Autogenous self-healing of cement with expansive minerals-II: Impact of age and the role of optimised expansive minerals in healing performance

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Abstract

This part of the study presents the optimisation of expansive minerals mix proportions and establishes a quantitative and qualitative correlation between self-healing and the cracking age of cementitious materials. The hydration degree of cementitious materials is considered as a quantitative measure of age and the corresponding healing performance was analysed to establish an age-healing relation. Healing performances were assessed in terms of load recovery, crack sealing efficiency and gas permeability. The microstructure of materials was investigated using XRD, TGA and SEM-EDX. The self-healing performance of particular cement mixes shows linearly increasing correlation with the reduction of hydration degree. However, cement mixes containing expansive mineral result in higher healing performance than mixes containing only Portland cement (PC). This observation was confirmed for all cracking ages. Blends containing only PC showed healing materials that were mostly calcite and portlandite, while the optimised use of expansive minerals produced denser healing materials with C-S-H, and complex Ca, Mg, Si, Al combined hydrated and carbonated products in addition to calcite and portlandite. The results further suggest that the proportions of calcite, portlandite and ettringite in healing compounds have an increasing trend with the age of hardened cementitious materials.

Keywords: Expansive minerals, self-healing, hydration degree, age-healing relation, microstructure.

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1. Introduction

Structural failure aggravates due to the formation of cracks and unpredictable damages in concrete over service life. Development of compatible self-healing concrete has the potential to mitigate this challenge. As such, expansive minerals can enhance three major stages in concrete healing process, i.e. the expansion, proliferation and crystallisation to form additional healing compounds [1–3]. Nevertheless, the age of concrete plays a major role in the evolution of the self-healing processes.

In recent years, publications have reported the direct relationship between the age of cement-based materials at the instance of crack formation and self-healing behaviour. Nardi et al. [4] showed that autogenous self-healing performance reduced with the age of pre-cracking of lime mortar mix. They have quantified the healing based on the recovery of the compressive strength and ultrasonic pulse velocity; however, the hydration state of lime cement and its influence on healing process was not covered in their study. Another study suggests that the self-repair effect reduces with the age of crack formation in cement-based materials incorporating bacteria [5]. Out of the specimens pre-cracked at the age of 7, 14, 28 and 60 days, bacteria showed efficient repairing to small cracks formed at 7 days. The healing performance explained to reduce due to the reduction of bacteria in the matrix after 28 days; however, no explanation was provided for the reduction of cement autogenous self-healing due to hydration over time.

Cracking age was reported to have vital impact on the self-healing of concrete or composite with the high proportion of cement and supplementary cementitious materials (SCMs) such as fly ash, slag based Engineered Cementitious Composites (ECCs) [6–13]. Two different types of fly ash (low lime and high lime) and ground granulated blast furnace slag (GGBS) about 1.2 times of PC in ECC were pre-damaged to 80% of the their deformed capacities at 7, 28 and 90 days, and their self-healing performance based on sorptivity and rapid chloride permeability tests (RCPT) showed decreasing healing trend with the increase in pre-damage age [9,10]. The self-healing of these fly ash and GGBS based ECCs was reported less effective when composites aged to maturity [11–13], although the use of hydrated lime [12] and CO$_2$-water curing [13] in ECCs reported to enhanced the healing efficiency.
Early age concrete rapidly heals itself through autogenous healing triggered by the remaining high proportions of unhydrated cement [14]. Although cement hydrates rapidly in the early ages, about 25% of cement still remains unhydrated in concrete even after 28 months [15]. These considerable proportions of unhydrated cement can initiate self-healing actions in mature concrete. The importance of hydration was further tagged as a major factor in establishing a model to characterize the self-healing efficiency [16]. While it is known that the autogenous self-healing potential decrease with the age of concrete, there are no studies to our knowledge that quantitatively relates the hydration state of cement with its intrinsic self-healing behaviour.

In this study, the experimental findings presented in Part-I [2] will be used to lead towards the optimisation of expansive minerals (MgO, bentonite and quicklime) mix proportions in PC blends. The results presented will be further used to establish correlations between the cracking age and the autogenous self-healing of cement based systems with or without expansive minerals. The age of the sample is numerically correlated with the hydration degree of cement paste, and healing parameters together with healing materials formation functionalities are assessed accordingly.

