Research on the production of cement composites with autonomous self-healing performance

Tudor Panfil Toader[1,2*], *Călin G.R.*Mircea[2], *Andreea* Hegyi[1], *Brăduț Alexandru* Ionescu[2], *Anamaria* Boca[2] *and Oana* Ciascaiu[2]

[1]NIRD URBAN-INCERC, Cluj-Napoca Branch, 400524 Calea Florești 117, Cluj-Napoca, Romania
[2]Technical University of Cluj-Napoca, Civil Engineering Faculty, 400020 Daicoviciu 15, Cluj-Napoca, Romania

Abstract. In a time when the attention paid to identifying the possibilities of reducing problems due to urban pollution is increasing, the construction industry has a lot to gain if it aligns itself with the new trends of sustainable development in the field. In this context, the objective of obtaining a concrete with self-healing properties of cracks is more than appropriate, becoming a sustainable alternative for reducing the maintenance costs of transport infrastructure by increasing their operating time and by decreasing the need for the volume of repair and maintenance works, thus indirectly contributing to the reduction of environmental pollution. Preliminary results obtained using a cementitious composite with waterproofing admixture content by mass crystallization are encouraging by identifying the existence of an autonomous healing degree (closure of cracks with average opening 20-40 μm) in a proportion of at least 65% after only 96 hours of exposure in a wet-dry environment, respectively and of at least 96% after 480 hours of conditioning. The degree of novelty and value of this research is mainly due to the approach of this type of composite produced by adapting the general principles to local raw materials, including the use of specific industrial waste and by-products available in Romania (fly ash and limestone slurry).

1 Introduction

Reinforced/prestressed concrete is a material prone to cracking, therefore under the action of external aggressive agents. access ways to the reinforcement are created through the cracks. The reaction between aggressive agents in the atmosphere (rain, snow, fog) and reinforcement, leads to the oxidation of the reinforcement, which can later lead to early loss (partial or total) of its load-bearing capacity. Intervention to deal with and close cracks and micro-cracks is necessary, otherwise failure of the structure can occur [1-5].

For conception of classical concrete elements, the amount of 20-30% of cement used in its preparation remains unhydrated. When cracks appear in the concrete elements and they encounter water, the hydration reaction of the unhydrated cement particles is initiated, through which the cracks close partially or completely. This mechanism of closing the cracks is known as autogenous self-healing [6].

In the literature there are concretes with different characteristics from the classical ones, namely concretes with different self-healing mechanisms [7]. Depending on the mechanisms of self-healing of the concrete, represented schematically in Fig.2.1. these concretes are classified as:

- concrete with autogenous self-healing (intrinsic mechanism) which does not require the use of other additives in the cement matrix and is produced due to the subsequent hydration reaction of cement particles left unhydrated from the concrete mass or calcium carbonate precipitation (CaCO3) [8];

- concrete with autonomous self-healing (extrinsic mechanism). The self-healing mechanism is produced because of chemical reactions of a self-healing agent embedded directly, embedded in capsules or introduced through vascular networks when designing and making the concrete mixture. Among the most used systems are superabsorbent polymers [9], [10], crystalline mixtures [11], [12], microencapsulated sodium silicate [13], tubes with adhesives [14-16] and bacteria [17-20].

The autonomous self-healing mechanism of concrete is achieved by modifying the autogenous self-healing mechanism by incorporating in the composition of the cement matrix other materials such as microorganisms, fly ash, polyvinyl alcohol (PVA), fibres, silica dust or even by using chemical reactions to fill cracks such as calcium-sulphate-aluminate reaction, [21 - 23].

The capacity of the self-healing mechanism can be improved by adding some mineralizing waterproofing additives (ICW)to the composition of the concrete that react in the presence of water and generate thin crystals capable of filling pores, capillaries, and micro-cracks [12], [24].

