

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

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7 **Abstract**

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

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

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1 **1. Introduction**

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

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

18 Cracking age was reported to have vital impact on the self-healing of concrete or composite with the
19 high proportion of cement and supplementary cementitious materials (SCMs) such as fly ash, slag
20 based Engineered Cementitious Composites (ECCs) [6–13]. Two different types of fly ash (low lime
21 and high lime) and ground granulated blast furnace slag (GGBS) about 1.2 times of PC in ECC were
22 pre-damaged to 80% of the their deformed capacities at 7, 28 and 90 days, and their self-healing
23 performance based on sorptivity and rapid chloride permeability tests (RCPT) showed decreasing
24 healing trend with the increase in pre-damage age [9,10]. The self-healing of these fly ash and GGBS
25 based ECCs was reported less effective when composites aged to maturity [11–13], although the use
26 of hydrated lime [12] and CO₂-water curing [13] in ECCs reported to enhanced the healing efficiency.

1 Early age concrete rapidly heals itself through autogenous healing triggered by the remaining high
2 proportions of unhydrated cement [14]. Although cement hydrates rapidly in the early ages, about
3 25% of cement still remains unhydrated in concrete even after 28 months [15]. These considerable
4 proportions of unhydrated cement can initiate self-healing actions in mature concrete. The importance
5 of hydration was further tagged as a major factor in establishing a model to characterize the self-
6 healing efficiency [16]. While it is known that the autogenous self-healing potential decrease with the
7 age of concrete, there are no studies to our knowledge that quantitatively relates the hydration state of
8 cement with its intrinsic self-healing behaviour.

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

15 **2. Materials and experimental procedure**

16 **2.1 Materials and sample preparation**

17 Table 1 illustrates the mix composition of cement pastes used in this study. The mix proportions in
18 Table 1 were based on the findings of Part-I [2]. Cement mixes with 5% MgO show good
19 improvement in self-healing performances. In those mixes with expansive minerals, the
20 microstructure and ternary diagrams analysis of healing materials (refer to Fig. 14 and Fig. 15 in Part-
21 I) [2] correspond to additional formation of efficient healing materials. However, the substitution of
22 PC in the mixes over 15% with expansive minerals was not improving the healing performance
23 considerably, and in fact resulted in the reduction of mechanical strength. Therefore, in this Part-II
24 test series, MgO proportions were set within 5-7.5%, while bentonite and quicklime were substituted
25 within 2.5-5% respectively.

1 The control mix (CON) was a 100% PC (CEM 1 42.5N) cement paste mix, while the rest of the five
 2 mixes contained different percentages of minerals as PC substitutions (Table 1). Water to cement ratio
 3 (w/c) was kept constant at 0.35 and superplasticiser (Sikament 700 satisfying [17]) was used as a
 4 water-reducing admixture to balance similar workability in each mixes based on the flow table test.
 5 The w/c was kept constant in Part-II mixes intentionally to compare the healing performance of all
 6 mixes at same w/c, while Part-I [2] investigates healing performance with varying w/c according to
 7 each mixes standard consistency.

8 **Table 1.** Cement mix compositions by percentage weight.

Mix	PC	MgO 92/200	Bent- onite	Quick- lime	w/b 0.35	Superpl- asticiser	Flow table test avg.
	%	%	%	%	% of binder	% of binder	mm
CON (PC100)	100	0	0	0	35	0.00%	199.5
PC87.5M7.5B2.5L2.5	87.5	7.5	2.5	2.5	35	1.05%	206.0
PC85M7.5B5L2.5	85	7.5	5	2.5	35	2.08%	203.5
PC85M7.5B2.5L5	85	7.5	2.5	5	35	1.09%	201.0
PC87.5M5B5L2.5 (OPT-1)	87.5	5	5	2.5	35	2.08%	205.0
PC87.5M5B2.5L5 (OPT-2)	87.5	5	2.5	5	35	1.09%	204.5

9
 10 Cubes, prisms and disks were prepared for this study. For the results to be comparable all samples
 11 were prepared the same as described in Part-I [2]. The crack mouth opening of the prisms was
 12 restricted at 0.3 mm which resulted in a residual crack of 0.20 ± 0.03 mm after unloading.

13 2.2 Experimental procedure

14 The compressive strength of 28 days matured cubes were measured following BS EN 196-1:2005
 15 [18]. Healing performance was compared using visual crack sealing, strength recovery and durability
 16 improvement against gas permeability. Triplicate samples were investigated in all the compressive
 17 strength and healing performance experiments.

1 At first, the early age (24 hr) self-healing of cement mixes was investigated up to 28 days to
2 determine optimum mix composition with expansive minerals for autogenous self-healing. Then CON
3 (PC100) and two potential optimum cement mixes were further assessed to determine the impact of
4 cracking age on healing behaviour. To perform this, prism and disk samples were cracked at 1, 7 and
5 28 days after casting, and their healing was investigated subsequently after 28 days of cracking. The
6 compressive strength was also measured at the age of 1, 7 and 28 days. Healing properties were
7 further compared with the microstructural analysis of starting cement mix and healing materials.

