Development of Cement-Based Materials Enriched with Polymeric Coated Reactive Grains as Long-Term Promoter of Matrix Continuous Hydration

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Abstract. The continuing hydration of unhydrated cement grains was proven to be one of the most important processes for promoting the self-healing effect within cementitious composites, by generating the CSH gels as valuable healing products, not only sealing the microcracks but also being able to provide some mechanical recovery of the material, as well [1]. It was also concluded that the process slows down in time, being strongly connected to concrete age. In order to ensure the continuous hydration potential for the cementitious materials, also as essential self-healing (SH) promoter, the addition of reactive grains is considered. This paper presents preliminary aspects regarding the possibility of polymeric encapsulation of some reactive grains and the feasibility of the concept in terms of matrix compatibility to the addition and also their SH performance under induced, controlled cracking. The considered self-healing addition behaves intelligent as it would react with water only when the cracking occurs, creating gaps in the waterproofing coating. The object of this research is less focused on regaining the mechanical characteristics of concrete, like pre-cracking strength, but mainly on preventing aggressive agents from entering in the concrete mass and aggressing the reinforcement.

1. Introduction
The concept of Self-Healing (SH) of cementitious materials is fundamentally connected to the state of cracking - micro-cracking in the structure of the material, as a form of induction of degradation in the mass of the material. The Self-Healing effect materializes by closing the cracks, sealing them, partially or totally. Most of the time the initiated recovery is not only at the physical level, connected to the microstructure of the material, but also to its functionality, recovery of the initial mechanical characteristics [2].

The Self-Healing of cementitious materials represents a research direction gaining consistent attention among worldwide research groups and also the construction industry, taking into consideration the substantial potential for ensuring, via prevention and intelligent materials design, the durability of infrastructure and considerable reduction of repair and maintenance activities, and consequently the costs savings [3].

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Autogenous self-healing processes (SH) in concrete have been noticed since ancient times; also, their efficiency in closing micro-cracks and consequently in preventing the damage of cementitious composites microstructure and preserving their durability was considered to bring effects in the survival of ancient structures, from the Middle Ages or even antiquity (Figure 1).

Figure 1. Examples of Self-Healing effect on ancient structures: (a) Roman Forum (1st century BC - I d.Hr; (b) Old bridge in Amsterdam; (c) Colosseum, Rome.

Sustained research [1, 2, 4, 5] has shown that the phenomenon of autogenic curing of cementitious composites represents the consequence of mechanical processes (particles swelling), physical processes (crack filling with fine particles usual present in the water entering the crack) and most important, the chemical processes (continuous hydration and calcium carbonate precipitation); they can occur simultaneously and interfere or they can happen independently.

The continuing hydration of unhydrated cement grains represents an important chemical process generating self-healing of cementitious composites, generating the CSH gels as crack closing valuable products, not only sealing the microrcracks but also generating mechanical recovery of the material, as well [1]. The intensity of the process slows down in time, strongly connected to concrete age: In time the unhydrated clinker nuclei are consumed and the generation of further hydration products is less productive. Another factor with significant contribution to the decrease of the binder continuous reactivity in time is the nowadays cement production and technology: the clinker is strongly grounded and the cement finesse today is superior with respect to the previous years. Consequently, cement grains are easily accessible to the fast, initial hydration, reaching their peak till 28 days. After reaching their strength class, at the age of 28 days, a small further strength growth is recorded, confirming the assumption. The continuous hydration potential of the cementitious materials for the self-healing (SH) effect inducing as well is considered to be stimulated by the means of reactive grains addition is considered. The added grains would be polymeric coated for further preservation of their
reactivity for when it would be necessary: initiation of a crack and the necessity of its sealing, when also the humidity is provided.

This paper presents preliminary aspects regarding the encapsulation techniques that could be used for the considered reactive grains and their compatibility to the cementitious matrix, as well as their potential use as Self-healing effect promoter within the material.

