presence  
 281 of ettringite as healing products was commonly found for C<sub>100</sub>, C<sub>70</sub>MK<sub>30</sub> and C<sub>70</sub>S<sub>30</sub>. This  
 282 product appears due to continuous hydration of unreacted particles of cement.

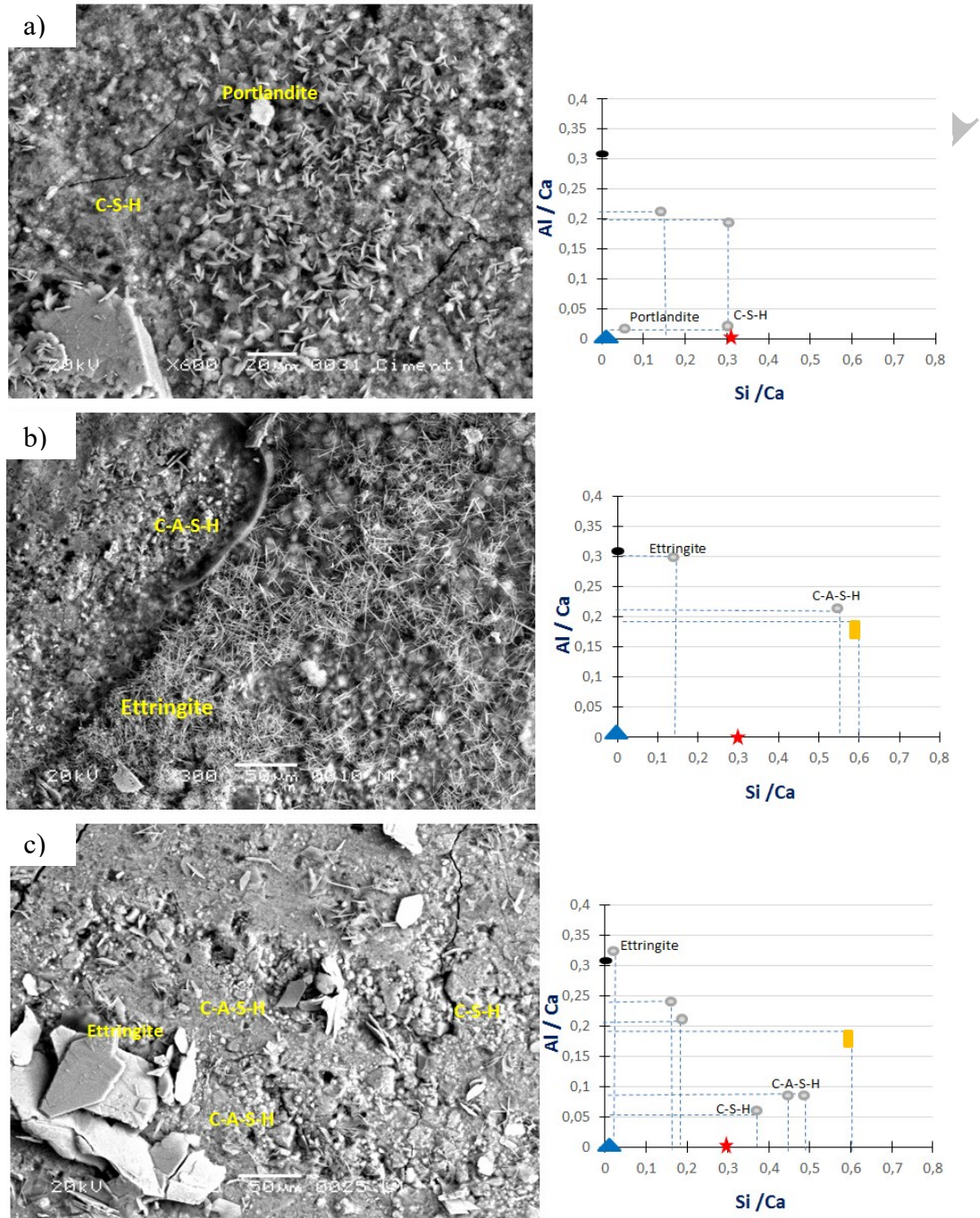
283 Fig.5 shows also the EDS analysis plotted as Al/Ca ratio against of Si/Ca (atomic %). For  
 284 binary mixture C<sub>70</sub>MK<sub>30</sub> (Fig.5b), C-A-S-H sheets were detected in addition to the  
 285 ettringite as healing products. Metakaolin contains silica and alumina in an active form,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

