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Development of ultra-high performance concretes with self-healing micro/nano-additions

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HIGHLIGHTS

- Self-healing UHPCs are developed by using a set of two additions.
- Healing additions reduce the mechanical performance but refine the microporosity.
- An effective autonomous self-healing capacity is assessed in the fabricated UHPC.
- Self-healing capacity is not improved when increasing the additions content used.
- The crack width and the healing period influence the self-healing efficacy.

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ABSTRACT

UHPC are developed in present paper incorporating an innovative self-healing system based on two micro/nano-additions: silica microcapsules containing epoxy sealing compound (CAP) and amine functionalised silica nanoparticles. Although CAP are well integrated within the cementitious matrix, their inclusion promotes a reduction in the mechanical performance so CAP could act as weak points. However, the inclusion of these additions refines pore distribution thus increasing the expected durability in aggressive media. An effective autonomous self-healing capacity is assessed/confirmed which is unexpectedly higher in the concretes with the lower healing additions content studied. This capacity depends on the crack width and the healing period considered.

1. Introduction

During the lifetime of many concrete structures, the assurance of high durability is a key parameter to ensure their safety service life. In this sense, the continuous increase in the durability requirements of the concrete structures led to the development of ultra high performance concretes (UHPC) where excellent durability is mandatory [1]. The UHPC term was introduced by De Larrard in 1994 [2] and, since then, more and more researches have been conducted on the design/formulation and characterization of this type of concretes [3]. The design of UHPC implies the use of very low w/c ratios, high cement contents, high supplementary cementitious materials contents (mainly silica fume), fibre reinforcements, etc., with the subsequent decrease in porosity, improvement in microstructure and homogeneity, and increase in toughness [1–5]. Simultaneously, during the last two decades the increase of the durability requirements on concrete structures has also led to investigate, design and improve the self-healing capability of cementitious materials that allows an autonomous way of sealing of cracks [6–18]. In this way, the service life of the structure is extended and the maintenance costs are reduced [10,11].

Depending on its origin/nature, self-healing in concrete can be classified as autogenous or autonomous [11,19,20]. Autogenous healing is an intrinsic characteristic of concrete that heals small cracks mainly by further hydration of cement and/or precipitation of calcium carbonate [8,21]. On the contrary, in the autonomous approach the healing is caused by engineered additions specific for this action and added to the cementitious matrix [6,9–18]. In recent years, addition of different microcapsule systems to cementitious materials to confer self-healing capacity has been studied obtaining very promising results [9–15,17].

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The final objective is always to improve the long-term durability by sealing the initially formed microcracks thus preventing their growth and/or limiting the ingress of aggressive solutions. This objective is even more essential when ultra-high performance concretes (UHPC) are considered, as the performance requirements are high and the expected service-life is very long. For this reason, the combination of these two innovative concrete technologies is assessed in the present paper. Nevertheless, it is well known that UHPC has certain autogenous-healing capacity, for cracks smaller than 30 μm, due to the presence of unhydrated cement particles with latent reactivity that get activated in presence of moisture upon cracking [8,22,23]. Although fibre reinforcement helps to control crack growth it seems unlikely that they are kept small enough for an effective autogenous healing. Thus, the present study has tried to improve the healing ability of UHPC by means of adding engineered additions (autonomous approach), and therefore trying to obtain the healing of wider cracks. In this case, the design of the UHPC is based on that designed by Richard and Cheyrezy [4] and the self-healing mechanism is based on the one reported by White et al. [6] but modified to make it chemically more compatible with the heterogeneous cementitious matrix.

The self-healing system proposed is based on a two component epoxy-amine system. On the one hand, the epoxy is introduced encapsulated in silica microcapsules (CAP) which are added during the mixing process and get bound to the matrix as it hardens. On the other hand, amine functionalised silica nanoparticles (NS) are added dispersed in the mixing water to react with the clinker during the hydration process. The objective is to generate an amine functionalized cementitious matrix, that is, the amine group is covalently bound to the silicate chains that form the cementitious matrix. The formation of a microcrack would break some microcapsules releasing the epoxy which would spread through the crack. The epoxy then would come into contact with the amine groups in the matrix which would cure the epoxy thus sealing the crack [24,25].

