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Scientific paper

Autogenous Healing Effect of Ultra-High Performance Cementitious Composites

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Received 16 July 2018, accepted 1 November 2018

doi:10.3151/jact.16.549

Abstract

This paper presents the results of research concerning the potential ability of ultra-high performance cementitious composites to self-heal the cracks that appear at various curing stages, and the effect of additional hydrothermal treatment on this ability. Test specimens were fractured in a 3-point bending test. The preload was induced during the initial curing period, i.e. 24 hours after the mix was made, and also in matured materials: concrete that was cured for 28 days in water or subjected to low-pressure steaming or autoclaving. Flexural strength and total fracture energy tests were carried out on reference specimens and also on specimens with a crack healed by immersion in water and by the additional use of steaming at 90°C and autoclaving at 250°C. The results of studies performed with respect to mechanical properties and microstructure observations show that material that was cracked at early curing stages can be most effectively healed (i.e. its strength restored) by the autoclaving process. The main reason for this is the crystallisation of xonotlite and tobermorite whiskers in the healed crack. The self-healing effect tested in matured composites where binder hydration was determined to be of around 40% turned out to be virtually negligible.

1. Introduction

One issue related to the durability of cement composites is the determination of their self-healing ability. Of particular interest is the assessment of the materials potential for spontaneous (autogenous) or externally stimulated (autonomous) healing of micro-defects in the form of cracks and fractures that occur in the material during its curing and subsequent use. This issue is currently an intensively researched aspect of the production of “smart” materials, and not just cementitious ones (Alaneme and Bodunrin 2017; Barrasa *et al.* 2014; Bekas *et al.* 2016; de Rooij *et al.* 2013). It concerns material durability, and thus also touches upon the subject of sustainable development (Li and Herbert 2012).

The autogenous healing of cracks caused, *inter alia*, by shrinkage, thermal deformations, external loads or finally expansive corrosion products is the result of processes that may occur in the material, involving components that are naturally present in the hardened cementitious composite. This mainly pertains to the presence of unhydrated relict cement grains, hydraulic and/or pozzolanic additives as well as calcium carbonate precipitation (Lv and Chen 2012; Sahmaran *et al.* 2013). Self-healing processes result not only in increasing the tightness of cement composite structures, and thus in restoring their physical continuity, but also in restoring to some degree the mechanical properties lost

as a result of cracking. In general, there are three types of mechanisms that result in autogenous healing:

- physical – sealing caused by water absorption by the material, which results in the swelling of the C-S-H phase,
- chemical – a reduction in porosity caused by the hydration of relict cement grains and carbonation, which continues until the crystallization of CaCO_3 occurs (Li and Herbert 2013; Ranaivomanana *et al.* 2013; Şahmaran *et al.* 2008; van der Zwaag 2007). Further reaction with CO_2 causes bicarbonate to emerge, resulting salt becoming more soluble, and thus unfortunately to unsealing the structure,
- mechanical – the structure is sealed by the introduction of fragments of native material together with the migrating liquid or by the crystallization of other salts resulting from the oversaturation of solutions during the evaporation of water from open pores (Snoeck and De Belie 2015).

There are also certain means of triggering the self-healing effect in materials; in this case, the process is referred as autonomous healing (de Rooij *et al.* 2013). This consists in deliberately introducing into the composite, at the stage of preparing the mix, inclusions that are carriers of the agent that fills the emerging cracks. One of the first ideas (Dry 1997), which was patented, for achieving the effect of induced self-healing was the introduction of hollow fibres filled with a repair agent into the concrete mix. In the case of cementitious composites, the healing mechanism was triggered by mechanical damage of the composite structure and simultaneous damage of the fibre, which resulted in the release of the repair agent and the defect being filled. The most commonly discussed type of repair materials that can fill structure defects are either two-component ep-

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oxy resins with hardeners or epoxy resins cross-linked by the presence of calcium hydroxide, which is present naturally in concrete (Abd Elmoaty 2011; Łukowski and Adamczewski 2010). A completely different group of materials in which the self-healing process can be induced are bioconcretes. This concept is based on the addition of (usually *Bacillus*) bacteria to the concrete mix, which produce calcium carbonate during their metabolic processes (Souradeep *et al.* 2017; Tziviloglou *et al.* 2017). In addition to polymer or biologic fillers as a repair agents, inorganic ones are used as well (Ahn and Kishi 2010). Usually these have the form of capsules that contain salts such as calcium nitrate (Al-Ansari *et al.* 2017) or sodium silicate (Huang and Guang 2011; Restuccia *et al.* 2017), which results in the precipitation of additional C-S-H phases in cracks in the presence of Ca^{2+} ions.