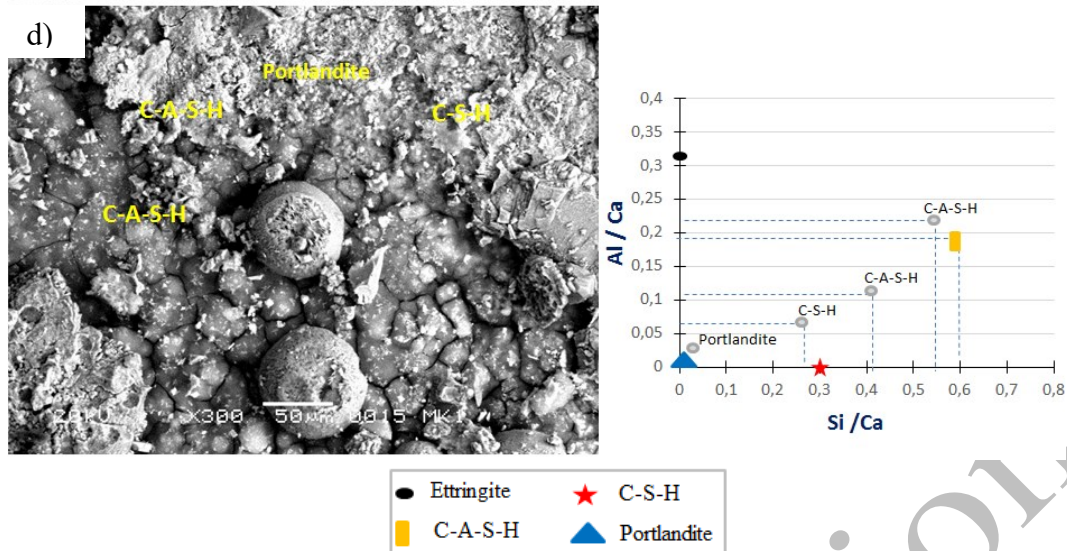
287 As presented in Fig.5d (C<sub>70</sub>MK<sub>15</sub>S<sub>15</sub>), the healing products are most like C-A-S-H. It can  
 288 be explained by the pozzolanic reaction of metakaolin and the hydration reaction of slag.

289 From EDX analysis, it was difficult to determine the composition of products due to high  
 290 level intermixing with metakaolin, slag, ettringite and C-A-S-H. However, we do not  
 291 notice the presence of stralingite, which is also considered as one of the hydration  
 292 products of metakaolin [39].



293 Moreover, the healing products as can be seen in Fig.5 c) ( $C_7S_3O$ ) are most like C-S-H,  
 294 ettringite and C-A-S-H. Whenever slag particles are present into contact with portlandite,  
 295 their reaction can directly appear by the presence of C-S-H [43]. Therefore, this can lead  
 296 to a better self-healing process than that of ordinary mortar mixture.





297  
 298 **Fig.5** SEM/EDS analysis of an artificial cracks after 26 days of healing: (a) C<sub>100</sub>, (b)  
 299 C<sub>70</sub>MK<sub>30</sub>, (c) C<sub>70</sub>S<sub>30</sub>, (d) C<sub>70</sub>MK<sub>15</sub>S<sub>15</sub>. Scale bar of BSE images corresponds to 50 μm.  
 300 Graphical treatment of EDX points analysis obtained for healed products, Al/Ca ratio is  
 301 plotted as a function of Si/Ca ratio (in atomic percentage).