* Corresponding author: tudor.toader@incerc-cluj.ro

2 Experimental method – materials and methods

To make self-healing concrete the most important step is the determination of the raw materials. The raw materials used in this paper are of local origin, in order to study the possibility of producing this type of composite material in Romania. In the second part of this paper, the determinations made on the raw materials will be presented in order to find both the type and the optimal quantity to obtain the physical-mechanical properties and the self-healing properties of the concrete.

2.1 Materials

For the design and production of micro concrete compositions with self-healing properties, the following component materials were used:

1) Portland Cement type cement EN 197-1 - CEM I 42.5 R, produced at Aleşd cement factory, in Bihor county (density 1,07 g/cm^3);
2) ash from the thermal power plant from Mintia commune, Hunedoara county, resulting from the burning of coal to obtain electricity (density 0,89 g/cm^3);
3) standardized polygranular sand according to EN 196-1;
4) marble slurry, resulting from the cutting of marble rock - source from Cluj-Napoca (density 1,19 g/cm^3);
5) Master Glenium 51 superplasticizer;
6) MasterLife WP 1000 integral crystallization waterproofing;
7) PVA type fibers, L = 8 mm (density 1,3 g/cm^3);
8) Water.

2.1.1 Cement

Produced at the Aleşd cement factory, Bihor county, with the essential characteristics specified in Table 1.

2.1.2 Aggregates - Standardized sand

Originally from Germany, for which the granularity was determined and the granulometric analysis was performed by sieving.

2.1.3 Fly ashes

The important feature of power plant ash is the pozzolanic activity and it is used in concrete as a substitute for cement to improve the workability of the material and for economic reasons (the fly ash being considered as waste in the power generation industry). Studies have shown that industrial by-products can be used successfully for the partial replacement of cement in concrete, but also as a raw material in the chemical activation for the production of innovative materials [25-28].

Table 1. Characteristics of Portland cement – CEM I 42,5 R.

Characteristics	Units	Declared Performance
Initial setting time	min	min.60
Stability (expansion)	mm	max.3
Compressive strength: initial	MPa	min.24
Compressive strength: standard	MPa	min.46
Sulfate content (as SO_3)	%	max.4
Chloride content	%	max.0.1

2.2 Methods

After mixing the fresh mortar samples were obtained with mold dimensions 40 x 40 x 160 mm using plastic foil to cover the molds, stored in a climatic chamber at a relative humidity of 90% (RH) and a temperature of (20±2) ºC. The samples were removed from the molds after 24 h, and cured for 28 days in water under room conditions (RH = 50%, 20±2ºC). The samples were pre-loaded up to 90% of the mean flexural strength and subjected to preliminary three-point bending tests The samples were tested after 28 days.

With a Leica microscope (DMC2900) the width of the micro-cracks was measured after 1 day, 4 days, 8 days, 14 days, 20 days, 16 h immersed in water and 8 h exposed in dry, in room conditions (RH = 50%, 20±2ºC).

Time-dependent self-sealing parameters are discussed with regard to the raw segment data and to individual micro- cracks:

- the closure of the crack considers the decrease in the average crack width at day t of conditioning, related to the initial moment after preloading

$$\text{Crack closure } [\%] = \frac{w_{av}(0) - w_{av}(t)}{w_{av}(0)} \times 100 \tag{1}$$

- the average crack width was determined w^i_{av}, on the crack segments:

$$w^i_{aw} = \frac{A^i_{cr}}{l^i_{cr}} \tag{2}$$

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$$w_{av} = \frac{\sum_i A^i_{cr}}{\sum_i l^i_{cr}} \quad (3)$$

A^i_{cr} is the area of the crack segment i;

l^i_{cr} is the midline crack segment

3 Results and discussions

The research methodology consisted of the following steps: compositional design (according to Table 1) of mixture T0 (control mixture) and T1.

The results obtained regarding the flexural strength of the mixtures are presented in Table 2.