2. Materials and experimental procedure

2.1 Materials and sample preparation

Table 1 illustrates the mix composition of cement pastes used in this study. The mix proportions in Table 1 were based on the findings of Part-I [2]. Cement mixes with 5% MgO show good improvement in self-healing performances. In those mixes with expansive minerals, the microstructure and ternary diagrams analysis of healing materials (refer to Fig. 14 and Fig. 15 in Part-I) [2] correspond to additional formation of efficient healing materials. However, the substitution of PC in the mixes over 15% with expansive minerals was not improving the healing performance considerably, and in fact resulted in the reduction of mechanical strength. Therefore, in this Part-II test series, MgO proportions were set within 5-7.5%, while bentonite and quicklime were substituted within 2.5-5% respectively.
The control mix (CON) was a 100% PC (CEM 1 42.5N) cement paste mix, while the rest of the five mixes contained different percentages of minerals as PC substitutions (Table 1). Water to cement ratio (w/c) was kept constant at 0.35 and superplasticiser (Sikament 700 satisfying [17]) was used as a water-reducing admixture to balance similar workability in each mixes based on the flow table test. The w/c was kept constant in Part-II mixes intentionally to compare the healing performance of all mixes at same w/c, while Part-I [2] investigates healing performance with varying w/c according to each mixes standard consistency.

Table 1. Cement mix compositions by percentage weight.

<table>
<thead>
<tr>
<th>Mix</th>
<th>PC</th>
<th>MgO 92/200</th>
<th>Bentonite</th>
<th>Quicklime</th>
<th>w/b 0.35</th>
<th>Superplasticiser</th>
<th>Flow table test avg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CON (PC100)</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>35</td>
<td>0.00%</td>
<td>199.5</td>
</tr>
<tr>
<td>PC87.5M7.5B2.5L2.5</td>
<td>87.5</td>
<td>7.5</td>
<td>2.5</td>
<td>2.5</td>
<td>35</td>
<td>1.05%</td>
<td>206.0</td>
</tr>
<tr>
<td>PC85M7.5B5L2.5</td>
<td>85</td>
<td>7.5</td>
<td>5</td>
<td>2.5</td>
<td>35</td>
<td>2.08%</td>
<td>203.5</td>
</tr>
<tr>
<td>PC85M7.5B2.5L5</td>
<td>85</td>
<td>7.5</td>
<td>2.5</td>
<td>5</td>
<td>35</td>
<td>1.09%</td>
<td>201.0</td>
</tr>
<tr>
<td>PC87.5M5B5L2.5 (OPT-1)</td>
<td>87.5</td>
<td>5</td>
<td>5</td>
<td>2.5</td>
<td>35</td>
<td>2.08%</td>
<td>205.0</td>
</tr>
<tr>
<td>PC87.5M5B2.5L5 (OPT-2)</td>
<td>87.5</td>
<td>5</td>
<td>2.5</td>
<td>5</td>
<td>35</td>
<td>1.09%</td>
<td>204.5</td>
</tr>
</tbody>
</table>

Cubes, prisms and disks were prepared for this study. For the results to be comparable all samples were prepared the same as described in Part-I [2]. The crack mouth opening of the prisms was restricted at 0.3 mm which resulted in a residual crack of 0.20±0.03 mm after unloading.

2.2 Experimental procedure

The compressive strength of 28 days matured cubes were measured following BS EN 196-1:2005 [18]. Healing performance was compared using visual crack sealing, strength recovery and durability improvement against gas permeability. Triplicate samples were investigated in all the compressive strength and healing performance experiments.
At first, the early age (24 hr) self-healing of cement mixes was investigated up to 28 days to determine optimum mix composition with expansive minerals for autogenous self-healing. Then CON (PC100) and two potential optimum cement mixes were further assessed to determine the impact of cracking age on healing behaviour. To perform this, prism and disk samples were cracked at 1, 7 and 28 days after casting, and their healing was investigated subsequently after 28 days of cracking. The compressive strength was also measured at the age of 1, 7 and 28 days. Healing properties were further compared with the microstructural analysis of starting cement mix and healing materials.