302

### 303 3.2 TGA analysis

304 Fig.6 illustrates the DTA/DTG profiles of bulk cement paste and healing products formed  
 305 in cracks after curing up in water to 26 days. Overall TGA graphs show common  
 306 hydration products peaks around 110 °C to 200 °C for hydrates like ettringite, C-S-H gel  
 307 [42], [44], around 410 °C to 550 °C for portlandite [45], and the peaks between 660 °C  
 308 and 840 °C is mainly due to the decomposition of calcite [46].

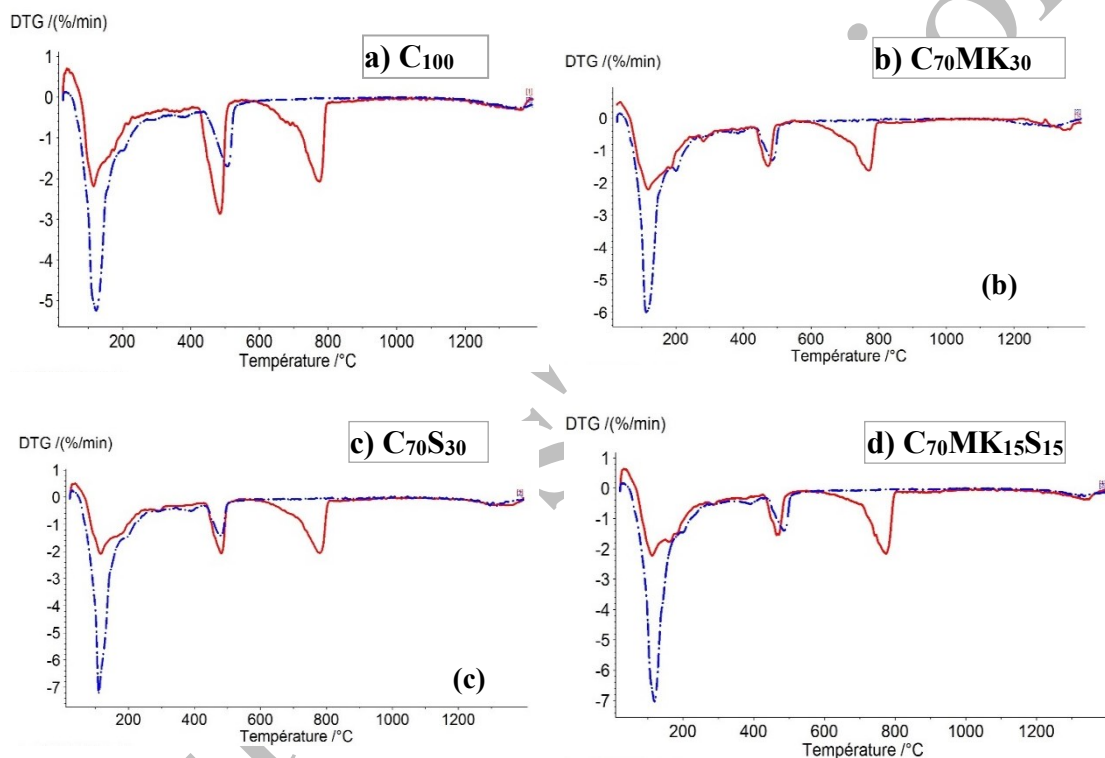
309 For DTG profiles of the healing products for binary and ternary blends (C<sub>70</sub>MK<sub>30</sub>,  
 310 C<sub>70</sub>S<sub>30</sub> and C<sub>70</sub>MK<sub>15</sub>S<sub>15</sub>), small peaks are observed at about 190-280 °C. They  
 311 represent the decomposition of crystalline part of C-A-H, C-A-S-H and the presence of  
 312 monocarboaluminate and gehlenite hydrates [42]. Thus, they participate in the  
 313 diversification of healing products [47].

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

317 [38]. Moreover, the ingress of CO<sub>2</sub> between each two slices is accelerated by the porous  
318 structure of reaction products present between the gaps [15].

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

323



324

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

327

### 328 3.3 XRD analysis

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

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

333 mainly consisted of portlandite and calcite. These products are observed in common for  
334 the four different mixtures. In contrast, C-S-H sheets are hardly noticeable by XRD  
335 analysis due to their low degree of crystallization. The microstructure of the healing  
336 products varies with the chemical composition of minerals additions used. For ordinary  
337 C<sub>100</sub> mixture, the C<sub>2</sub>S remains visible after 28 days of aging.