Table 2 Mix design ratio of mixture T_0 and T_1

Mixture	Density (kg/m^3)	Flexural Strength (MPa)	Mean flexural strength (MPa)
T_0	1919	15.8/16.2/15.4	15.8
T_1	1926	16.5/16.4/16.2	16.4

Mixture T0

- The maximum initial crack opening is in the range (0.114 - 0.029) mm and decreases with the conditioning period, Fig. 1.

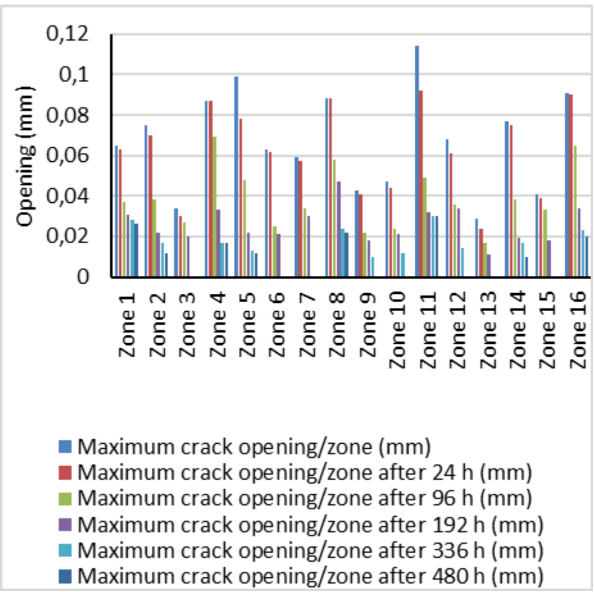


Fig. 1. Maximum initial opening of cracks for mixture T0.

- The average initial opening of the cracks falls within the range (0.019 - 0.0944) mm and decreases with the conditioning period, Fig. 2.

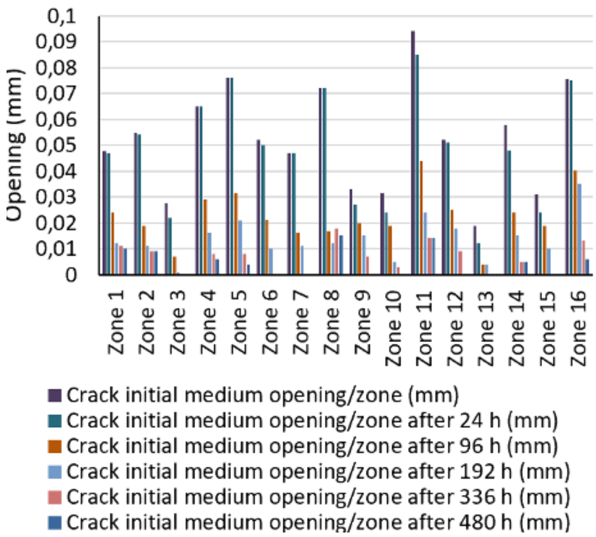


Fig. 2. Crack initial medium opening of cracks for mixture T0.

- The degree of healing of the maximum crack opening, represented in figure 3, increases as the conditioning period passes, reaching 100%, after 336 h in the case of zones 3, 6, 7, 13, 15, respectively after 480 h in the case of zones 9, 10, 12, the following cracks remain completely unclosed (Table 3):

Table 3 Cracks remained unclosed after exposure to self-healing cycles

Zone	Opening (mm)
1	0,0478
2	0,0547
4	0,065
5	0,0764
8	0,0721
11	0,0944
14	0,058
16	0,0755

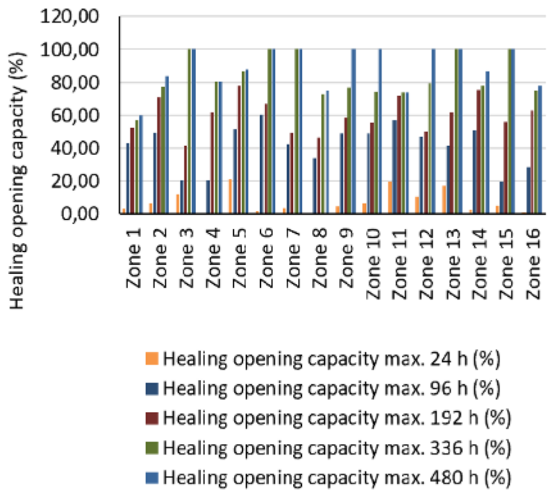


Fig. 3. Healing opening capacity of cracks for mixture T0.