So-called ultra-high performance concretes (UHPCs), which also include RPCs (reactive powder concretes), are currently among state-of-the-art composites with a cementitious matrix. The production of these materials has been made possible mainly by the progress in cement binder technology, the availability of highly efficient superplasticizers, and also comprehensive studies of the mechanisms of action of mineral additives. Similarly as the High Performance Concrete (HPC) group of materials, which has been known for many years, these composites are the result of long-term research on methods which can be used to mitigate the drawbacks typical of ordinary concretes. Studies on concrete composites belonging to this group can be considered to have started in the 1970s with the production of DSP (Densified Small Particles) cementitious materials and MDF (Macro Defect Free) materials (Aïtcin 2001). In the mid-1990s, primarily in France, a formula for a composite referred to as reactive powder concrete (RPC) was developed (Richard and Cheyrezy 1994, 1995). According to the authors, depending on the technological procedures applied, this multi-component material could achieve compressive strengths ranging from approximately 200 to approximately 800 MPa and flexural tensile strengths ranging from approximately 20 to 140 MPa. Among the many material and technological factors which ensure such favourable mechanical properties is reducing the amount of mixing water to below stoichiometric values. Therefore, the assumption is that hardened composite must include relics of unreacted clinker. This is the main reason why in the case of Ultra High Performance Cementitious Composites, such as reactive powder concretes (RPCs), the self-healing effect is mostly described as an autogenous process. Moreover, due to additional phenomena that occur during cement hydration, such as water being trapped in gel or capillary pores, the degree of cement hydration in composites being cured under natural conditions can be as low as 15% (Zanni *et al.* 1996). The first mentions of the self-healing effect in reactive powder concrete can be found in the paper by (Acker and Behloul 2004) who

presents a damaged relict clinker grain with a healed space within the grain. The healing occurred as a result of a reaction with water molecules that migrated from the external environment.

Interesting research in this area was conducted by (Granger *et al.* 2007, 2009) who analysed changes in post-critical stresses in pre-cracked UHPC. The test results obtained confirmed that the damage caused was clearly healed. After a crack with a width of around 30 μm had been initiated and 50% of load capacity had been lost, the material was immersed in water for a period of 20 weeks. After this time, its flexural tensile strength was approximately 30% higher than that of the reference material that was stored in air-dry conditions. Also, the research conducted by (Kunieda *et al.* 2012) unambiguously confirms the ability of UHPC to self-heal its structure. Investigations of this phenomenon conducted by the authors were based, *inter alia*, on the characteristics of the composites ability to transport liquid and gas media. Samples containing PE fibers were subjected to uniaxial tensile tests, thus producing many cracks in the material with a width of approximately 10 to 20 μm . The obtained tests results confirm that after 90 days of healing in water the level of transport of liquid (water) and gas (air) again reached a reference level i.e. before loading. Further healing in water lasting up to 360 days resulted in the reduction of air permeability coefficient by more than an order of magnitude.

The issue of autogenous healing is also discussed in connection with other cementitious composites. However, comparisons between the studies published to date are very difficult. This is due to the fact that tests of recovered mechanical properties of cementitious composites are very sensitive to multiple factors. First of all, these include environmental factors such as composite curing conditions: in air at variable relative humidities, in water and finally at variable temperatures. Second, methods of testing the restored mechanical properties (compression, bending, tension) and, most importantly, methods of preloading concrete elements have a considerable impact on results. These factors are different most publications. Moreover, reinforcement in the form of steel fibres is very often present in the composition of the cementitious composites tested. The manner of calculation of strength recovery coefficients also varies. However, it can be generally stated that concretes in which exclusively Portland cement is used as binder exhibit very limited recovery of mechanical properties. Tests (Şahmaran *et al.* 2008) conducted on self-compacting concretes (SCC) demonstrated that compressive strength recovery of material preloaded to 90% of the maximum load and stored in water over a period of 30 days was around 5%, which is the natural level of variability of this property. Much better results were achieved for a composite that included fly ash, which replaced 55% of Portland cement by weight, since compressive strength recovery amounted to around 20% in

that case. It should also be mentioned that a programme for testing the recovery of mechanical features similar to the one presented in the present article was conducted by (Restuccia *et al.* 2017). The research concerned the autonomous healing of standard mortar which contained encapsulated water glass solution as a repair agent. The tests consisted in causing 250 µm cracks during three-point bending of a notched concrete prism. After 28 days, the recovery of flexural tensile strength did not exceed 10%. The test results presented below demonstrate that depending on the time and the curing method, ultra-high performance composites may exhibit significantly higher levels of recovery of mechanical properties. As it has been shown, this is related, *inter alia*, to the binder hydration degree.

The matrix of ultra-high performance composites is known as a very brittle material. A linear relationship between stress and deformation is observed during both squeezing and bending until the composite reaches maximum load. In other words, UHPC matrix when is deprived of fibres hardly exhibits any plastic deformation, and the formation of a crack is associated with its immediate propagation, which leads to a sharp drop in recorded post-critical stress (Zdeb 2009, 2016). Thus the research programme presented below is based on the following assumptions:

- the effect of autogenous healing of ultra-high performance composite will be observed on specimens equipped with counter-weights and preloaded during 3-point notch bending up to deflection where the values of post-critical stress were negligible (200 µm);
- the self-healing effect is due to the low value of the water-binder ratio typical of this group of materials, which results in a low degree of cement hydration, allowing the relict clinker grains on the fracture surface of the specimen to further react with water.