Microstructure of the materials were investigated using: X-Ray diffraction (XRD) in a range of 5-60° of 2θ at a rate of 2 s/step and scanning resolution of 0.05°/step; thermogravimetric analysis (TGA) in 50-800 °C temperature range at a rate of 10 °C/min in nitrogen (50 ml/min) environment with ~20 mg of dried powdered samples; and a high definition scanning electron microscopy (SEM-EDX). The detailed sample preparation techniques are discussed in Part-I [2].

3. Results and Discussions

3.1 Determination of optimum mineral mix proportion

The compressive strength and healing performance of early age (24 hr) samples were first investigated. This was to determine the optimum mineral mix proportion with PC for maximum possible compressive strength and efficient self-healing performance at early cracking age.

Compressive strength results are presented in Fig. 1. The strength was found lower in mineral containing mixes compared to CON (PC100) mix. However, compressive strength showed a similar trend as reported in Part-I test series, where bentonite has considerably reduced compressive strength development compared to MgO and quicklime. This is due to the fact that, bentonite absorbs higher proportions of water and act as a filler material rather much contributing in the cement hydration process. MgO and quicklime, on the other hand, are less water demanding and much compatible with PC during the hydration process.
The healing period of early age (24 hr) samples was 28 days. The healing performance was assessed in terms of crack sealing efficiency (CA%), strength recovery percentage (SR%) and gas permeability improvement. Self-healing results are presented in Fig. 2. The mineral containing mixes sealing efficiencies were considerably higher than PC100 (Fig. 2a and 2b). Higher proportions of quicklime showed faster and higher crack sealing tendencies as similarly reported in the previous series (part-I, [2]). This was similarly evident when PC87.5M5B2.5L5 mix demonstrated the best performances followed by the other mixes. While sealing efficiency was around 100% after 28 days in all mineral mixes, it was only about 70% for PC100 mixes. Similarly, strength recovered up to 67% in a mineral containing mixes which was much higher compared to that of 15% by PC100 mixes (Fig. 2c). The gas permeability coefficient was affected by self-healing as such, lower the coefficient greater the durability improvement due to healing. The impact of mineral combinations on gas permeability reduction after healing was more dominant than crack sealing and strength recovery results. PC100 mix discs were cracked (PC100-cracked) and not cracked (PC100-un cracked) respectively to compare the gas permeability of reference samples with expansive mineral containing mixes. Compared to PC100-cracked samples, the permeability coefficient of PC87.5M7.5B2.5L2.5, PC85M7.5B5L2.5, PC85M7.5B2.5L5, PC87.5M5B5L2.5, and PC87.5M5B2.5L5 was reduced 66%, 68%, 71%, 69% and 75%, respectively. However, the permeability coefficients of these mixes were 2.4-1.8 times higher than the completely un-cracked discs (PC100-un cracked). Although the
permeability reduction results show a similar trend as crack sealing (Fig. 2 b and d), strength recovery was found efficient with 5% each MgO and bentonite mixes. Therefore, optimum mineral mix proportions could be attributed to MgO:bentonite:quicklime ratios at 5~7.5:2.5~5:2.5~5 with a maximum of 15% cement substitution.

**Fig. 2.** Early age healing performances of Table-1 mixes after 28 days: (a) typical crack sealing image, (b) crack sealing efficiency, (c) strength recovery percentage, and (d) gas permeability coefficient improvement.
Out of all mineral containing cement mixes, PC87.5M5B5L2.5 and PC87.5M5B2.5L5 mixes have resulted in a minimum reduction in the compressive strength compared to PC100, while overall self-healing performances were found maximum. Hence, the impact of cement paste cracking age on the self-healing performance was only investigated among that two potential optimum combination mixes (OPT-1: PC87.5M5B5L2.5 and OPT-2: PC87.5M5B2.5L5) and PC100 mix. Here, OPT-1 has more strength recovery potential and OPT-2 has more crack sealing and durability improvement potential. Prism and disk samples were cracked on 1, 7 and 28 days and subsequently healed for 28 days to compare the impact of sample age at cracking on healing performance.