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

13 **3. Results and Discussions**

14 **3.1 Determination of optimum mineral mix proportion**

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

18 Compressive strength results are presented in Fig. 1. The strength was found lower in mineral
19 containing mixes compared to CON (PC100) mix. However, compressive strength showed a similar
20 trend as reported in Part-I test series, where bentonite has considerably reduced compressive strength
21 development compared to MgO and quicklime. This is due to the fact that, bentonite absorbs higher
22 proportions of water and act as a filler material rather much contributing in the cement hydration
23 process. MgO and quicklime, on the other hand, are less water demanding and much compatible with
24 PC during the hydration process.

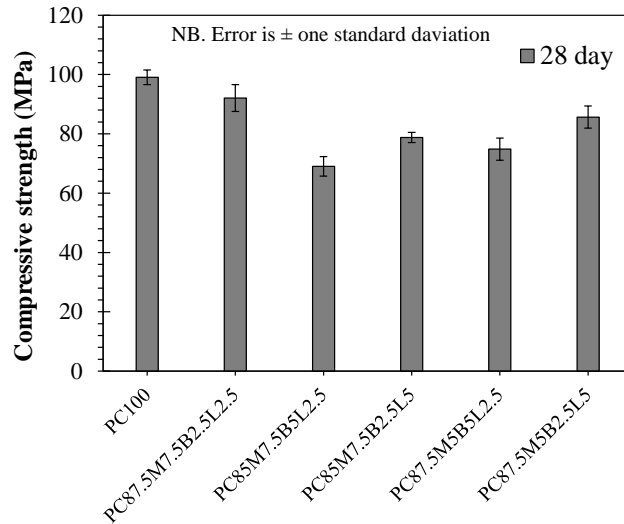


Fig. 1. The compressive strength of 28-day cubes.

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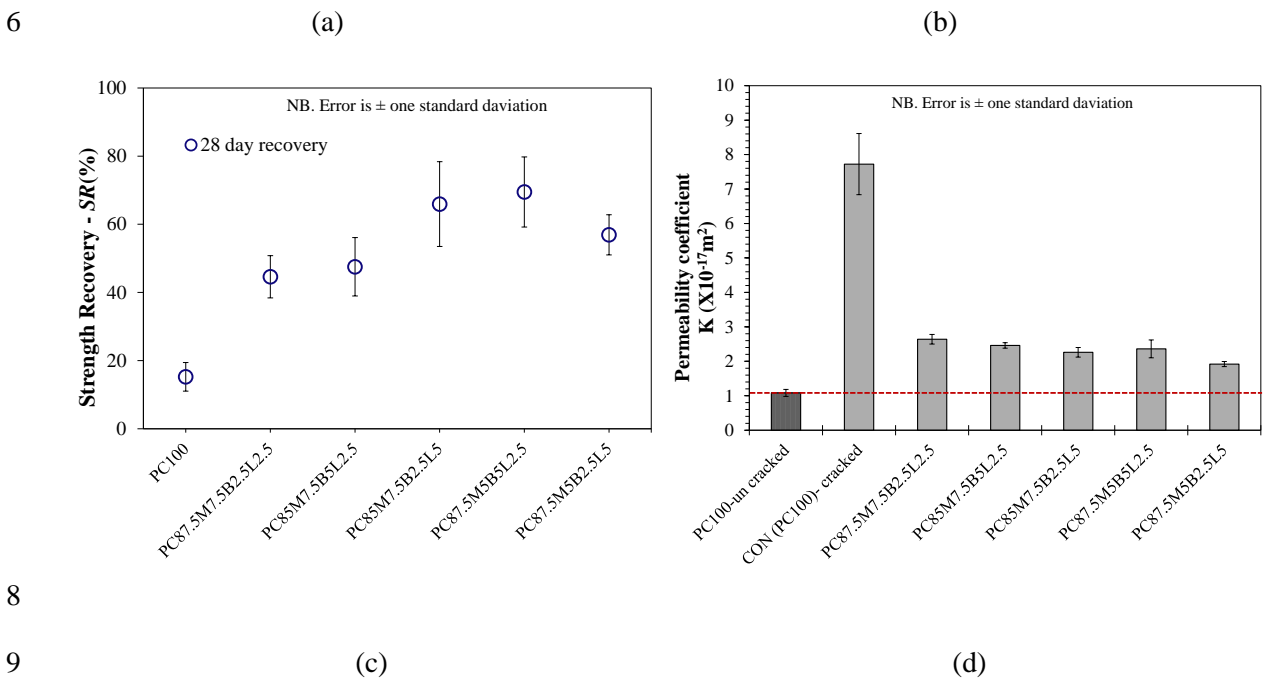
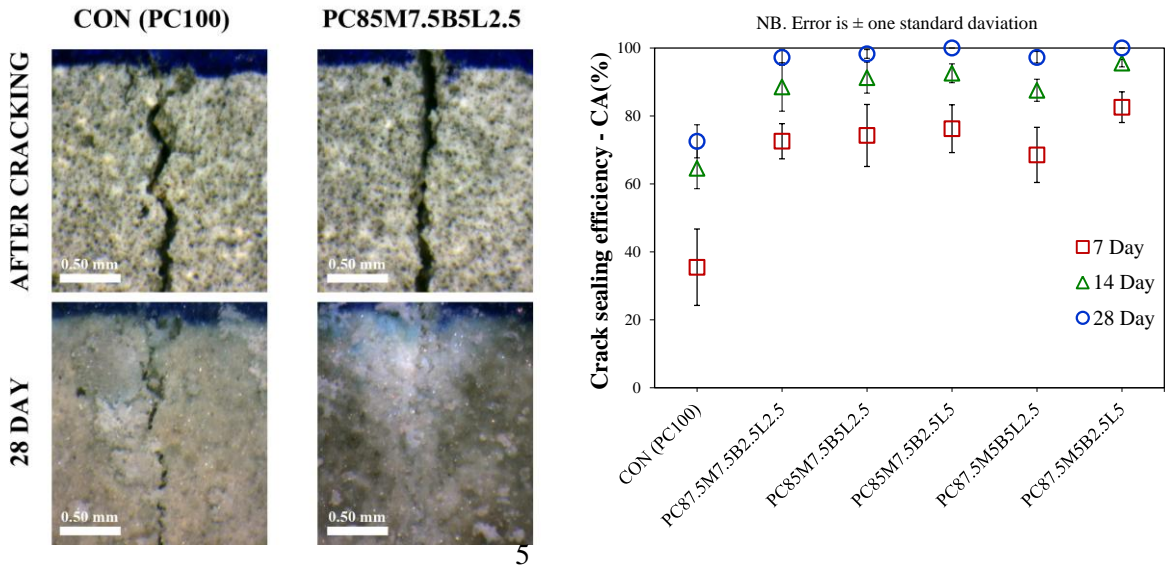
The healing period of early age (24 hr) samples was 28 days. The healing performance was assessed in terms of crack sealing efficiency (CA%), strength recovery percentage (SR%) and gas permeability improvement. Self-healing results are presented in Fig. 2. The mineral containing mixes sealing efficiencies 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 containing 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