2. Experimental part

2.1 Origin and purpose of research

In the ultra-high performance cementitious composites discussed, also frequently named reactive powder con-

cretes, the paste volume (including cement, pozzolans and water) often exceeds 50 – 60% of the overall composite volume. The natural consequence of this fact is the considerable shrinkage, especially in the early phase of curing. This is a shortcoming of such composites. Microstructure observations of the composites cured in water reveal micro-defects in the form of shrinkage cracks, often causing a cohesive discontinuity of the structure, which passes through clinker grains (see Fig. 1). The newly created surface, which is caused by 3-point bending of test elements, is intended to simulate a crack that appears during shrinkage and should include non-hydrated relict cement grains.

The purpose of the tests carried out was to determine the autogenous healing effect in ultra-high performance composites cured in different hydrothermal conditions and cracked in the initial curing stage, i.e. after 24 hours. This situation simulates the emergence of a destructive crack caused e.g. by material shrinkage, and its self-healing as a result of natural curing, assisted by low-pressure steaming or autoclaving (Fig. 2a). These variable curing conditions were applied because the composites discussed here are largely used for the manufacture of prefabricated elements. During their manufacture, hydrothermal treatments are frequently applied in order not only to increase the rate of binder hydration, but also to reduce shrinkage deformations.

In the second stage, the possibility of self-healing in composites cracked after achieving its full mechanical properties, i.e. after 28 days of curing in water or after hydrothermal treatment, i.e. after low-pressure steaming or autoclaving, was investigated. The general test scheme is shown in the diagram (Fig. 2b).

2.2 Materials and concrete mix composition

The investigated composite included the following components: CEM I 52.5 R Portland cement, which basic properties and both chemical and phase compositions are presented in Table 1; silica fume characterized by a specific surface (BET) of 22.4 m²/g, density of 2.23 g/cm³ and LOI = 0.74% wt.; quartz flour 0 / 0.2 mm and quartz sand 0 / 0.5 mm with LOI 0.25 and 0.15% wt. respectively, both are characterized by high purity (SiO₂ > 98.5% wt.) and polycarboxylate superplasticiser. Component proportions were determined in such a manner as to obtain the appropriate consistency of the concrete mix as well as to ensure that the hardened material is as compacted as possible and exhibits minimum porosity and maximum strength as a result. The method for designing the composition of the material is described in detail in (Zdeb 2009, 2013). It is mainly based on packing dry composite components as densely as possible. To this end, the optimal grain size distribution curve proposed by (Funk and Dinger 1994) was used:

$$y_i = \left(\frac{D_i^n - D_{\min}^n}{D_{\max}^n - D_i^n} \right) \cdot 100\% \quad (1)$$

Fig. 1 Shrinkage-induced cohesive micro-crack in the material structure.

Table 1 Basic properties and chemical and phase composition of the cement CEM I 52.5 R.

Physical properties	
Initial setting time [min]	130
Final setting time [min]	220
Specific surface (Blaine) [cm ² /g]	4100
Compressive strength (2 days) [MPa]	34.5
Compressive strength (2 days) [MPa]	34.5
Compressive strength (28 days) [MPa]	70.8
Chemical composition [% wt.]	
CaO – 65.6; SiO ₂ – 23.0; Al ₂ O ₃ – 4.4; Fe ₂ O ₃ – 2.1; SO ₃ – 3.3; MgO – 1.0; Na ₂ O _e – 0.5; Cl ⁻ – 0.009; LOI – 1.4	
Phase composition [% wt.]	
C ₃ S – 59.1; C ₂ S – 18.0; C ₃ A – 8.1; C ₄ AF – 6.4	

where:

y_i – cumulative % of the i -th fraction

D_i – diameter of the i -th fraction [μm]

D_{max} – diameter of the maximum grain [μm]

D_{min} – diameter of the minimum grain [μm]

n – a constant equal to 0.37

Knowing the grain size distribution of the components which constitute the micro-aggregate of the composite, on the basis of relationship (1) it is possible to determine their proportions so as to maximise the pack-

ing density of the material. Additionally, this relatively simple analysis makes it possible to detect any excesses or deficiencies with respect to individual micro-aggregate fractions. In this particular case, the proportion of ground quartz to quartz sand to be used was determined at 30/70. The volumetric proportion of binder to micro-aggregate and the proportion of silica fume mass to cement mass were determined on the basis of experience, with the main characteristics diagnosed were mechanical ones, i.e. flexural and compression

Fig. 2 Scheme for testing the self-healing effect in composites cured in different hydrothermal conditions: a) stage I; b) stage II.

Table 2 Mix composition of the composite. [kg/m³]

Portland cement CEM I 52.5R	903
Silica fume	181
Quartz flour 0/0.20 mm	312
Sand 0/0.50 mm	729
Water	217
Superplasticizer	19
w/b	0.20

strengths. The proportions obtained were $V_{\text{binder}} / V_{\text{aggregate}} = 60 / 40$, while the optimal amount of silica fume in relation to cement mass was 20%. The material obtained in this way, reinforced with steel fibers in the amount of 2% by volume was characterized by compressive strength about 210 MPa after 28 days of setting in water, 220 MPa subjected to steaming at $T_{\text{max}} = 90^{\circ}\text{C}$ and 300 MPa after autoclaving at $T_{\text{max}} = 250^{\circ}\text{C}$. The quantitative composition of the tested material calculated for 1 m³ is presented in **Table 2**.