3.2 The impact of cement paste ages at cracking on the self-healing process

In order to quantitatively correlate the impact of cracking age on the healing process, compressive strength development, XRD and TGA were used to determine the state of cement mix hydration after 1, 7 and 28 days. These are to confirm the status of cement hydration during different cracking age, i.e. ages of cement mix at crack formation after casting. Self-healing performance was then assessed using crack sealing, strength recovery and gas permeability. Finally, XRD and SEM-EDX were used to observe the microstructure of formed healing compounds.

The compressive strength development of three selected mixes (OPT-1, OPT-2, and PC100) is presented in Fig. 3. It could be noted that compressive strength was reduced in OPT-1 and OPT-2, compared to the control PC100 mix. The higher proportions of bentonite reduced the compressive strength in OPT-2 compared to OPT-1. The reason is that bentonite reduces hardening property through limited hydration compared to PC, MgO and quicklime. Bentonite also contains considerable proportions of water in the matrix which later results in the development of porous matrix and ultimately reduced the compressive strength. The amount of total mineral substitution, i.e. 12.5% is also causing the reduction of compressive strength in OPT-1 and OPT-2 mixes compared to PC100. These results show similar trends as reported in previous studies where bentonite addition reduced the compressive strength development [2,19]. Compressive strength and self-healing results refers that
different healing performance improves with the compensation of reduced compressive strength in a certain limit.

**Fig. 3.** Compressive strength development after 28 days.

### 3.2.1 The microstructure of cement mixes prior crack formation

The microstructure of the starting cement mixes prior initiating self-healing was investigated using XRD and TGA. Figure 4 presents XRD data of the initial cement mixes cracked at different ages. The XRD patterns showed similar features in the main cement hydration phases (portlandite, ettringite, jennite type crystalline C-S-H) and unhydrated phases (C₃S, C₅S and MgO in OPT-1 and OPT-2). However, the intensity of C-S-H peaks in all mixes, and brucite peaks in OPT-1 and OPT-2 increased with the cement hydration ages. Similarly, the peaks for anhydrite phases were decreasing with the increasing hydration ages.

The corresponding TGA result of those samples is illustrated in Fig. 5. Overall TGA graphs show the weight losses of corresponding mineral hydration phases due to the addition of different minerals in OPT-1 and OPT-2 cement mixes. Common hydration peaks were found for ettringite around ~68 °C, C-S-H gel around ~150 °C similar as [20], major product portlandite decomposition between 425-550 °C [21] and different phases of calcite around ~640–700 °C. The brucite decomposition peaks around ~350 °C [22] were noted in both OPT-1 and OPT-2. The non-evaporative water loss content of cement hydration was determined quantitatively from the major hydration products step observed in the weight loss curve between 100 °C and 550°C (Fig. 7d). The percentages of weight loss were
increasing with the increasing samples hydration ages. This weight loss percentage can be correlated as a function of compressive strength development and age of individual mixes.

![XRD graphs of the cement mixes on different cracking ages (1 day, 7 day and 28 day)](image)

**Fig. 4.** XRD graphs of the cement mixes on different cracking ages (1 day, 7 day and 28 day) (Graph notations: A= Anhydrate, E= Ettringite, Hy= Hydrotalcite, N/HM= Nesquehonite/Hydromagnesite, B=Brucite, C= Calcite, CSH= C-S-H, CS= C$_2$S and C$_3$S, P= Portlandite, M= MgO/MgCO$_3$).

The optimum mineral combinations in OPT-1 and OPT-2 were resulting in an increased weight loss compared to PC100. This could be due to the chemical binding of additional water by expansive minerals during the hydration process. At early age hydration, bentonite could absorb a certain amount of water molecules, due to its large parallel sheet-like surface area. Another factor related to the increasing weight loss content is the adsorption of free water by MgO and quicklime during the initial hydration process. Similar observations were reported by [23] while investigating the impact of replacement materials in ordinary PC hydration. However preliminary study [2,24] suggested that...
individual substitution of MgO reduces the water loss due to its restricted hydration. Therefore, bentonite interlayer water absorption and quicklime early age hydration mostly contributed to the increasing water losses of OPT-1 and OPT-2 mixes.