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

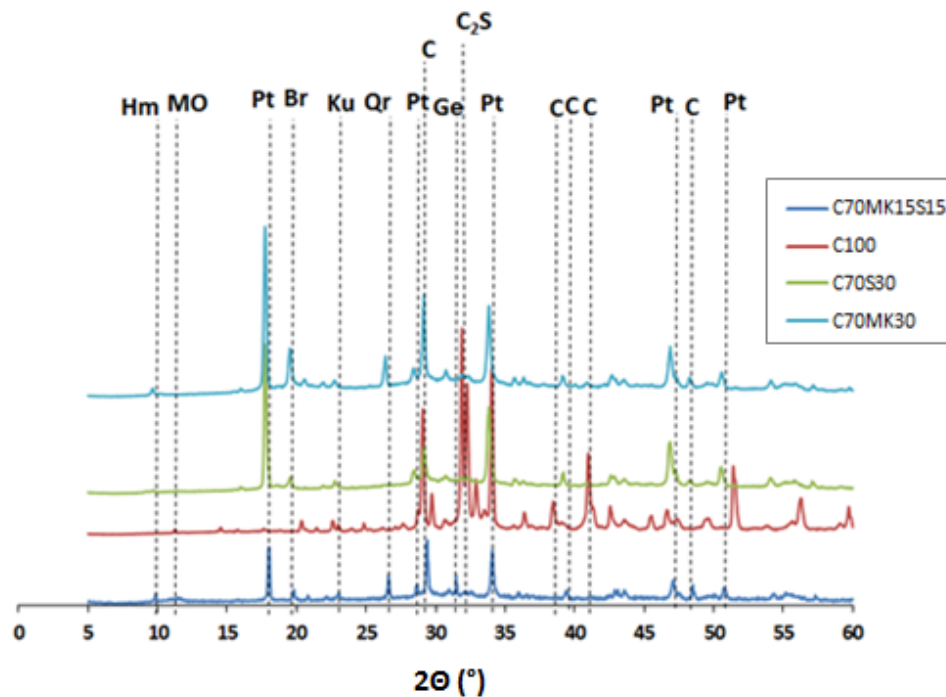
344 It is well known that the lower hydration reaction of slag in comparison to that of cement  
345 clinker makes it possible to find, even after years of casting, a large amount of unreacted  
346 particles in slag cement paste [15]. Therefore, further reactions of slag particles explain  
347 their significant role in self-healing phenomenon [48]. It was confirmed that the self-  
348 healing performance was improved when slag that can supply Al ions was incorporated  
349 [23], [45]. As reported by many researchers, the complex mechanism reaction of slag  
350 leads to a complex mineralogy of healing products in slag cement paste compared to self-  
351 healing in Portland cement paste [23]. Moreover, the space factor may also influence the  
352 morphology of the reaction products. There is a difference in mineralogy structure of  
353 reaction products formed in cracks compared to the hydration products in bulk matrix  
354 [10].

355 As indicated in Fig.7, hydrotalcite is not detected as labeled by TGA analyzes for binary  
356 mixture that contained slag as a supplementary addition (C<sub>70</sub>S<sub>30</sub>). It should be noticed that  
357 since the XRD pattern of hydrotalcite is closed to monocarboaluminate, it is possible that

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

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

374



375

376 **Fig.7** XRD patterns of healing products formed in cracks created at 2 days and healed for  
 377 26 days from single, binary and ternary compositions including slag and metakaolin. HM  
 378 (hemicarboaluminate), MO (monocarboaluminate), Pt (portlandite), Br (Brucite), Ku  
 379 (kuzelite), Qr (quartz), C (calcite), Ge (gehlenite).