2.3 Detailed research programme

The mixing of concrete components took place according to the following procedure: pre-mixing of dry components for 1.5 minutes; adding 75% of the assumed amount of water with the superplasticiser; further mixing for 1.5 minutes; 2-minute break in mixing to ensure proper contact between dry components and water; adding the remaining water and mixing for 3 minutes.

The amount of superplasticiser was adjusted so that the flow diameter of the mix measured by means of a flow table according to EN 1015-3 was around 25 cm. Immediately after the mixing process had been completed, series of 3 specimens of 40 x 40 x 160 mm each were moulded and then stored in the chamber with RH = 98% for 24 hours. Such conditions limited the evaporation of water.

In the first stage of testing, after a 24-hour initial curing period, a 1 mm wide and 20 mm high notch was introduced in the centre of the specimens span, and then were subjected to a 3-point bending test during which the load-deflection relationship was recorded up to 200 μm .

In order to enable the healing process and prevent further destruction of the newly created surface, samples were immediately installed on a stand and tightened

with a torque wrench, using a constant load of 100 N. Under these conditions, the width of the crack at the cross-section, as measured by an optical microscope, ranged from 35 to 50 μm . The average crack width was 42 μm with a standard deviation of 5.8 μm and a coefficient of variation of 14%. The stand allowed the sample to be stored in water in the steaming chamber as well as in an autoclave.

Subsequently, the specimens were cured under three different sets of conditions:

- natural curing in water at 20°C for 28 and 90 days;
- accelerated curing in the form of low-pressure steaming during an 18-hour cycle (raising the temperature to 90°C – 3 hours, isothermal heating at 90°C – 12 hours, cooling to 20°C – 3 hours) in saturated steam;
- curing under autoclaving conditions during a 36-hour cycle (raising the temperature to 250°C – 12 hours, isothermal heating at 250°C and at a pressure of 3.9 MPa – 12 hours, cooling to 20°C – 12 hours) in saturated steam.

Hydrothermal treatment parameters were selected and justified on the basis of the author's research (Zdeb 2016). Generally, the conclusion of that research is that the effectiveness of these technological treatments with respect to the mechanical properties of UHPC composites increases with temperature both in the case of steaming and autoclaving. Changes in temperature as a function of time during steaming and autoclaving are shown in **Fig. 3**. After completion of the hydrothermal treatment processes, the specimens were stored in water until the 28 and 90 day of curing according to the scheme presented in **Fig. 2a**.

In the second stage of testing, on the basis of new concrete samples, self-healing tendencies of matured materials were determined. Therefore the composites were preloaded after 28 days of curing in water or after steaming or autoclaving. In both types of hydrothermal treatment initial setting time, before the temperature raise, lasted 24 hours. The other parameters i.e. raising the temperature, isothermal heating and cooling proceeded in the same manner as described above (see **Fig. 3**). The preload was initiated immediately after the aforementioned treatments and subsequently the specimens were immersed in water at 20°C for a subsequent

Fig. 3 Curing regimes of a) low-pressure steaming at $T_{\text{max}} = 90^{\circ}\text{C}$; b) autoclaving at $T_{\text{max}} = 250^{\circ}\text{C}$

28 and 90 days. A scheme of material treatment in the second stage of testing is presented in **Fig. 2b**.

Regardless of the testing stage, after the pre-determined curing period, the specimens were subjected to 3-point bending according to the RILEM TC 187 procedure (Planas 2007) using the Zwick/Roell Z100 strength testing machine. This apparatus was equipped with articulated supports and an extensometer that can measure beam deflection to 0.1 μm and allows for testing to be carried out with a continuous increase in deflection of 0.01 mm/min. According to the procedure described, counterweights were installed at the ends of prismatic specimens to offset the force of gravity, which affects the load-deflection relationship during crack propagation (see **Fig. 4**).

On the basis of measurements of 3 samples each time, flexural strength f_f was calculated, taking into account the height of the notch. The total fracture energy G_f was calculated by integrating the load-deflection curve within the 0 – 200 μm deflection range and applying the result to the newly formed surface (sum of the pre and post-cracking energy). The comparison of strength testing and fracture energy results in the initial material during the initiation of the crack and after the crack self-healing process enabled a quantitative evaluation of the effectiveness of this phenomenon.

In addition, in order to determine the potential possibility of reaction between the cracked material and water, the degree of binder hydration was determined. Thermogravimetric analysis (TG-DTA) described in (Chen *et al.* 2014; Monteagudo *et al.* 2014) was used, which consists in determining the amount of non-evaporable water at a temperature range of 105 – 1050°C. The hydration level α was determined using the following relationships:

$$\alpha = \left[\frac{W_B(t) \cdot m_{\text{tot}}}{m_{\text{bind}} \cdot W_B(\infty)} \right] \cdot 100 \quad (2)$$

$$W_B = (Ldh + Ldx + 0.41 \cdot Ldc) - \left(\sum_{i=1}^n LOI_i \cdot \frac{m_i}{m'_{\text{tot}}} \right) \quad (3)$$

Fig. 4 The stand for 3-point bending of notched prisms with fastened counterweights.

where:

α – binder hydration degree [%]