1 permeability reduction results show a similar trend as crack sealing (Fig. 2 b and d), strength recovery

2 was found efficient with 5% each MgO and bentonite mixes. Therefore, optimum mineral mix

3 proportions could be attributed to MgO:bentonite:quicklime ratios at 5~7.5:2.5~5:2.5~5 with a

4 maximum of 15% cement substitution.



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10 **Fig. 2.** Early age healing performances of Table-1 mixes after 28 days: (a) typical crack sealing

11 image, (b) crack sealing efficiency, (c) strength recovery percentage, and (d) gas permeability

12 coefficient improvement.

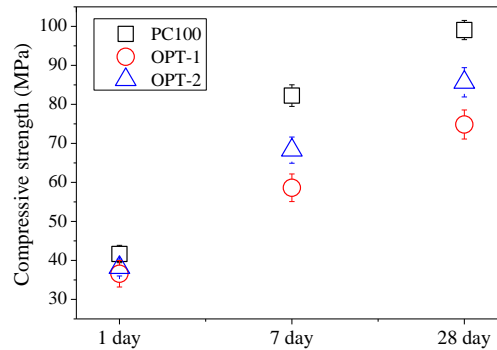
1 Out of all mineral containing cement mixes, PC87.5M5B5L2.5 and PC87.5M5B2.5L5 mixes have
2 resulted in a minimum reduction in the compressive strength compared to PC100, while overall self-
3 healing performances were found maximum. Hence, the impact of cement paste cracking age on the
4 self-healing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

9 **3.2 The impact of cement paste ages at cracking on the self-healing process**

10 In order to quantitatively correlate the impact of cracking age on the healing process, compressive
11 strength development, XRD and TGA were used to determine the state of cement mix hydration after
12 1, 7 and 28 days. These are to confirm the status of cement hydration during different cracking age,
13 i.e. ages of cement mix at crack formation after casting. Self-healing performance was then assessed
14 using crack sealing, strength recovery and gas permeability. Finally, XRD and SEM-EDX were used
15 to observe the microstructure of formed healing compounds.

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

1 different healing performance improves with the compensation of reduced compressive strength in a
2 certain limit.