In a previous paper, the influence of the incorporation of both additions in the microstructure evolution and the performance of cement pastes has been analyzed [15]. The aim of the present study and as a step forward, is to evaluate the feasibility of developing a self-healing UHPC and its resulting physico-mechanical, durability and self-healing properties. In this regard, since healing capacity depends on the crack size [10,11,16,21,26], two different crack mouth opening displacements (CMOD) have been considered: 150 μm and 300 μm, larger than those previously reported to be healed by the autogenous self-healing mechanism in UHPC [8] and even than those reported to be completely autogenously healed in other cementitious materials types [27].

2. Application and practice

The development of the self-healing UHPC considered in this study is based on the necessity to guaranty durable concrete structures under extreme environmental and/or operating conditions. The concept is based on combination of two innovative technologies, UHPC and autonomous self-healing concretes, in order to develop long lasting concrete structures. The developed concretes are expected to last under severe operating and environmental conditions with high durability requirements, such as high mechanical fatigue, extreme temperatures, etc.

New infrastructure projects require long service life spans, which often exceed those formulated in standards. In fact, materials that perform in more and more extreme operating conditions are increasingly required, for example, concretes to be used in offshore structures or underground structures (where large temperature gradients and high pressure are expected), or concrete structures to be installed along coast lines (high chloride contents), in sub-arctic/arctic areas (low temperatures, ice-abrasion), desert areas (high temperatures and drastic temperatures changes between night and day), etc. In most of these mentioned situations, service life longer than 100 years is required nowadays but these periods significantly exceed the conventional service life design. Moreover, it is widely accepted that service life can be extended more economically with a durable initial design than by future rehabilitation. In this sense, the self-healing UHPCs developed in this study are expected to increase the initial cost of the infrastructure but strongly reduce the maintenance costs which agrees with the new trends in the construction market where life-cycle costs are being increasingly used. In present study highly durable concretes are designed but its durability is even extended by self-healing engineered additions that are expected to improve the healing ability of the designed UHPC. Thus, the healing of wider cracks will be possible and this is essential when very aggressive environments or aggressive operating conditions of the concrete structures are considered.

3. Materials and methods

3.1. Self-healing UHPC developed

Three different ultra-high performance concretes were analyzed, two with the self-healing system (MIX5 and MIX10) and the other one (REF) without it. The characteristics and the synthesis process of the self-healing additions were presented elsewhere [24,25,28]. As shown in Table 1, the three UHPC had similar compositions but in the self-healing concretes silica fume (SF) was partially substituted by weight by the corresponding amount of epoxy resin filled silica microcapsules (CAP) and amine functionalized nanosilica (NS). This was done in order to minimize modifications of the granulometric distribution and the total silica content. Two different addition dosages have been considered, 5% and 10% of self-healing additions both according to silica microcapsules, so two different self-healing concretes have been fabricated: MIX5 and MIX10. The CAP to NS ratio was in both cases 0.75. Such value was chosen to warranty that there was enough activating component (amine functionalization) within the matrix to cure the epoxy. Two different sand types were used in these UHPC or microconcretes.

The different specimens were prepared as follows. Firstly, all the solids but the NS (i.e. the silica fume, CAP, the cement and the two types of sand) were mixed at low speed according to UNE-EN 196-1 for one minute. The NS were dispersed in the water with the superplasticizer for 5 min by an ultrasound probe (Bandelin Sonopuls Ultrasonic homogenizer, 20 kHz, at 75% of power) previous to pouring it over the solids. Then the paste was mixed for 1 min at slow speed and 3 min fast (as specified in the UNE-EN 196-1 standard) before letting it rest for 2 min. Mixing proceeded at fast speed for two more minutes and then half of the

Table 1
Composition of the UHPCs.

Components (g)	REF	MIX5	MIX10
CEM I 52.5N	680	680	680
Water	204	204	204
Siliceous aggregates (∅ < 1 mm)	510	510	510
Limestone powder (∅ < 0.5 mm)	510	510	510
Silica Fume	170	91	11
CAP	–	34	68
NS	–	45	91
Superplastizicer	27.2	27.2	27.2
Fibres	119	119	119