$W_B(t)$ – the amount of chemically bound water in composite after time t [%]

$W_B(\infty)$ – the amount of chemically bound water in binder after hydration has been completed [%]

m_{bind} – binder mass in composite (cement + silica fume) [g]

m_{tot} – sum of masses of all composite components [g]

m'_{tot} – sum of masses of all dry composite components [g]

Ldh – relative mass losses as a result of dehydration [%]

Ldx – relative mass losses as a result of dehydroxylation [%]

Ldc – relative mass losses as a result of decarbonation [%]

LOI_i – loss of ignition of the i -th component of the composite [%]

m_i – mass of the i -th dry component of the composite [g]

n – number of dry composite components = 4 (cement, silica fume, ground quartz, sand)

TG-DTA measurements were made using the NETZSCH STA 449 F3 Jupiter, equipped with mass spectrometer QMS 403 Aeolos, which enabled the analysis of evolved gases. In this case, test samples were collected from the entire volume of the material. Other observations were made using the Zeiss EVO10 M scanning microscope equipped with an EDS detector and the Zeiss SteREO Discovery V20 optical microscope. In order to confirm the phase composition of products precipitated within the crack during autoclaving, XRD tests were performed using the X'Pert PRO diffractometer. The test specimen was prepared by mechanically removing the deposit from the healed surface after testing mechanical properties.

3. Results and discussion

3.1 Autogenous self-healing – mechanical properties

(1) Effects of self-healing in composites preloaded at early curing stage

As indicated in the diagram (**Fig. 2a**), in the first stage of the research, the self-healing effect was tested directly after the hydrothermal treatments conducted and after additional 28 and 90 days of the specimen having been immersed in water. In order to verify the composites self-healing effect each time three specimens were tested and compared to those recorded at the time when the crack had been initiated, i.e. after 24 hours of curing. In addition, tests of not preloaded, reference materials, cured under the same conditions and the same time, were made. The average values of mechanical properties of all healed specimens and reference ones are presented in **Table 3**.

On the basis of the load-deflection relationship (**Figs.**

Table 3 Mechanical properties of self-healed crack in RPC subjected to different curing regimes and mechanical properties of reference specimens.

Self-healing conditions	Feature	Preload after 24 h in mould	Reference load just after heat treatment	Reload just after heat treatment	Reference load 28 days	Reload 28 days	Reference load 90 days	Reload 90 days
Water $T_{\max}=20^{\circ}\text{C}$	f_r [MPa]	4.3	-	-	9.6	1.9	14.5	3.1
	G_f [J/m ²]	28.0	-	-	65.9	11.2	117.6	15.9
Steaming $T_{\max}=90^{\circ}\text{C}$	f_r [MPa]	4.3	9.5	0.3	10.7	0.5	12.9	1.1
	G_f [J/m ²]	28.0	81.3	4.1	82.8	4.3	248.0	9.9
Autoclaving $T_{\max}=250^{\circ}\text{C}$	f_r [MPa]	4.3	8.4	2.6	9.7	3.1	10.8	4.7
	G_f [J/m ²]	28.0	66.5	12.6	114.9	14.0	117.7	25.1

5a–7a), the flexural tensile strength and the total fracture energy were determined. **Figures 5b–7b** show the average as well as minimum and maximum values of the analysed parameters. On the basis of the results obtained, it may be concluded that the mechanical properties of the composites healed in water have clearly been recovered. After 28 days, the degree of strength recovery compared to the initial strength was 44%, and after 90 days it was as high as 72%. Relationships between the initial total fracture energy and fracture energy after the self-healing process are similar. After 28 days of curing, this energy amounted to 40%, and after 90 days was around 60% of the initial value. Load-deflection graphs also indicate that the junction formed in the healed crack also results in a reduction in the deformability of the element subjected to bending. On the one hand, this can be ascribed to the lower rigidity of young material (24 hours). On the other hand, however, as (Huang *et al.* 2013) claim, the main components which crystallise in the crack during the self-healing of cement paste at ambient temperature are portlandite, CaCO_3 and the C-S-H phase. According to studies (Fu *et al.* 2018; Lee *et al.* 2016), the elastic modulus tested using the nano-indentation method for the HD-C-S-H phase is around 33 GPa, that of $\text{Ca}(\text{OH})_2$ around 40 GPa, and for calcite it is 60 GPa. Thus, the slow recrystallisation of CaCO_3 as a result of a reaction with CO_2 dissolved in water may be associated with an increase in the stiffness of the crack which is subject to healing in water. This effect is more pronounced after 90 days of curing. With respect to the reference samples aged in the same conditions and the same period the self-healing effect it is obviously smaller. However, there is an interesting ongoing tendency between the increase in the strength of cracked and uncracked samples in the period from the 28th to the 90th day of natural hydration. The flexural strength and total fracture energy of the preloaded specimens remain constant at 20% and 15% respectively, compared to the one characterized by a continuous structure.

