Cement & Concrete Composites 57 (2015) 116–127

Contents lists available at ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Influence of mineral additives and environmental conditions on the self-healing capabilities of cementitious materials

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ARTICLE INFO

Article history:
Received 16 June 2014
Received in revised form 15 October 2014
Accepted 11 November 2014
Available online 7 January 2015

Keywords:
Mineral materials
Environmental conditions
Self-healing
Cementitious

ABSTRACT

The effects of the addition of minerals of various compositions (i.e., silica-based materials, chemical expansive agents, swelling minerals and crystalline components) on the self-healing performances of cementitious materials were investigated. The self-healing capabilities were assessed by performing water permeability tests, quantifying the widths of the surface cracks and studying the water absorption of mortars that were pre-cracked by either splitting or compression. The results showed that the cracks that appeared early on healed more efficiently when they were cured in still rather than flowing water. High pHs and high temperatures accelerate crack healing. The healing efficiency can be further improved by utilizing a combination of minerals rather than a single mineral. A self-healing mechanism was discussed by combining these results with micro-observations. The precipitation of calcium carbonate, which is aided by higher pH values and higher calcium ion contents, was found to be the main contributor to the healing of surface cracks.

1. Introduction

Recently, increased attention has been given to the study of the self-healing of cracks in cementitious materials. Self-healing is conventionally achieved using methods that employ microcapsules or hollow glass fibers that contain healing adhesives [1,2], bacteria [3], or shape memory alloys [4,5]. These techniques can be used to improve the durability and longevity of materials, but they must be carefully carried out. For instance, the addition of microcapsules and hollow glass fibers make the casting of concrete difficult and may weaken the mechanical response of the host matrix because they are less rigid in comparison. It is difficult for bacteria to survive in concrete because it is a highly alkaline environment. Shape memory materials are quite expensive and better for structural maintenance. Most of all, the inorganic cementitious matrix and the added phase (either organic or metallic) must be compatible so that the long-term performance of the concrete is not adversely affected.

Indeed, cementitious materials have an inherent healing capability, typically termed "autogeneous healing". As indicated by Van Breugel, the self-healing capacity of ordinary concretes is an inherent property of the material and cannot be manipulated via mixing [6]. In fact, in autogeneous healing, cracks heal on their own as a result of the interaction of the cement, water and the surrounding environment. As revealed by most analyses, the main mechanisms of natural healing feature the continued hydration of unhydrated cement grains and the crystallization of calcium carbonate. The crystallization of calcite plays a major role in the crack healing mechanisms of mature concrete [7–9]. Natural healing can lead to the recovery of a material's dynamic elastic modulus and water impermeability, but its strength is typically not improved to a large degree [10].

Some mineral additives have been found to promote the self-healing of cementitious materials. For instance, the expansion and crystallization of mineral materials can produce products that fill and heal cracks. In other words, autogeneous healing can be accelerated and improved. This method is compatible with and takes advantage of the inherent characteristics of the cement matrix, such as its high alkalinity and moist environment.

When self-healing is accomplished via the hydration of the cementitious components, it is based on the fact that unhydrated cement grains are present in the system. If most of the cement is fully hydrated before cracking takes place, the efficiency of the self-healing process can be very low, unless silica-based minerals are involved. Such methods have been used to improve of the transport properties and restore the mechanical behavior of materials that possessed cracks no more than a few tens of microns in width; however, when the material possessed cracks with widths larger than 100 μm little improvement in these properties and

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http://dx.doi.org/10.1016/j.cemconcomp.2014.11.014
0958-9465/

behaviors were observed [11,12]. Moreover, self-healing is a time-dependent process; both the inherent and external environmental conditions can greatly influence healing efficiency.

Expansive products (physical or chemical) fill the cracks and thus contribute to the improvement of the transport properties and the enhancement of the mechanical performance. However, when the volume is expanded too far, additional cracking may be induced by restrained deformation [13].

Inhomogeneous nucleation occurs during the precipitation of calcium carbonate in solution [14]. The crystallization, sedimentation and kinetic crystal growth of calcium carbonate are mainly influenced by the temperature, concentration, pH of the solution and the partial pressure of CO_2. Kishi et al. [15] used carbonates, such as Na_2CO_3 and Li_2CO_3, to accelerate the deposition of calcium carbonate into cracks. The results showed that the healing products were very loose; thus, the healing did not positively affect the mechanical performance of the material. To overcome this problem, expansive agents were used in addition to the carbonates. However, very little is known about the internal and external factors that affect the crystallization and sedimentation of calcium carbonate. These factors will be investigated in this study. Herein, the self-healing capabilities (water permeability, crack width and water absorption) of cement mortars incorporating a single silica component, a chemical expansive agent, a swelling mineral and a crystalline material (or a particular combination of these) were assessed experimentally. The related healing mechanisms were explored by combining microscopic observation.

2. Experimental plan

2.1. Specimen preparation

Mortars with a water to cement ratio of 0.45 and a sand ratio of 2 were made using ordinary Portland cement (CEM I 52.5N). Four different mineral materials (i.e., silica-based, chemical expansive, swelling and crystalline additives, denoted *a*, *b*, *c* and *d*, respectively) were used. Table 1 lists the four specific mineral additives.

The proportions of the mixtures are given in Table 2. The one denoted by P represents the control specimen in which mineral materials were not added. The cement was partially replaced by either a single type of mineral or a combined mixture of more than one type for the remaining mortars.

Mixing was performed in accordance with ASTM C192-06 [16]. The mortars were then cast in molds with a size of 70.7 mm × 70.7 mm × 70.7 mm. The mortars were demolded after

Table 1
Mineral additives used in the experiment.

Type of minerals	Functions	Typical materials
Silica-based (*a*)	Producing gel by the reaction with the hydration products of cement	Silica fume, fly ash, etc.
Chemical expansive (*b*)	Producing AFt by the reaction with the hydration products of cement	UEA, etc.
Swelling (*c*)	Swelling by absorbing water, containing ions migration between layers	Bentonite, etc.
Crystalline (*d*)	Promoting crystallization and sedimentation in the matrix of cement-based materials	Sodium carbonate and talcum powder, etc.

Table 2
Mixture proportion of the mortars by mass ratio.

Mortar	Cement	Water	River sand	Mineral materials			
				a	*b*	*c*	*d*
P	100	45	200	0	0	0	0
A	92			8	0	0	0
B				0	8	0	0
C				0	0	8	0
D				0	0	0	8
ABC	88			5	4	3	0
ABD				5	4	0	3
BCD				0	4	3	5
ACD				5	0	3	4
ABCD	86			6	4	2	2

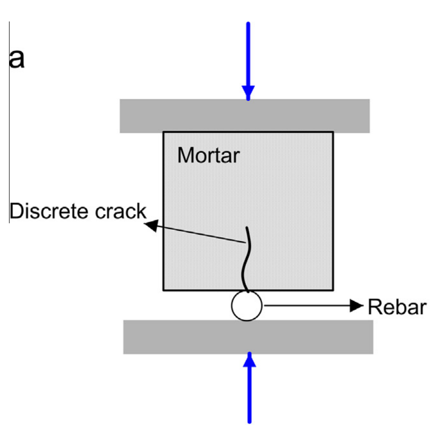

Fig. 1. A schematic of the test set-up for crack fabrication: (a) splitting and (b) compression.