2. Materials and methods
Developing an intelligent, self-healing addition, based on an active hydraulic material (grain), covered with a layer of waterproofing material and then testing its positive effect involves the compliance with some specific requirements: identifying active hydraulic material grains with compatible waterproofing coating, controlled cracking of the samples and accelerated aging of concrete for a fast initial evaluation, identifying an appropriate method for highlighting the self-healing inducing of the addition, correctly emphasised and distinct from the natural, autogenous self-healing capacity of concrete.

The design concept of the intelligent addition includes some specific requirements for the reactive grains and for the waterproof polymeric coating, as well. The graphical representation of the theoretical concept is presented in Figure 2.

![Graphical representation of the theoretical design for the reactive grains concept.](image)

Regarding the hydraulic material, it must be able to generate new compounds by reaction with water or ions dissolved therein, compounds which can be deposited in the crack and diminish/cancel the access for the aggressive agents. In the same time, the reactive grain should not contain or generate sulphates, chlorides, alkalis or other aggressive concrete ions, as the presence of sulphates can lead to the formation of ettringite with a remedial action by creating a barrier to water access. There is identified the risk of an out-of-control reaction which can lead to the destruction of concrete; simultaneously, it must not negatively influence the hydration and hardening properties of Portland cement in case of accidental break of the waterproof protection.

The waterproof polymeric coating must protect the reactive material from water until the cracking would occur and also it has to be brittle and sensitive enough so it would break when necessary (when cracking happens), in order to allow the water in infiltrate and produce the healing compounds. It has
to withstand efforts during the concrete preparation process, be resistant in the alkaline concrete environment, do not suffer positive volume variations in alkaline environments and not negatively influence the cement hydration processes. The adherence between the reactive granules and the coating represents an important feature, responsible to provide the required strength to withstand to mechanical shocks during mixing.

From the economic point of view, both materials, the reactive grains and the polymeric coating, should be available in large quantities and they should have the ability to be used in technological processes, in order to be attractive to the industry and produce a real effect as concrete durability enhancement, maintenance and environment pollution reduction.

In order to obtain the intelligent addition a hydraulic active material was considered. 0.09-0.16 mm particles were the main choice for the physical development of the composite capsules. Regarding the encapsulation development, a polymeric material, soluble in ordinary solvents and with a reasonably low melting point, generally complying with the previous described features, was considered.

Two different methods were considered as possible encapsulation techniques for the chosen hydraulic active grains (H):

1) Mixing the granules with the polymer (P) dissolved in compatible solvent, at various solution concentration and also various H/P ratios;
2) Mixing the granules with melted polymer at a reasonable temperature (Figure 3).

![Figure 3](image)

**Figure 3.** Active hydraulic grain (H) aspect during the coating procedures: (a) after mixing with melted polymer (Method 2); (b) before the grinding and sieving operations.

As variable parameters, the ratio hydraulic active grains (H) to Polymer (P), H/P and also the concentration of the polymer solution were considered (Method 1). An active hydraulic material with the size of granules ranging from 90 and 160 μm, wrapped in a polymer film of a thickness of 4-7 μm was obtained. Further on, the material is grinded for breaking the adhesions between the shells of the granules and then sieved through the 0.5 mm sieve, considered to generate the proper dimensions of the final coated grains.

Although mixing the reactive granules with the polymer solution or with the melted polymer generates complete coating of them, during the grinding operation, partial polymeric cover is removed and the full grain coating is lost. The coating efficiency, necessary to be evaluated, is determined by using a conductivity method, considering that the chemical reaction rate in a heterogeneous system depends on the contact surface between the two phases, the solid and the liquid. The conductivity of the distilled water, containing a certain amount of reactive addition / protected reactive addition is measured. The coating efficiency actually represents the decrease of conductivity, expressed as a percentage, and it is related to the reactive material conductivity. It was noticed that the relevant conductivity changes happened in the first 60 s after the mixing of distilled water with the considered amount of reactive grains (virgin and coated). Conductivity tests were performed for several types of coated grains, in terms of polymer concentration and H/P variation.
The Degree of coating (GA, %) was determined by using equation (1):

\[
GA \, (\%) = 100 \times \frac{\text{Cond}_{hp} - \text{Cond}_{h}}{\text{Cond}_{h}} \tag{1}
\]