The effect of low-pressure steaming on the self-healing effect has been found to be considerably less compared to that observed for immersion in water. Immediately after the steaming process, the recovery of flexural tensile strength only amounted to 0.3 MPa,

which represents 7% of the strength reached during preload i.e. after 24-hour hydration. Additional curing for 28 and 90 days in water resulted in a slight further increase in strength of 0.5 and 1.1 MPa, respectively, which represented 12% and 26% of the initial strength. As stated in (Kurdowski 2014), the increase in temperature may increase the tendency of the hydrated calcium silicates to crystallise, which in turn results in a reduction of the specific surface area of the C-S-H gel in relation to one precipitated under natural conditions. Moreover, according to (Kurdowski 2014), where the resulting C-S-H phase is treated with steam at an elevated temperature, this causes a decrease in the content of H_2O bound within it. This is also confirmed by research results (Maruyama *et al.* 2014a, 2014b), where the authors describe changes in C-S-H phase morphology at elevated temperatures. Under such conditions, the agglomeration of C-S-H globules may occur, and the C-S-H interlayer space may be reduced or even destroyed. As a result, the adhesion of hydration products to the inert, opposite surface is reduced. Additionally, the acceleration in cement hydration through steaming results in the rapid formation of a watertight layer of hydration products, mainly C-S-H phase and CH (Huang *et al.* 2013), on the surface of the clinker grains, which limits the transport of water particles, and thus also the beneficial effect of self-healing. The changes described correspond to observations of the microstructure of the fracture surface subjected to healing after being exposed to low pressure steaming (see **Fig. 11**). The hydration products visible exhibit a clearly more crystalline morphology compared to those produced under immersion in water. Additionally, these products cover the entire healed surface so tightly that it is not possible to observe any exposed grains of clinker which are the potential for the composite autogenous healing. In addition to the low values of maximum stress recorded after steaming, the junction formed in the healed crack exhibited a slightly higher deformability compared to the one resulting from immersion in water. Hence the proportions between total fracture energy and flexural strength in comparison to material healed in water are imbalanced. In comparison to the reference samples cured in the same conditions and the same time, the self-healing effect becomes practically negligible. It varies from 3 to

9% depending on the period of further hydration. However, a slight tendency to increase the proportion of flexural strength with time of the healed composite and having a continuous structure can be observed. Total fracture energy remained on the constant level of about 5% in comparison to reference samples regardless of the curing period.

The process that had the most beneficial effect on recovery the mechanical properties of the composite was autoclaving. Immediately after the autoclaving process, the recovery of flexural tensile strength amounted to 2.6 MPa, which represents 60% of the initial strength. In a development that is difficult to explain, a further significant increase in flexural strength was observed between

28 and 90 days of additional immersion in water despite the use of high-pressure thermal treatment. After 28 days, it was 3.1 MPa, i.e. 72% of the initial value, and after 90 days it was 4.7 MPa, i.e. the strength had not only been restored but actually increased (to 110%). In this case, the total fracture energy was close to the reference value, but the joint formed as a result of autoclaving was characterised by the highest stiffness. Total fracture energy values of materials subjected to self-healing under autoclaving conditions were proportional to the flexural tensile strength values obtained. It should also be added that taking into account the same method and hydration period of the composite, recovery of flexural strength is observed at the level of 30 to 45%, also,

Fig. 5 Self-healing effect as a result of immersion in water for 28 and 90 days: a) load-deflection relationship; b) flexural strength and total fracture energy.

Fig. 6 Self-healing effect as a result of low-pressure steaming at 90°C and subsequent immersion in water for 28 and 90 days: a) load-deflection relationship; b) flexural strength and total fracture energy.

Fig. 7 Self-healing effect as a result of autoclaving at 250°C and subsequent immersion in water for 28 and 90 days: a) load-deflection relationship; b) flexural tensile strength and total fracture energy.

Table 4 Traces of mechanical properties of self-healed crack in matured RPC cured in water and mechanical properties of reference specimens.

Self-healing conditions	Feature	Preload after 28 days in water	Reload after additional 28 days	Reference load 90 days	Reload after additional 90 days
Water $T_{\max}=20^{\circ}\text{C}$	f_r [MPa]	9.6	0.09	14.5	0.12
	G_f [J/m ²]	65.9	0.2	117.6	0.3

Table 5 Binder hydration degree.

Time/manner of RPC curing	α [%]
24 hours/Water at 20°C	23
48 hours/Steaming at 90°C	36
72 hours/Autoclaving at 250°C	49
28 days/Water at 20°C	38
28 days/Steaming at 90 (48 h) + Water at 20°C (26 days)	37
28 days/Autoclaving at 250 (72 h) + Water at 20°C (25 days)	49

as in the case of steaming, with an upward tendency over a longer 90-day period of time.

This valuable healing under autoclaving conditions can be attributed to fibrous xonotlite and tobermorite microcrystals, which were observed during the analysis of the microstructure of the composite within the crack. As described in (Zdeb 2016), the length of the resulting whiskers depends on the temperature and pressure achieved during autoclaving. At a temperature of 250°C they can reach lengths of up to $20\text{ }\mu\text{m}$. It can therefore be assumed that a crack of approximately $40\text{ }\mu\text{m}$ in width can be effectively healed by applying the hydro-thermal treatment discussed above.