Fig. 5. Thermogravimetric analysis of the cement mixes on different cracking ages: (a) PC100, (b) PC87.5M5B5L2.5, (c) PC87.5M5B2.5L5, and (d) Percentage of non-evaporative water loss.

The compressive strength, XRD and TGA results of cement mixes at different ages confirms that higher content of expansive minerals and cement remains un-hydrated at early ages (1 day). Higher proportions of primary hydration products such as brucite, portlandite and anhydrite phases also presented in early age, and these products keep forming reducing the unhydrated phases in the matrix over time. In order to investigate the relationship between hydration degree and self-healing performance, next section presents the self-healing results of corresponding mixes.
3.2.2 Self-healing performance

Self-healing performance in this section was compared in terms of crack sealing efficiency, strength recovery percentage and gas permeability improvement.

Crack sealing efficiency and strength recovery results are presented in Fig. 6. Both OPT-1 and OPT-2 mixes showed promising crack closure trends compared to PC100 samples. This was due to the efficient crack sealing performance of added expansive agents. However, sealing efficiency was expected to decrease with the age due to more hydration of the cementitious mix. OPT-1 and OPT-2 mixes resulted in similar improvement, where 5% bentonite mix (OPT-1) shows slightly higher strength recovery performance than 5% quicklime mix (OPT-2) in one day cracked samples. Although OPT-1 and OPT-2 mixes showed efficient crack sealing and strength recovery compared to the control samples, both crack sealing and strength recovery were reduced with the increasing cracking age. This was obvious because higher proportions of cement and expansive minerals are hydrated with time. Hence the autogenous self-healing performance reduced with the increasing cracking age after casting.

![Crack sealing efficiency and strength recovery](image)

**Fig. 6.** Self-healing efficiency of different cracking age samples after 28-day recovery: (a) Crack sealing efficiency and (b) Strength recovery percentage after healing.
Cracking ages have strongly impacted the strength recovery compared to crack sealing performances. Within 1 day to 28 day cracking ages of both OPT-1 and OPT-2 mixes, crack sealing efficiency had dropped by ~20% whereas strength recovery had reduced by ~45-55%. These observations were made due to the reduction of the amount of unhydrated cement, substituted minerals and primary hydration products. These compounds have dictated the amount and type of self-healing materials formatted at different ages of cement mixes. In the more mature samples (i.e. cracked at 28 days), healing compounds were mostly crystalline and less strengthening due to the less availability of unhydrated cement and substituted expansive minerals. The dominant crystalline nature of the self-healing compounds may have attributed to a considerable sealing performance rather than strength recovery efficiencies.

Figure 7 shows the permeability coefficient of disks cracked at different age (1, 7, 28 days) and subsequently healed under water for 28 day period. In the graph, CON-UN and CON-CR were the reference 28 days mature PC100 (CON) disks which were not cracked and cracked, respectively. Gas permeability on these two types was performed to compare results between two extreme cases, where CON-UN represent permeability on an assumed defect free sample at the age of 28 days, and CON-CR represent permeability on a fractured disk just after cracking. Both OPT-1 and OPT-2 resulted in a lower permeability performances compared to PC100 where OPT-2 shows the least permeability due to the higher proportions of quicklime presences in the cement mix. Although the best case healing samples (OPT-2 cracked at 1 day) showed slightly higher (1.78 times) permeability coefficient compared to CON-UN, the coefficients were much lower (0.10 times) than CON-CR samples indicating the effect of self-healing durability improvement. The permeability results confirmed that compacted and higher amount of healing compounds forms in early age (1 day cracked) samples due to the presence of high content unhydrated cement, minerals and primary hydration products. However, this trend diminishes with the age of cement paste mixes. Overall, permeability increases with increasing sample age at crack formation. These permeability results are in good agreement with crack sealing and strength recovery measurements.
Fig. 7. Gas permeability coefficient of cracked disks after 28-day healing (note: the red column and the red dashed line indicate the permeability limit for completely un-cracked PC100 disks).