Where:
- GA (\%) = Degree of coating;
- Cond_{hp} = conductivity of the coated grains suspension;
- Cond_{h} = conductivity of the uncoated grains suspension;

The results, presented in Table 1 show a small range of variation, proving a general reliable coating efficiency of the reactive addition and also the efficiency of the testing methodology. Seven of the tested compositions prove a GA exceeding 80\%, four of them almost reach a convenient 90\%, which is considered a very good performance.

Table 1. Degree of coating for relevant compositions.

| Composition code | GA (%) |
|------------------|--------|
| 2                | 83     |
| 4                | 85     |
| 6                | 88     |
| 8                | 89     |
| 20               | 88     |
| 30               | 85     |
| 5                | 79     |
| 10               | 66     |
| 15               | 71     |
| 20               | 70     |
| Melted polymer (Method 2) | 87     |

The compatibility of the smart addition to the cementitious matrix was determined by integrating it in mortar samples produced in accordance to EN 196-1 [6]. CEM I 52.5R was used in order to obtain cement grain fast complete hydration and consequently, to reduce the natural, autogenous self-healing capacity of the mortar, for further better emphasise of the crack sealing effect of the smart addition. A small amount of polypropylene fibres was added to the mixes, including to the reference (R), which contains no other addition. The smart addition was added to the mortar samples as sand (0/0.5 mm fraction) replacement, as follows: Mix 130P40 contains 130 kg/m\(^3\) smart addition, Mix 260P40, contains 260 kg/m\(^3\) smart addition (developed by Method 1, polymer solution); Mix 225PT contains 225 kg/m\(^3\) smart addition (developed by Method 2, melted polymer).

The influence of the smart addition to the mechanical resistance is observed by the means of the specific flexural (3PB) and compressive tests, by using the 40 x 40 x 160 mm\(^3\) prismatic specimens, at the age of 28 days, in accordance to EN 196-1 [6]. It was recorded no negative influence of the smart addition to the cementitious material, on the contrary, a slight strength increase was recorded, attributed to the hydraulic active material, available from the remaining uncovered area.

The method considered reliable and conclusive for the initial evaluation of healing efficiency in terms of crack sealing and regenerating the concrete is based on a ASTM methodology [7]. The method principle is related to the specific electric load passing through the samples: cracked concrete and healed concrete. Prismatic specimens 40 x 90 x 160 mm\(^3\) were prepared using the mixes previously mentioned (R, 130P40, 260P40 and 225PT). Accelerated aging of the samples is obtained by 2 weeks exposure to hygrothermal curing at temperature T 80°C, in humid conditions (water bath). The pre-cracking of the specimens, namely the cutting of a 5 mm thick and 15 mm deep channel, is
performed by the help of a diamond disc saw, across the sample, in the median area, in order to determine the path for the further natural cracking, induced by mid span loading; the set-up is equipped with an horizontal LVDT for obtaining the desired crack width of 0.3 mm. The set-up used for the pre-cracking state of the specimens is presented in Figure 4.