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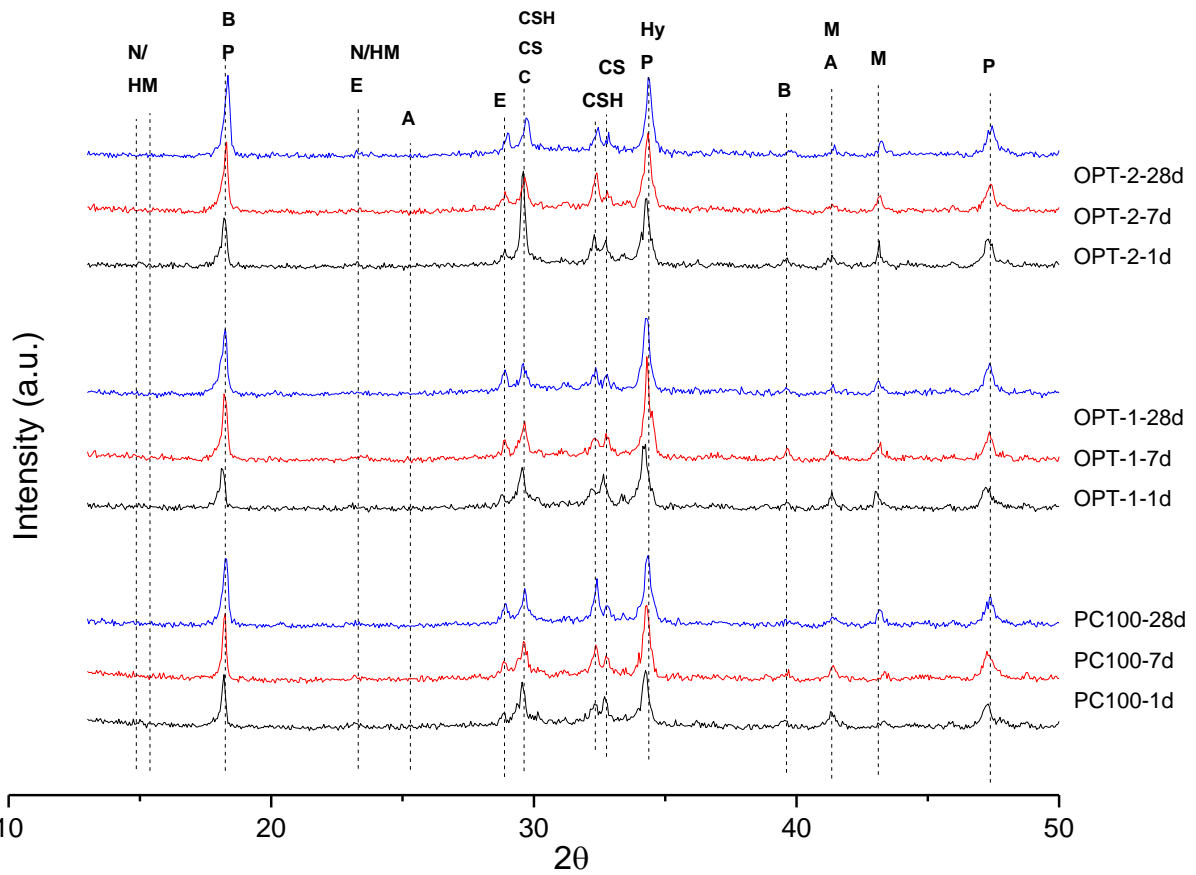
Fig. 3. Compressive strength development after 28 days.

5 **3.2.1 The microstructure of cement mixes prior crack formation**

6 The microstructure of the starting cement mixes prior initiating self-healing was investigated using
7 XRD and TGA. Figure 4 presents XRD data of the initial cement mixes cracked at different ages. The
8 XRD patterns showed similar features in the main cement hydration phases (portlandite, ettringite,
9 jennite type crystalline C-S-H) and unhydrated phases (C_2S , C_3S and MgO in OPT-1 and OPT-2).
10 However, the intensity of C-S-H peaks in all mixes, and brucite peaks in OPT-1 and OPT-2 increased
11 with the cement hydration ages. Similarly, the peaks for anhydrite phases were decreasing with the
12 increasing hydration ages.

13 The corresponding TGA result of those samples is illustrated in Fig. 5. Overall TGA graphs show the
14 weight losses of corresponding mineral hydration phases due to the addition of different minerals in
15 OPT-1 and OPT-2 cement mixes. Common hydration peaks were found for ettringite around ~ 68 °C,
16 C-S-H gel around ~ 150 °C similar as [20], major product portlandite decomposition between 425-550
17 °C [21] and different phases of calcite around ~ 640 – 700 °C. The brucite decomposition peaks around
18 ~ 350 °C [22] were noted in both OPT-1 and OPT-2. The non-evaporative water loss content of
19 cement hydration was determined quantitatively from the major hydration products step observed in
20 the weight loss curve between 100 °C and 550°C (Fig. 7d). The percentages of weight loss were