3.2.3 The microstructure of formed self-healing materials

The microstructure of self-healing materials was investigated using XRD and SEM-EDX on self-healing materials. Samples were collected from re-cracked prisms after 28 days healing.

The XRD analysis is shown in Fig. 8. Typical healing materials are composed of rehydrated cement products, such as a mixture of calcium phases (calcite and portlandite), calcium with silicone and sulphate phases (crystalline jennite phase C-S-H and Ettringite). While calcite peaks intensity was found dominant in PC100 samples, the production of magnesium phases (brucite, nesquehonite/hydromagnesite and hydrotalcite) was found in OPT-1 and OPT-2 mixes. These products have improved the healing efficiency as reflected in the self-healing performances. The XRD peaks are similar for healing materials formed at the different age of samples at cracking. Initially, cement and substituted expansive mineral keeps hydrating then the secondary reactions and carbonation of active portlandite have more dominating effect in the healing product formation. However, as the cement paste becomes more mature, unhydrated cement and expansive mineral contents reduce as a consequence of continuous hydration before cracking. Post cracking, the secondary reactions become dominant. Therefore, with the increasing cracking age of hardened cement, calcite and portlandite contents increase in the healing products. This was in agreement with
the XRD results when the peak intensities of calcite and portlandite found increases with the age of sample at cracking.

**Fig. 8.** XRD diagrams of the self-healing materials (Graph notations: E= Ettringite, Hy= Hydrotalcite, N/HM= Nesquehonite/Hydromagnesite, B=Brucite, C= Calcite, CSH= C-S-H, CS= C$_2$S and C$_3$S, P= Portlandite, M= MgO/MgCO$_3$).

The microstructure of the formed healing products is different to the hydration products of the starting cementitious mixes (Fig. 4 and Fig. 8). The healing products vary with the different combinations of expansive minerals used. Combinations of MgO, bentonite and quicklime promoted the production of Mg-based hydration products together with C-S-H as shown in Fig. 8. These expansive hydration products not only have increased the volume of the healing products but also enhanced the strength of the healing compounds.
The SEM surface morphology of the typical self-healing materials with semi-quantitative elemental detection using EDX is shown in Fig. 9. Healing substances were mostly composed of calcite and portlandite in the PC100 samples (Fig. 9 a, d and g). In OPT-1 and OPT-2 samples, Ca and Mg-rich hydrated and carbonated products combined with a bentonite layer structure were commonly visible (Fig. 9b). However, the bentonite layers become more interlocked in the microstructure with increasing age of the cementitious matrix i.e. age at cracking. Overall, bentonite has contributed in the formation of Al-rich hydrotalcite, and aluminate hydrates while quicklime led to Ca-rich hydromagnesite and ettringite formation. Sulphate hydrate products were also found in OPT-1 and OPT-2 mixes (Fig. 9 c, e, h and i) where other hydration products (eg. portlandite, brucite, calcite) were found proliferating inside that structure. These expansive products solidified the healing compounds, which resulted in an increase in durability as evident in the gas permeability results. The observations of healing compounds morphology and their corresponding elemental detections are in agreement with XRD results, as well as the healing performances of cement mixes at the different cracking ages.
Fig. 9. Typical SEM images and EDX elemental composition of the self-healing materials after the 28 day healing of each cracking age samples: 1 day cracking age samples, (a) PC100, (b) OPT1 and (c) OPT-2; 7 day cracking age samples, (d) PC100, (e) OPT1 and (f) OPT-2; and 28 day cracking age samples, (g) PC100, (h) OPT1 and (i) OPT-2.
3.2.4. Overall correlation between cracking age and healing performance

The overall correlation of self-healing recovery parameters (CA%, SR%, k) against non-evaporative water loss in TGA, and between compressive strength and non-evaporative water loss in TGA are presented in Fig.10. In case of individual mix proportions, the self-healing recovery performances (CA% and SR%) were found reducing with the increase of non-evaporative water loss in TGA (Fig. 10a-c). The gas permeability coefficients show an increasing trend with the increase of non-evaporative water loss in TGA. This non-evaporative water loss in TGA is related to the age of cement mix, i.e. cracking age (1, 7, 28 days) in this case. Therefore, the self-healing performances show an inverse relation with the age of cement mixes at cracking due to the further hydration of cement, mineral and primary hydration phases. Also, a linear trend is noted between compressive strength and non-evaporative water loss in each mixes (Fig. 10d), since increasing degree of hydration increases the compressive strength of cement mix over time. Therefore, compressive strength development over time can be indirectly correlated to the cracking age and self-healing performances by individual types of cement mix.