![Figure 4. Experimental set-up for fixed-width of 0.3 mm mid-span crack inducing into the specimens.](image)

In order to increase the self-healing process of the specimens, they were cured by exposure in high moisture environment. After 3 days the samples were extracted from the water bath and another channel, similar to the previous one, was induced across the sample, located at 27 mm from the edge of the prismatic specimen. This way the same specimen includes both the cracking state and the totally healed cracked state, for a reliable healing evaluation via electric load passing through the two specified media. Two polyethylene tubes 50mm in diameter were stuck on the casting face using a silicone seal, one in the central area above the crack and one above the channel centred at 27mm from the prism end. The samples were dried in an oven and saturated with water in a vacuum of 20mm Hg. The samples thus prepared were introduced at the same level in a tray containing a 0,1N NaOH solution. A 3% NaCl solution is inserted into the polyethylene tubes. A difference in potential of 24V was applied for 15 minutes and the intensity of the electrical current through the cracked I_{fr} and uncracked I_{nR} area of each sample was measured, including the I_{fr} and I_{nR} reference area. The self-healing efficiency in accordance to this procedure represents on-going research and the concluding data analysis is currently performed.

3. Results and discussions
The first results of the current research are offering some optimist conclusions related to the general viability of the concept.

The conductivity testing confirms the efficiency of the polymeric coating of the reactive grains, for both methods: Seven from the eleven tested compositions proved a coverage efficiency of over 80%, four of them approaching 90%. Figure 5 shows the conductivity development over time, for the reactive grains, without coating vs. a) the coated grains (Method 1) and b) the coated grains (Method 2).

The mechanical performance of the mortar proves not to be affected by the smart addition. Figure 6 shows the graphical comparative analyses of the 28 days results, obtained for all the mortar mixes considered. Initial specific testing performed on specimens show significant healing degrees even after short curing exposure, thus proving the research superior potential.
Figure 5. Graphical variation of the conductivity over time: uncoated vs. coated grains.

Figure 6. 28 days flexural and compressive strength for samples with or without smart addition.

Figure 7. Graphical variation of the conductivity over time: uncoated vs. coated grains.
Simultaneously, the visual analyses performed by SEM microscopy coupled with EDAX (Figure 7), showed hydraulic active material granules with broken shell next to the crack and also its hydraulic active material, inside, starting to hydrate, developing new hydration, healing compounds, especially hexagonal crystals of Ca(OH)$_2$; intact coating at the edge of the crack was also noticed, offering further protection of the grain.

4. Conclusion and perspectives
The initial testing and the corresponding results are offering positive conclusions regarding the viability of the concept. A composite smart addition, consisting in hydraulic active grains, waterproof coated by a 4 - 7 μm polymer shell has been developed.

The two methods used for the encapsulation technique show good waterproof performance, in terms of conductivity evaluation, proving their efficiency.

The compatibility of the coated reactive grains to the cement based matrix was tested in terms of mechanical performance evaluation with respect to the reference matrix, with no addition; the tensile and compressive strength did not experience any decrease due to the smart addition, but a slight increased attribute to the reactive grains becoming active during mixing.

The self-repairing effect of intelligent addition is evaluated on the mortars by electro diffusion of chloride ions. Crack healing degrees of more than 70% were obtained for some of the tested compositions, according to the initial data analysis.

Optimization of the smart addition and supplementary validation performance of its repairing effect in concrete still needs to be performed.

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5. References
[1] De Belie N, Gruyaert E, Al-Tabbaa A, Antonaci P, Baeră C, Bajare D and Litina C 2018 Adv. Mater. Interfaces 5(17) 1800074
[2] Snoeck D 2015 Self-healing and microstructure of cementitious materials with microfibres and superabsorbent polymer (Belgium: Ghent University)
[3] Joseph C, Lark R, Jefferson T and Gardner D 2009 Potential application of self-healing materials in the construction industry (Cardiff: Cardiff University)
[4] De Rooij M, Van Tittelboom K, De Belie N and Schlangen E 2013 Self-healing phenomena in cement-Based materials: state-of-the-art report of RILEM technical committee 221-SHC: self-Healing phenomena in cement-Based materials vol 11 (Berlin: Springer Science & Business Media)
[5] Van Tittelboom K and De Belie N 2013 Mater. 6(6) 2182–217
[6] EN 196 2016 Methods of testing cement. Determination of strength, Romanian Standard Association, Bucharest, Romania
[7] ASTM C 1202 2005 Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration (Washington: ASTM International)