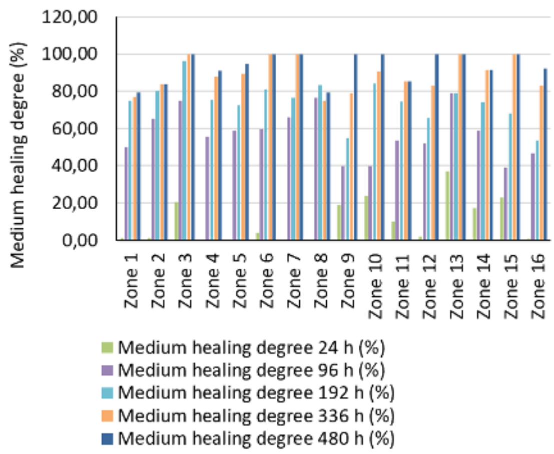


Fig. 4. Medium healing degree for mixture T0.

- The degree of healing of the maximum crack opening, represented in figure 3, increases as the conditioning period passes, reaching 100%, after 336 h in the case of zones 3, 6, 7, 13, 15, respectively after 480 h. In the case of zones 9, 10, 12, the following cracks remain completely unclosed (Table 4):

Table 4 Cracks remained unclosed after exposure to self-healing cycles

Zone	Opening (mm)
1	0,065
2	0,078
4	0,087
5	0,099
8	0,088
11	0,114
14	0,077
16	0,091

Mixture T1

- The initial maximum crack opening falls in the range (0.027 - 0.060) mm and decreases as the conditioning period progresses, Fig. 5.

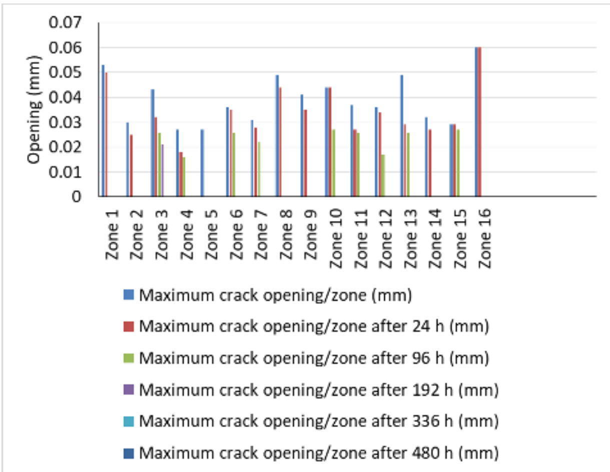


Fig. 5. Maximum initial opening of cracks for mixture T1.

- The average initial crack opening falls in the range (0.019 - 0.051) mm and decreases as the conditioning period progresses, **Fig. 6.**

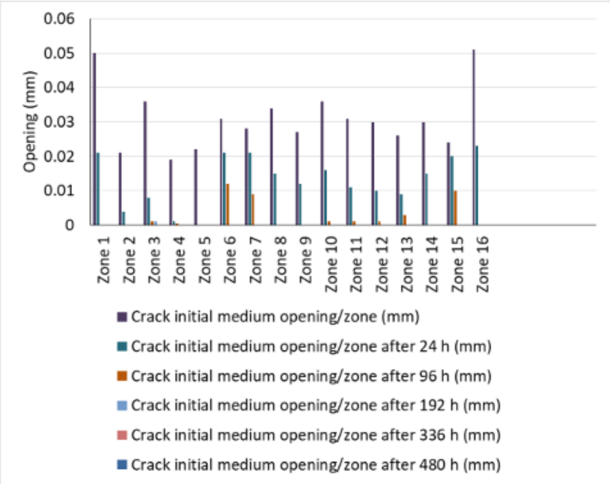


Fig. 6. Crack initial medium opening of cracks for mixture T1.