Although increasing the degree of hydration for an individual mix shows reducing healing performance, this is not necessarily comparable among different cement mix combinations. In this case, the OPT-2 mix has resulted in higher crack sealing and lower gas permeability performance, while its compressive strength was higher than the OPT-1 mix (Fig. 10 b-d). On the contrary, OPT-1 mix showed higher strength recovery performance than OPT-2. This is due to the fact that individual cement mixes keep hydrating in a particular trend over time, which results in an increasing compressive strength and reducing healing performance in that particular trend. The self-healing performance of both OPT-1 and OPT-2 was influenced by the corresponding expansive mineral substitutions in PC. Nevertheless, the results discussed here provide substantial indications that the autogenous self-healing performances of any particular cement or concrete mix could be associated with the degree of hydration as a function of age. Therefore self-healing capacity of cement based materials could be predicted at any age.
Fig. 10. Overall cracking age impact on the self-healing recovery and gas permeability: (a) PC100, (b) OPT-1, (c) OPT-2, and (d) Compressive strength relation to non-evaporative water loss in TGA.

4. Conclusions

This study identified the optimum minerals mix proportion in PC with expansive minerals (MgO, bentonite, and Quicklime) for efficient autogenous self-healing and established a quantitative correlation between the age of cement paste at cracking and self-healing performance. Two potential optimum mix proportions (OPT-1: PC87.5M5B5L2.5 and OPT-2: PC87.5M5B2.5L5) are recommended based on compressive strength and self-healing performances. OPT-1 shows higher strength recovery, moderately high crack sealing and durability performance, and OPT-2 shows higher compressive strength (than OPT-1), crack sealing and durability improvement, as well as moderately high strength recovery performance.
The autogenous self-healing capacity of cementitious materials directly relates to the age of cement paste mix at crack formation. This age factor is quantitatively correlated with the degree of hydration of cementitious materials. The strength recovery and crack sealing at 1 day to 28 day cracking age samples reduced from 15% and 73% to 4% and 55%, respectively in PC100, from 69% and 97% to 11% and 75%, respectively in OPT-1, and from 57% and 100% to 14% and 78%, respectively in OPT-2. The gas permeability on the other hand at 1 day to 28 day increased from 7.7 to 16.0, respectively in PC100, 2.7 to 10.2, respectively in OPT-1, and 1.9 to 7.8, respectively in OPT-2. The overall healing performance is as such, longer the cracking age of cement mix (after casting) and hydrated the cement matrix, less the self-healing performances. Although the healing performances of OPT-1 and OPT-2 cement mix combinations were much promising compared to that of only PC mix (PC100), healing performances were reduced with the cracking age of both OPT-1 and OPT-2.

Common healing compounds in all cement mixes were calcite, portlandite, ettringite, and CSH. Expansive minerals encouraged the formation of brucite, other magnesium hydro-carbonate products, and magnesium combined calcium and aluminium hydration compounds. A Higher percentage of unhydrated cement, expansive minerals and primary hydration products present in cement mix at an early age. These result in the production of compacted healing compounds, which eventually lead to improved healing performance. The production of healing compounds and their densifying structure reduces with the age of cement mix at crack formation. Additionally, with the ageing of the mix, the volume of healing compounds formation decreases and the content of calcite and portlandite increases. This ultimately reduces the self-healing performances.

Overall results suggested that expansive minerals improved the self-healing capacity of PC mixes. The autogenous self-healing performance of any particular cement mix could be numerically predicted based on their hydration degree which is an indicator of cement mix state at any particular age.
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