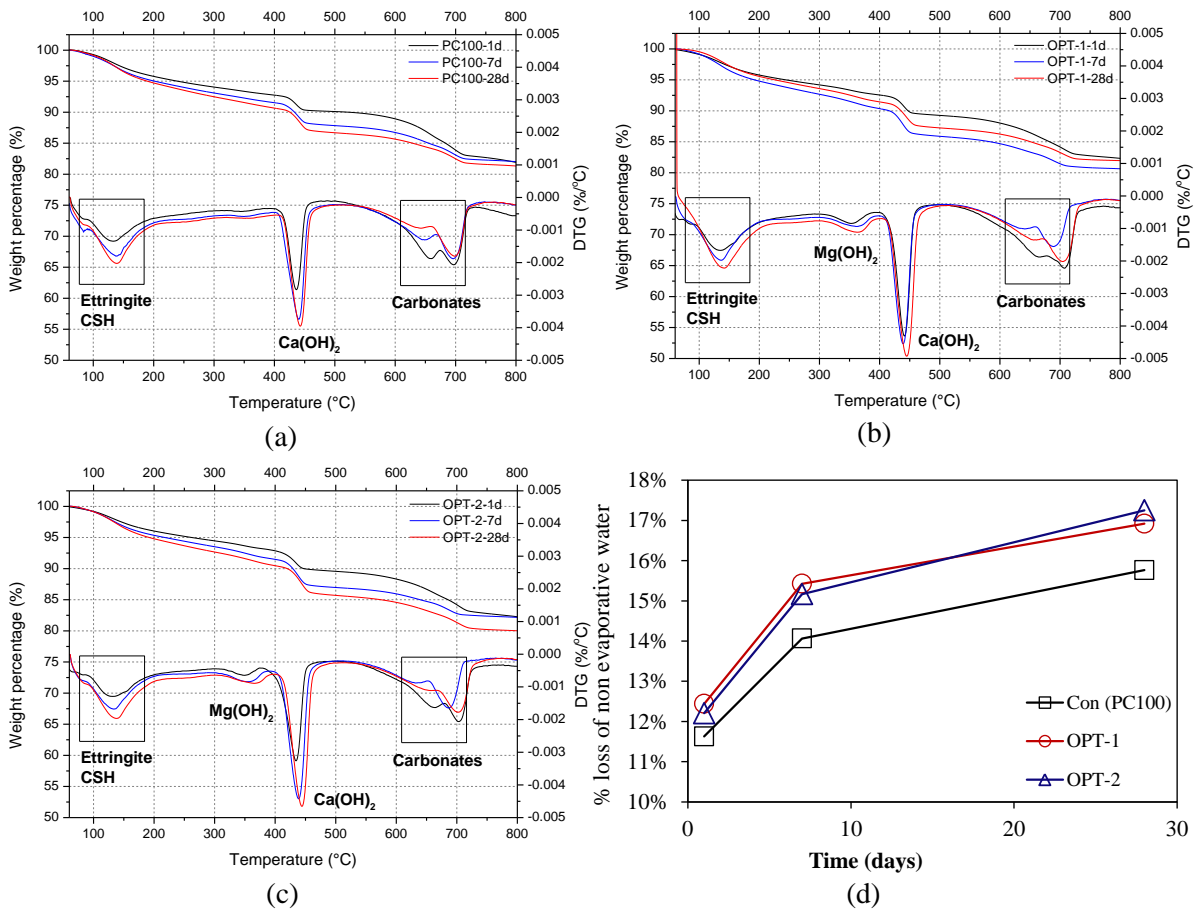
1 increasing with the increasing samples hydration ages. This weight loss percentage can be correlated
 2 as a function of compressive strength development and age of individual mixes.



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 4 **Fig. 4.** XRD graphs of the cement mixes on different cracking ages (1 day, 7 day and 28 day) (Graph
 5 notations: A= Anhydrate, E= Ettringite, Hy= Hydrotalcite, N/HM= Nesquehonite/Hydromagnesite,
 6 B=Brucite, C= Calcite, CSH= C-S-H, CS= C_2S and C_3S , P= Portlandite, M= $MgO/MgCO_3$).

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

1 individual substitution of MgO reduces the water loss due to its restricted hydration. Therefore,
 2 bentonite interlayer water absorption and quicklime early age hydration mostly contributed to the
 3 increasing water losses of OPT-1 and OPT-2 mixes.