The degree of healing of the maximum crack opening, shown in Figure 7, increases as the conditioning period progresses, reaching 100% after 24 h for zone 5, after 96 h for zones 1, 2, 8, 9, 14 and 16, after 192 h for zones 4, 6, 7, 10, 11, 12, 13 and 15, after 336 h for zone 3.

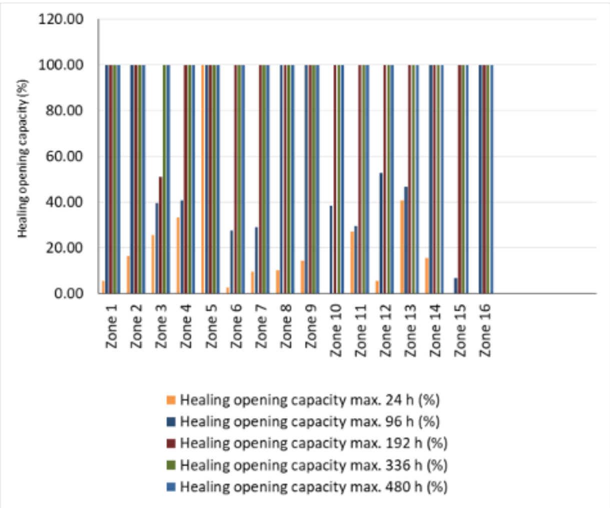


Fig. 7. Healing opening capacity of cracks for mixture T1.

- The average degree of healing of the identified cracks, shown in Figure 8, increases as the conditioning period progresses, reaching 100% after 24 h for zone 5, after 96 h for zones 1, 2, 8, 9, 14 and 16, after 192 h for zones 4, 6, 7, 10, 11, 12, 13 and 15, after 336 h for zone 3.

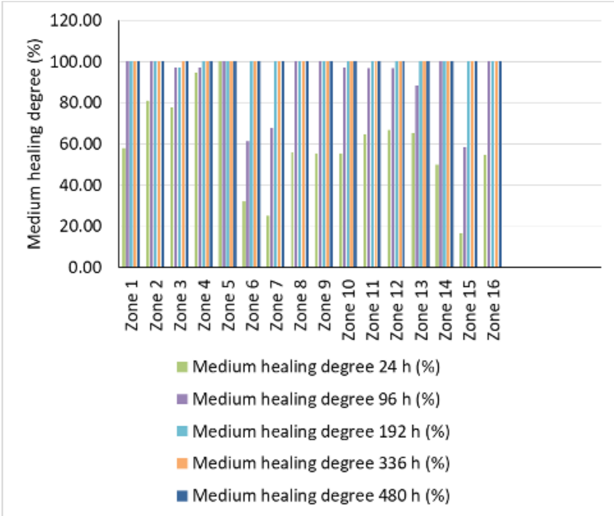
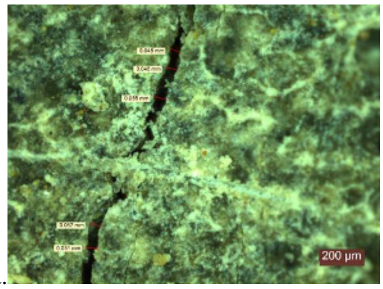
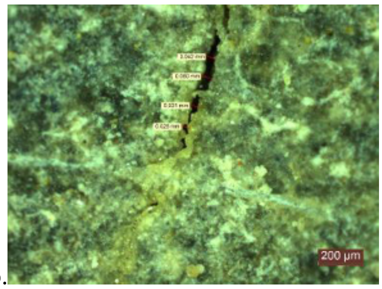


Fig. 8. Medium healing degree for mixture T1.