380

### 381 **3.4 Quantification of mechanical regains due to self-healing**

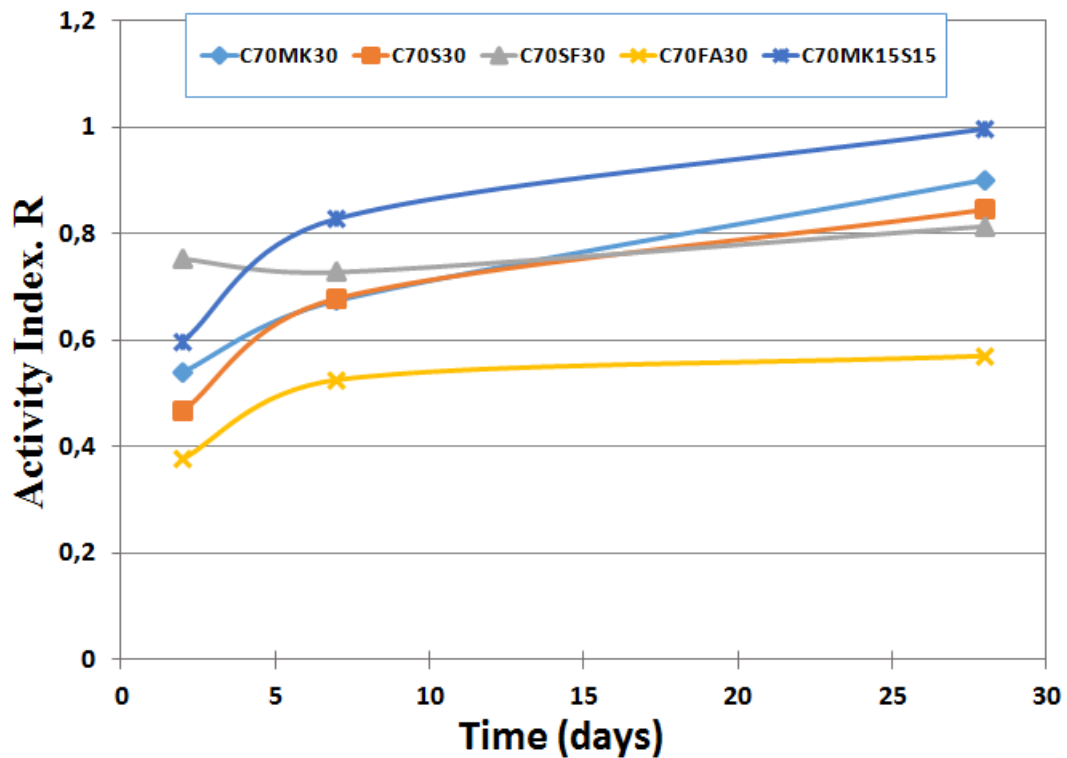
382 In Fig.8 the activity index of SCM mixtures is plotted at different ages: 2, 7 and 28 days.

383 It can be observed that the relative compressive strength significantly varied depending  
 384 on the type of SCM.

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

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

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



410  
411 **Fig.8** Activity index for different mixtures (w/b = 0.4)

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

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

419 CMOD of reloading curves are set to 0 in order to have the same initial state, in order to  
420 show the effect of mineral additions on mechanical properties after healing process. The  
421 recovery in material stiffness is more evident for specimens prepared with the following  
422 mixtures: C<sub>70</sub>MK<sub>15</sub>S<sub>15</sub>, C<sub>70</sub>MK<sub>30</sub> and C<sub>70</sub>S<sub>30</sub>. We can notice that reloading stiffness tends  
423 to be the same as for reference sample. These results indicate that new healing products,