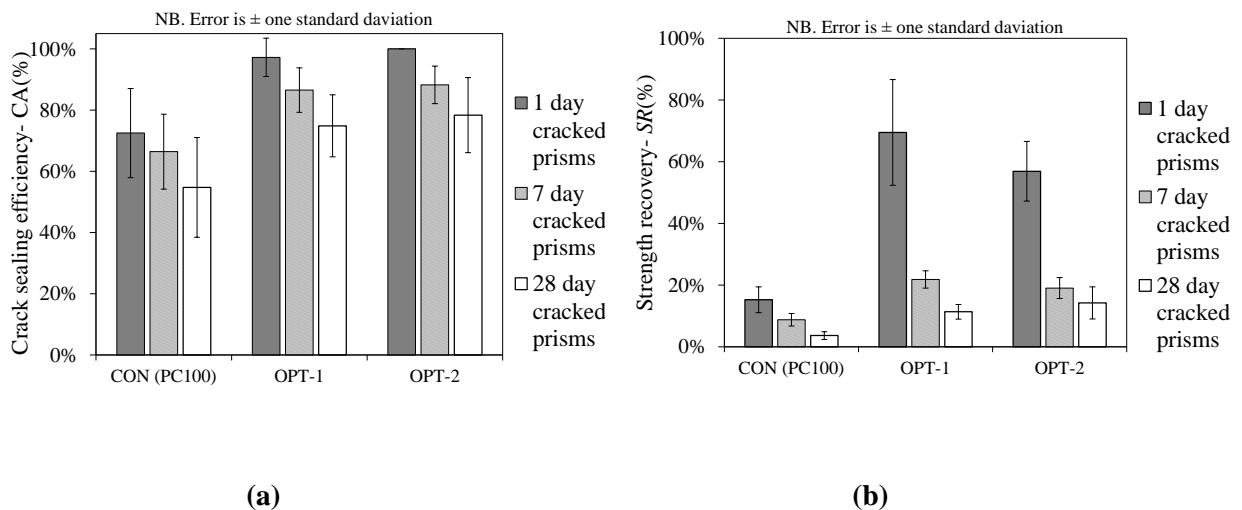
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 5 **Fig. 5.** Thermogravimetric analysis of the cement mixes on different cracking ages: (a) PC100, (b)
 6 PC87.5M5B5L2.5, (c) PC87.5M5B2.5L5, and (d) Percentage of non-evaporative water loss.

7 The compressive strength, XRD and TGA results of cement mixes at different ages confirms that
 8 higher content of expansive minerals and cement remains un-hydrated at early ages (1 day). Higher
 9 proportions of primary hydration products such as brucite, portlandite and anhydrite phases also
 10 presented in early age, and these products keep forming reducing the unhydrated phases in the matrix
 11 over time. In order to investigate the relationship between hydration degree and self-healing
 12 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.



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17 **Fig. 6.** Self-healing efficiency of different cracking age samples after 28-day recovery: (a) Crack

18 sealing efficiency and (b) Strength recovery percentage after healing.