(2) Self-Healing effects in matured composites

In the second stage of mechanical properties testing the matured materials self-healing abilities were investigated. Preload of the concrete took place either after 28-day hydration in water or just after hydrothermal treatment i.e. steaming or autoclaving. Generally speaking, the observed recovery of mechanical properties in fully cured material is either negligible or even unmeasurable depending on curing conditions. As it can be observed from the results of tests presented in **Table 3**, materials which have not been cracked (preloaded) and were cured in water exhibit the greatest increase in flexural tensile strength over time. This increase is around 50%

between 28 and 90 days. The analogous increases in the case of steaming and autoclaving are only 20% and 10%, respectively. Hence, traces of autogenous healing in cured composites were only observed for materials cured in water. Compared to the reference material (which was cured for 28 days in water), flexural strength after an additional 90 days of healing did not exceed 1%, only amounting to 120 kPa, and total fracture energy was 0.3 J/m^2 . **Figure 8** and **Table 4** show the negligible recovery of mechanical properties of the reference composite and of composites autogenously healed in water for a further 28 and 90 days. In the other cases (materials subjected to steaming and autoclaving before cracking), the recovery of mechanical properties was unmeasurable. In an attempt to explain this phenomenon, an analysis was conducted of the binder hydration degree at characteristic composite curing stages (see **Table 5**).

3.2 Material microstructure in the healed crack

According to Bhatti (1986), in order to determine the cement hydration degree the denominator in relationship (2) should have a constant value of 0.24. The issue of the amount of chemically bound water at full Portland cement hydration has often been discussed and the value ranges from 0.22 to 0.25 (Escalante-Garcia 2003; Kurdowski 2014; Taylor 1997; Wong and Buenfeld

Fig. 8 Self-healing effect in matured composites as a result of immersion in water for 28 and 90 days: a) load-deflection relationship; b) flexural tensile strength and total fracture energy.

2009). Additionally, the presence of additives among other things silica fume and the elevated temperature at which the hydration process takes place also affect the amount of chemically bound water. This is mainly related to the change in the phase composition of hydration products and the change in stoichiometry, mainly of the C-S-H phase. This matter was also examined by Pane and Hansen (2005). On the basis of the mentioned results, the value of the water-binder ratio adopted in order to estimate the degree binder hydration was 0.20.

Taking into account losses on ignition for all components and their mass fractions in the composite (see equation 3), the remaining mass loss in the temperature range examined was attributed to chemically bound water. As demonstrated by thermogravimetric testing together with evolved gas analysis over the entire temperature range, the mass loss is associated exclusively with dehydration of mainly C-S-H phase or dehydroxylation of portlandite traces. EGA tests show (Fig. 9b) that in the case of composites cured in water or subject to steaming within a temperature range from around 450 to 550°C, increased amounts of water evolved. As reported, among others, by (Alarcon-Ruiz *et al.* 2005), portlandite decomposes in this temperature range. The analysis of the TG curve demonstrates that the loss in mass due to dehydroxylation is at the level of 0.4% or below for both sets of curing conditions. This confirms the reduced portlandite content in these composites. It should also be noted that in the case of autoclaved materials, the endothermic peak in the DTA curve which is attributed to the decomposition of portlandite is not present. Additionally, no increased amount of evolved water is observed in the EGA curve for this temperature range. The 20% mass fraction (related to cement weight) of silica fume in tested materials is the main reason of a significant consumption of portlandite. Within the 700 – 900°C temperature range which is attributed to the decomposition of carbonates (Alarcon-Ruiz *et al.* 2005), there is no endothermic peak in the DTA curve (see Fig. 9a). The EGA curve shown in Fig. 9b also confirms the lack of CO₂ release during thermal decomposition. Summing up, the above information unambiguously

confirms that the rate of the carbonation process in the composites discussed is completely negligible irrespective of curing conditions. In other words, the Ldc parameter in equation (3) can be assumed to be zero.

Klimesch and Ray (1997) obtained results similar to those presented in Fig. 9 by subjecting autoclaved cement pastes containing silica to thermogravimetric analysis. Similarly as in the results presented, they observed a small endothermic peak in the DTA curve at 571°C, which was attributed to β -quartz inversion. The additional exothermic peak which appeared at temperatures above 800°C may be associated with β -wollastonite crystallisation (Huang *et al.* 2002; Klimesch and Ray 1997).

As the test results presented in Table 5 demonstrate, the potential for autogenous healing of cracks is related to the degree of binder hydration. It appears obvious that there is a greater chance of cracks in such composites being self-healed and of mechanical properties being recovered to some extent if such cracks appear at early curing stages. According to the results of flexural strength tests conducted, a binder hydration level of up to 20% makes it possible for the cracks formed to be filled to a significant extent with products of the hydration reaction. However, after 28 days of curing in water and also after low-pressure steaming at 90°C or autoclaving at 250°C, the hydration level ranges from around 40% to about 50%. This high level of hydration causes the autogenous healing effect to be negligible from mechanical properties point of view.