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

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

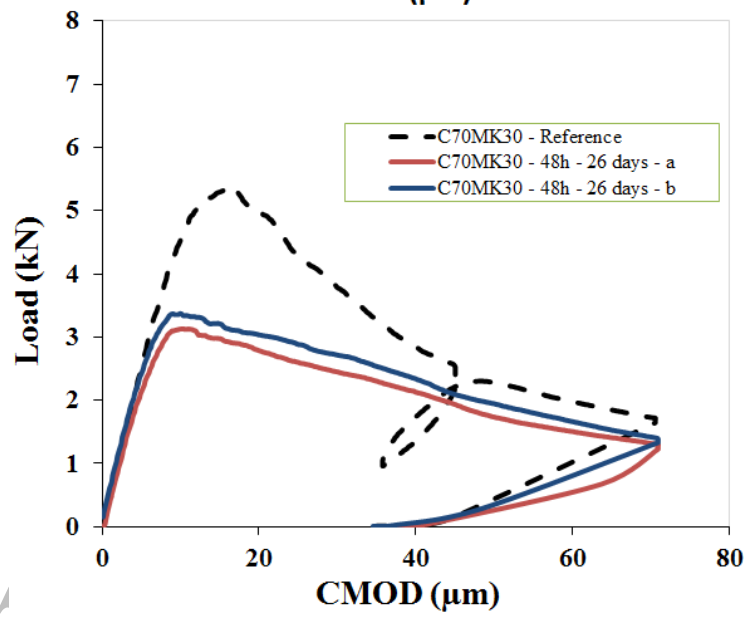
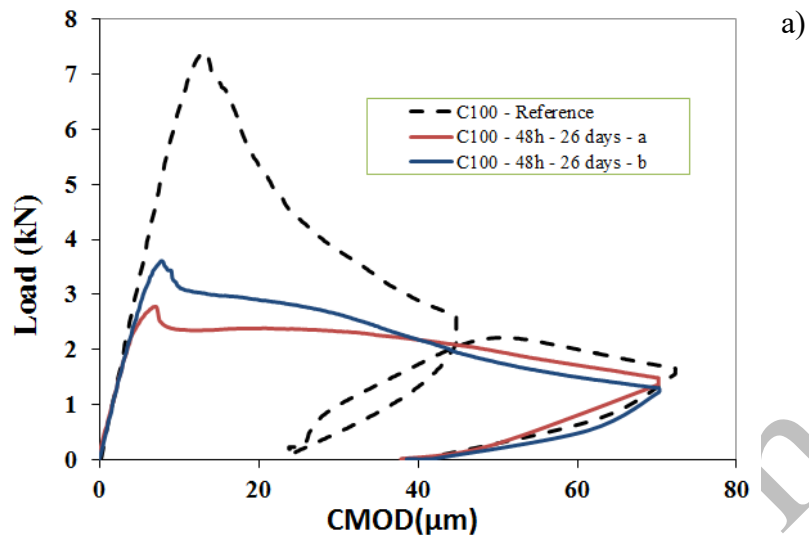
438 The index regains of each mixture test are shown in Fig.10. The strength regains are  
439 limited compared to the stiffness regains for all prepared mortars. Likewise, these results  
440 have been reported by [13] where a fast recovery of stiffness is noted for specimens  
441 cracked at 2 days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