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

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

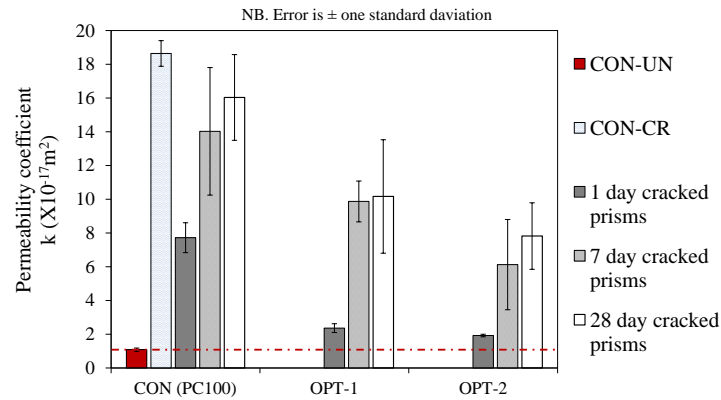


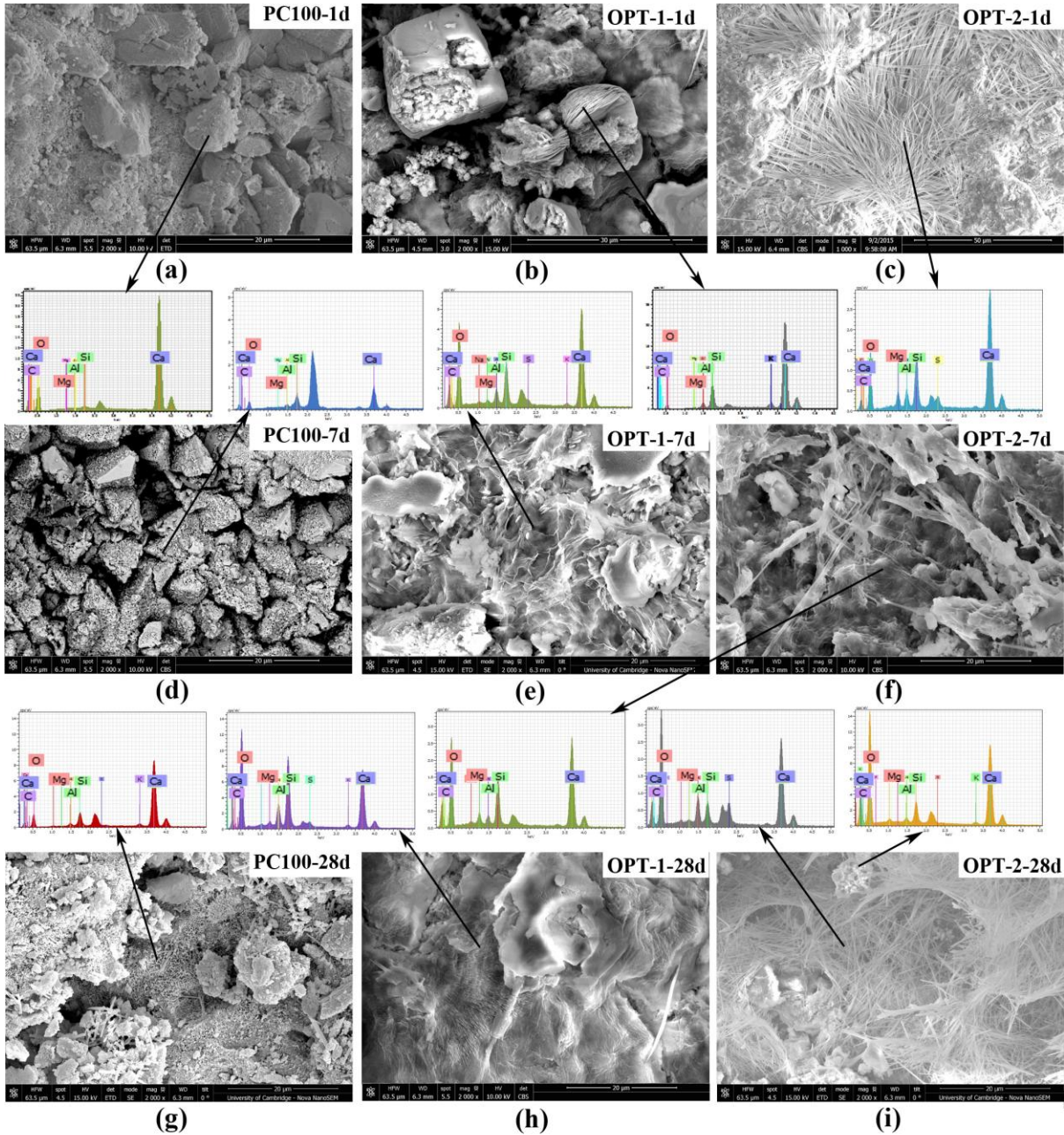
Fig. 7. Gas permeability coefficient of cracked disks after 28-day healing (note: the red column and the red dashed line indicate the permeability limit for completely un-cracked PC100 disks).

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

1 The SEM surface morphology of the typical self-healing materials with semi-quantitative elemental
2 detection using EDX is shown in Fig. 9. Healing substances were mostly composed of calcite and
3 portlandite in the PC100 samples (Fig. 9 a, d and g). In OPT-1 and OPT-2 samples, Ca and Mg-rich
4 hydrated and carbonated products combined with a bentonite layer structure were commonly visible
5 (Fig. 9b). However, the bentonite layers become more interlocked in the microstructure with
6 increasing age of the cementitious matrix i.e. age at cracking. Overall, bentonite has contributed in the
7 formation of Al-rich hydrotalcite, and aluminate hydrates while quicklime led to Ca-rich
8 hydromagnesite and ettringite formation. Sulphate hydrate products were also found in OPT-1 and
9 OPT-2 mixes (Fig. 9 c, e, h and i) where other hydration products (eg. portlandite, brucite, calcite)
10 were found proliferating inside that structure. These expansive products solidified the healing
11 compounds, which resulted in an increase in durability as evident in the gas permeability results. The
12 observations of healing compounds morphology and their corresponding elemental detections are in
13 agreement with XRD results, as well as the healing performances of cement mixes at the different
14 cracking ages.



1

2 **Fig. 9.** Typical SEM images and EDX elemental composition of the self-healing materials after the 28
 3 day healing of each cracking age samples: 1 day cracking age samples, (a) PC100, (b) OPT1 and (c)
 4 OPT-2; 7 day cracking age samples, (d) PC100, (e) OPT1 and (f) OPT-2; and 28 day cracking age
 5 samples, (g) PC100, (h) OPT1 and (i) OPT-2.

1 **3.2.4. Overall correlation between cracking age and healing performance**

2 The overall correlation of self-healing recovery parameters (CA%, SR%, k) against non-evaporative
3 water loss in TGA, and between compressive strength and non-evaporative water loss in TGA are
4 presented in Fig.10. In case of individual mix proportions, the self-healing recovery performances
5 (CA% and SR%) were found reducing with the increase of non-evaporative water loss in TGA (Fig.
6 10a-c). The gas permeability coefficients show an increasing trend with the increase of non-
7 evaporative water loss in TGA. This non-evaporative water loss in TGA is related to the age of
8 cement mix, i. e. cracking age (1, 7, 28 days) in this case. Therefore, the self-healing performances
9 show an inverse relation with the age of cement mixes at cracking due to the further hydration of
10 cement, mineral and primary hydration phases. Also, a linear trend is noted between compressive
11 strength and non-evaporative water loss in each mixes (Fig. 10d), since increasing degree of hydration
12 increases the compressive strength of cement mix over time. Therefore, compressive strength
13 development over time can be indirectly correlated to the cracking age and self-healing performances
14 by individual types of cement mix.