It should be noted that the potential for self-healing of the ultra-high performance composites is affected not only by the amount of binder reacted, but also by the tightness of the hydration products that coat relict clinker grains. After the hydrothermal treatment process has been completed, similarly as is the case after 24 hours of curing under normal conditions, the kinetics of the reaction between clinker grains and water is limited by diffusion. However, elevated temperature results in the formation of a tighter hydrate layer around clinker grains, which in turn limits the progress of hydration at later curing stages (Kurdowski 2014). The slightly

Fig. 9 a) thermogravimetric analysis and b) evolved gas analysis of the composites cured in for 28 days and directly after hydrothermal treatment.

lower binder hydration degree in the material cured for 28 days after the prior application of low-pressure steaming ($\alpha = 37\%$) as compared to cement in the material that was only cured in water for the same time ($\alpha = 38\%$) is consistent with the results reported in the literature.

The morphology of the hydrates formed in the healed crack is presented after 28 days of curing in water in **Fig. 10**, after low-pressure steaming and curing in water for

28 days in **Fig. 11** and after autoclaving and storing in water, also for 28 days in **Fig. 12**. The absence of hydrothermal treatment allows the precipitation of the amorphous C-S-H phase on the healed surface, which covers the surface of quartz grains at many places. In addition, it is characterised by numerous cracks whose number could have been further increased by the removal of unbound water molecules in the vacuum present in the SEM microscope chamber. As shown by

Fig. 10 a) SEM image and b) EDS point elemental analysis of the RPC fracture surface healed as a result of being immersed in water for 90 days.

Fig. 11. a) SEM image and b) EDS point elemental analysis of the RPC fracture surface healed as a result of steaming at 90°C and further curing in water to 90 day.

Fig. 12 a) SEM image and b) EDS point elemental analysis of the RPC fracture surface healed as a result of autoclaving at 250°C and further curing in water to 90. day.

the EDS analysis in the healed crack there are also carbon traces confirming that in addition to the precipitation of hydrated calcium silicates, calcium carbonates also crystallize.

On the other hand, low-pressure steaming caused a clear trend towards the formation of hydrated calcium silicates with a finer crystalline structure, but with the greatest number of micro-cracks at the same time. The expected reduced specific surface area of hydration products and their defected microstructure are reflected in mechanical properties. Analogously to self-healing in water, a peak assigned to carbon appears on the EDS diagram, which confirms the presence of carbonate salts in the crack.

In the case where mechanical properties have been recovered most effectively, i.e. through the autoclaving process, even at low magnifications, patches of native material detached from the adjacent surface, with a diameter of ca. 200 – 500 μm , can be observed on the healed surface. Crystallised hydrated calcium silicates are clearly present on the surface as well as under the aforementioned native material patches (see **Fig. 12**). This partially cohesive nature of the destruction demonstrates the very considerable potential of healing cementitious composites under autoclaving conditions.

In order to identify the phases present in the material that fills the crack in the composites healed through autoclaving, the growing crystals were mechanically removed and subjected to XRD analysis. As shown in the X-ray pattern (see **Fig. 13**), the whiskers appearing under autoclaving conditions i.e. at temperature 250°C and pressure 3.9 MPa in the presence of 20% of silica fume are tobermorite and xonotlite.

4. Summary and conclusions

Discussed ultra-high performance composites exhibit a

clear crack healing capability, which is assisted by all three sets of curing conditions analysed. However, in order to appear this effect with respect to the mechanical properties, the crack must emerge at the appropriate time, before binder hydration degree exceeds 20%.

The amorphous gel of the C-S-H phase as well as the carbonate salts produced during the immersion of the specimen in water for 28 and 90 days inside the crack initiated after 24 hours of curing will cause the crack to be healed to a significant degree, resulting in flexural tensile strengths of 1.9 and 3.1 MPa, respectively.

When the crack was initiated at the early material hardening stage, i.e. after 24 hours, the lowest degree of mechanical property recovery was achieved through low-pressure steaming. A relatively low flexural strength value of 0.3 MPa was recorded immediately after treatment. Further 28-day and 90-day hydration in water caused only slight changes in mechanical properties. The flexural strength increased from 0.5 to 1.1 MPa and total fracture energy from 4.3 to 9.9 J/m².

As the XRD analysis demonstrated, autoclaving process conducted at 250°C resulted in the crystallisation of xonotlite and tobermorite whiskers within the crack. This type of healing of the previously cracked material was the most effective. Tests of mechanical properties carried out immediately after the hydrothermal treatment demonstrated a recovery of mechanical properties, i.e. flexural strength, of 60% (amounting to 2.6 MPa), while after additional storage in water for 90 days, flexural strength exceeded the initial value by 10%, reaching a level of almost 5 MPa.

Matured materials i.e. subjected to 28-day curing in water or to low pressure steaming or to autoclaving process, exhibits a significant degree of binder hydration (around 40%). For this reason shows negligible self-healing effect from the mechanical properties point of view.

Fig. 13 X-ray pattern of the crystalline form of hydrated calcium silicates sampled from the material filling the crack in composite healed through autoclaving.

Acknowledgements

The results and paper preparation were supported by the funds of Cracow University of Technology within the framework of the L1/87/2018/DS research project. This study was carried out under the authority of the Testing Laboratory For Building Materials and Structures of Cracow University of Technology. Jacek Śliwiński is gratefully acknowledged for his support in this paper preparation. Also support by Teresa Stryszewska and Mariusz Wiecheć was highly appreciated.

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