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

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

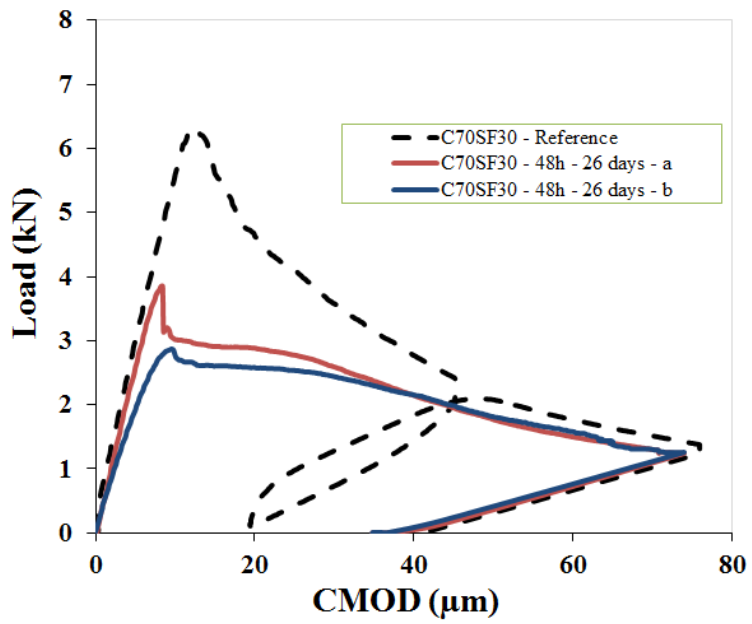
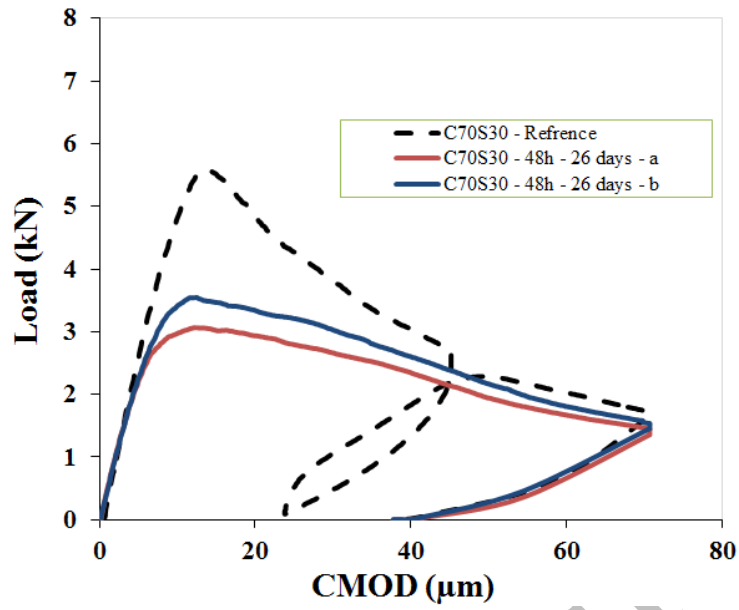
459 It should be noticed that hydration products fill the pore volume because their volume is  
460 twice greater than that of anhydrous cement phases, which lead to an increase in bulk  
461 density of cement matrix [35]. We can also conclude that the stiffness recovery due to  
462 healing by newly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

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



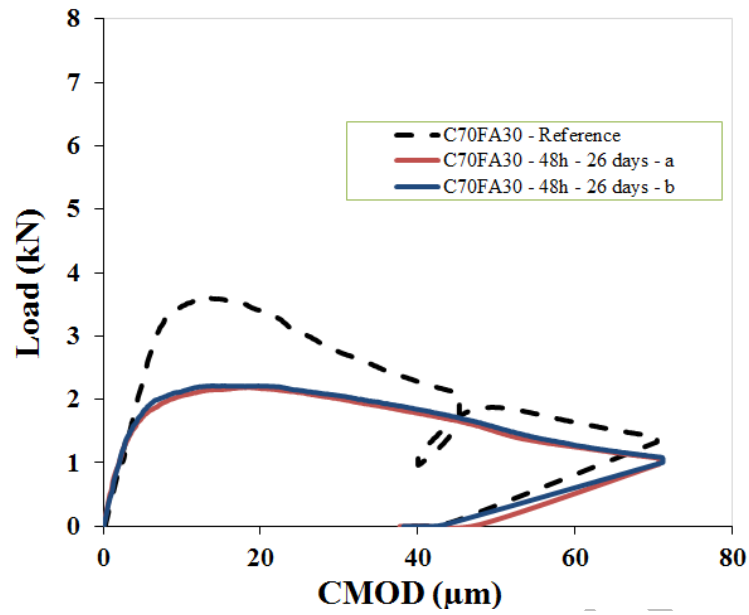
b)

c)