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

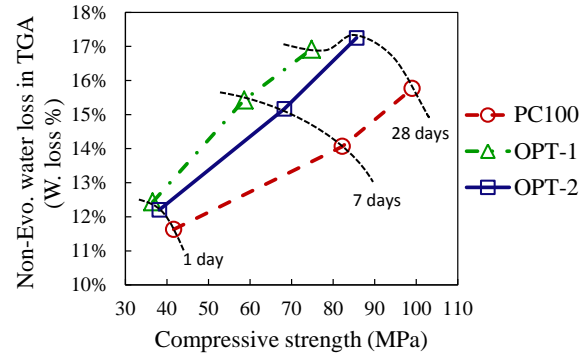
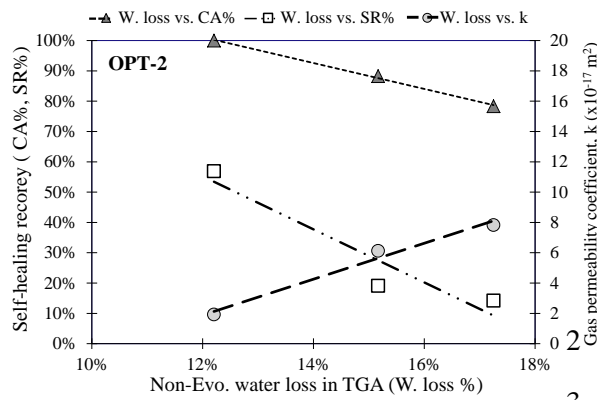
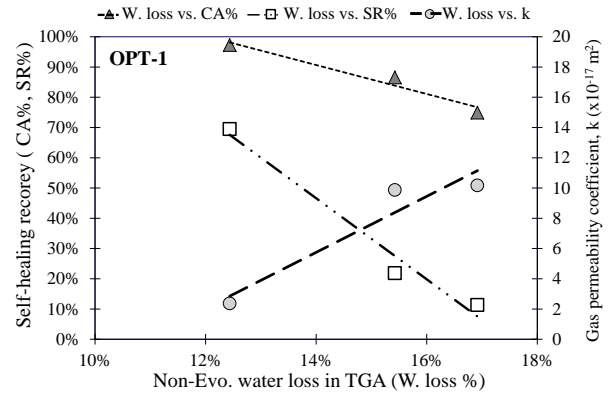
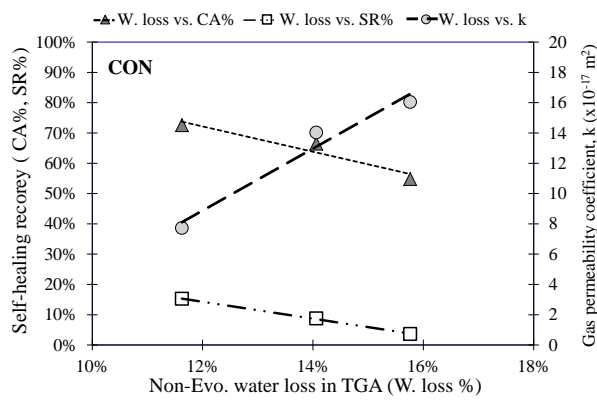


Fig. 10. Overall cracking age impact on the self-healing recovery and gas permeability: (a) PC100, (b) OPT-1, (c) OPT-2, and (d) Compressive strength relation to non-evaporative water loss in TGA.

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.

1 The autogenous self-healing capacity of cementitious materials directly relates to the age of cement
2 paste mix at crack formation. This age factor is quantitatively correlated with the degree of hydration
3 of cementitious materials. The strength recovery and crack sealing at 1 day to 28 day cracking age
4 samples reduced from 15% and 73% to 4% and 55%, respectively in PC100, from 69% and 97% to
5 11% and 75%, respectively in OPT-1, and from 57% and 100% to 14% and 78%, respectively in
6 OPT-2. The gas permeability on the other hand at 1 day to 28 day increased from 7.7 to 16.0,
7 respectively in PC100, 2.7 to 10.2, respectively in OPT-1, and 1.9 to 7.8, respectively in OPT-2. The
8 overall healing performance is as such, longer the cracking age of cement mix (after casting) and
9 hydrated the cement matrix, less the self-healing performances. Although the healing performances of
10 OPT-1 and OPT-2 cement mix combinations were much promising compared to that of only PC mix
11 (PC100), healing performances were reduced with the cracking age of both OPT-1 and OPT-2.

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

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

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