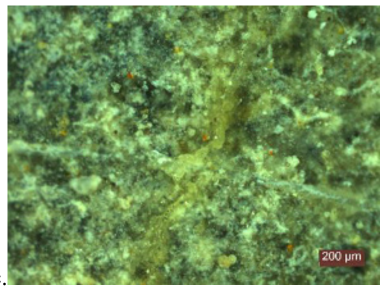
Fig. 9. shows the Self-healing T1 composition images with 3% addition of ICW



a.



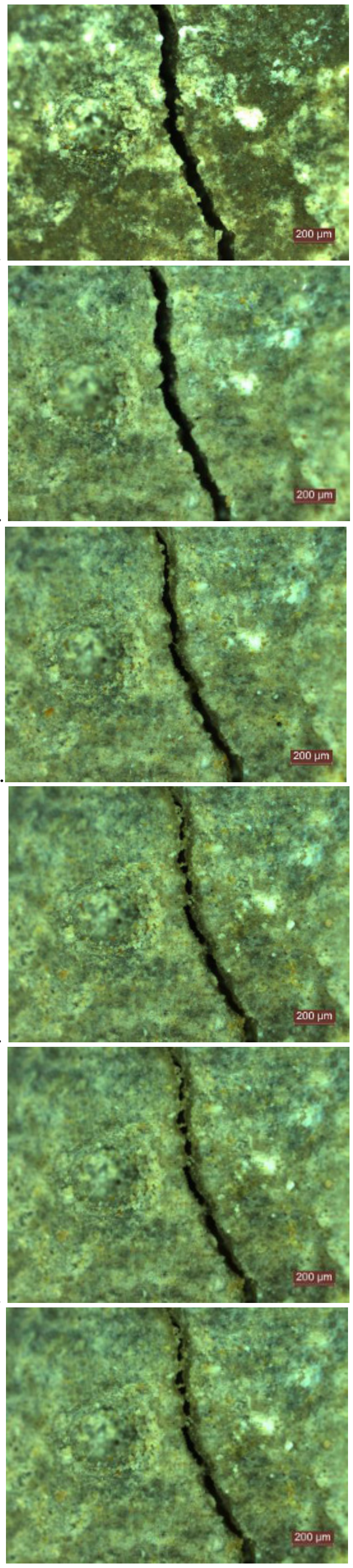
b.



c.

Fig.9. Evolution of the self-healing phenomenon for the composition T1 (Detail 1): a) induced crack appearance; b) crack appearance after 24 h conditioning for self-healing; c) crack appearance after 96 h conditioning for self-healing

Fig. 10 shows the Self-healing image of the control composition T0



a. b. c. d. e. f.

Fig.10 The evolution of the self-healing phenomenon for the composition of T0 (control sample) (Detail 1): a) induced crack appearance; b) crack appearance after 24 h self-healing conditioning ; c) crack appearance after 96 h conditioning; d) after 192 h conditioning; e) after 336 h conditioning; f) after 480 h conditioning.

4 Conclusions

The experimental study has shown that with an ICW content of 3%, the best crack closure ability is achieved. The analysed mixtures, with crack widths between 0,016 mm–0139 mm, showed a significant self- healing ability at early ages up to a month.

The autonomous self-sealing potential at early-age, proven by cementitious composites mortars, with a maximum grain size below 2 mm, is clearly shown and leads the way for using larger aggregates with self-sealing / self-healing abilities, that can achieve superior mechanical performance in time.

Results obtained on the cementitious composite samples using integral waterproofing admixture by mass crystallization showed the effectiveness of using this type of admixture in producing the self-healing effect of the cementitious composites and speeding the process, thus obtaining very good results.

This work contributes to the increase of knowledge in the field of cement materials with self-healing capacity, indicating a possibility of obtaining this effect using a waterproofing additive by mass crystallization, simultaneously with the presentation of the possibilities of use of industrial waste such as fly ash and lime-stone slurry.

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