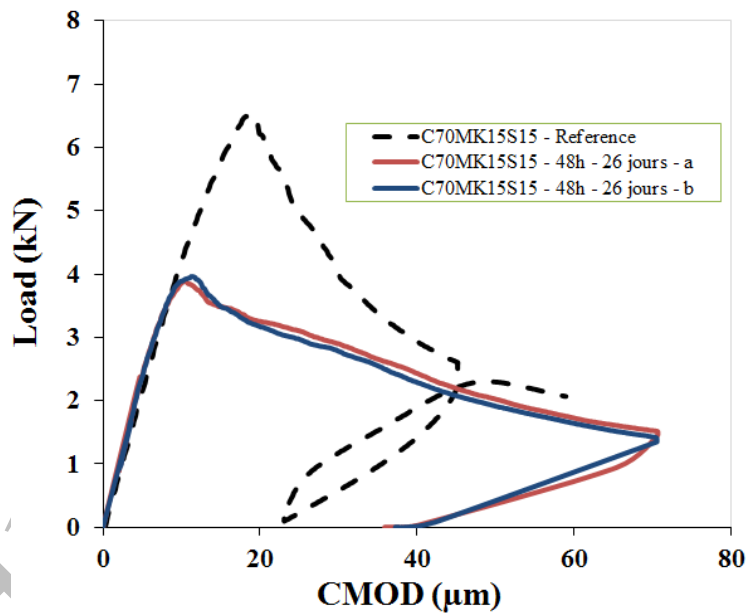


d)

e)

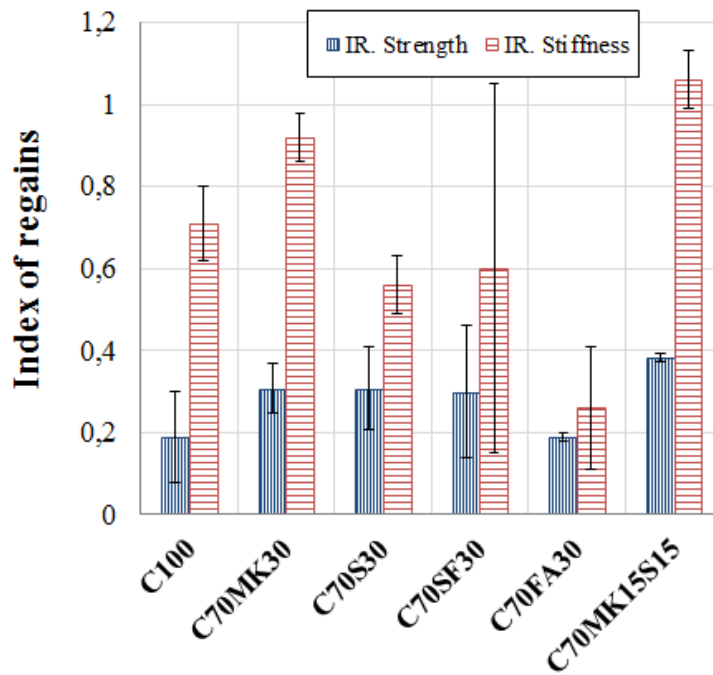


f)



470 **Fig.9** Mechanical behaviour of aged mortar specimens for different SCM's mixtures (load  
 471 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)  
 472  $C_{70}MK_{15}S_{15}$  (reloading of healed specimens is represented by continuous red/blue curve  
 473 while the reference one is represented by a dotted black curve).

474



475 **Fig.10** Effect of different minerals additions on mechanical properties: index of stiffness  
 476 and index of strength for healed mortars (10 $\mu$ m crack and 26 days of healing). The error  
 477 bars indicates the range of standard deviation.  
 478

479

#### 480 **4. Conclusion and perspectives**

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

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

- 493 monocarboaluminate, hydrotalcite and hemicarboaluminate besides previously  
494 reported C-S-H, portlandite and calcite.
- 495 - SEM observations are in agreement with TGA and XRD results as the self-healing  
496 products of ternary binders were found very various.
  - 497 - The compressive strength of the ternary composition C<sub>70</sub>MK<sub>15</sub>S<sub>15</sub> tends to  
498 increase progressively to reach approximately the compressive strength of  
499 Portland cement-based composition after 28 days of casting.
  - 500 - The partial replacement of cement by metakaolin and slag improves the self-  
501 healing efficiency of ternary binders as compared to ordinary formulations. This  
502 tendency was shown to be more significant for stiffness than strength probably  
503 due to the formation of various products like C-A-S-H phases as well as  
504 portlandite and C-S-H gel that make the structure denser.

505  
506

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512

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