Contribution to study of the self-healing effect activated by crystalline catalysts in concrete structures when subjected to continuous exposure to water

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ABSTRACT: This paper aims to contribute to the study of the self-healing effects on high performance concretes activated by crystalline catalysts when subjected to continuous water exposure, as part of a postgraduate research program developed at the Instituto Tecnológico de Aeronáutica (ITA) in Brazil. For this purpose, a specific crystalline catalyst was selected to investigate the potential to act as a self-healing agent in concrete. Specimens of high performance concrete were prepared having a constant water/cement ratio of 0.50, with and without addition of these crystalline catalysts. A uniaxial compression load was applied to generate microcracks in cylindrical concrete specimens pre-loaded up to 90% of the ultimate compressive load determined at 28 days for 2 minutes. Later, the extent of damage was determined as a percentage of loss in mechanical properties by determining compressive strength recovery and percentage of increase in permeation properties and water absorption rate by monitoring for 28 and 56 days after preloading, during a period necessary for self-healing of these microcracks. The results of the recovery of strength and permeability will be attributed to the self-healing of these pre-existing microcracks, due to hydration of anhydrous particles of cement and especially by the activating effect of the crystalline catalyst, on the surfaces of these microcracks. This is determined as a percentage of gain of mechanical properties and the percentage of decrease in the permeability properties. The knowledge developed in this study makes it possible for the self-healing technology to be specified in the high performance concretes mix design in various applications in air transportation and airport infrastructure buildings, especially in hydraulic structures and underground constructions.

1 INTRODUCTION

Concrete is a material with a very long history and universally used as a building material, and its importance will always continue to require more research to resolve the unavoidable cracks in reinforced concrete. Also, some research focuses on a scientific approach beginning with the casual observation self-healing phenomenon of the concrete cracks that was well-known since ancient times. If we can establish a comprehensive discussion of the laws which govern the chemical/physical/biological processes involved in self-healing technology, based on theoretical and experimental research, recommendations can then be made for the development of a high performance self-healing concrete to design more durable concrete structures subjected to continuous exposure to water.

1.1 *Self-healing phenomenon*

The term self-healing phenomenon has puzzled researchers for over a hundred years. In most studies the apparent decrease in permeability is incorrectly ascribed to a self-healing phenomenon. This mistake is especially common in investigations where only the inflow is recorded and through flow remains unknown. The latter is of primary importance, as the self-healing phenomenon is not a product of a particular testing procedure, but results from the interaction between the microstructure and permeating fluid (Edvardsen, 1999). The self-healing phenomenon, which is largely attributed to the dissolution and redeposition of hydrates induced by active catalysts, should be differentiated from autogenous healing, which is due to continuing hydration of unhydrated material with calcite ($CaCO_3$) nucleation and subsequent crystal growth. Two major differences are (a) self-healing effect is observed in a system closed to CO_2, where carbonation of dissolved $Ca(OH)_2$ is not possible, and (b) the condition under which the self-healing effect becomes significant is after extensive microcracking, usually caused by drying and/or mechanical loading during the service life of a concrete structure. Both are water exposure dependent, while continued hydration may proceed under stagnant conditions (Hearn, 1998).

Recently, several researchers have observed the formation of cementitious products such as Aft (ettringite), AFm (monosulphate) and $CaCO_3$ in the cracks and $Ca(OH)_2$ crystals in air voids in cracked concrete. It was hypothesized that these hydration products had been leached and recrystallized in water that had flown through the crack.

It was found that the crystalline self-healing catalyst selected in this study significantly affected the formation of re-hydration products with high chemical stability as well as rapid self-healing velocity; it didn´t show loss of re-crystallization products, which are mainly composed of fibrous phases from crystalline catalyst and calcite. This indicates these fibrous phases play an important role in crack bridging between cracks (Ahn & Kishi, 2010).

Various active healing catalysts have been proposed for enhancing the self-healing capacity of concrete. While most healing agents are chemically based, more recently the possible application of bacteria as self-healing agent has also been considered (Wiktor & Jonkers, 2011).

1.2 *Self-healing concrete technology*

Therefore, the aim of this study is to develop self-healing concrete technology for practical application in the near future, but it is also significant to know about the actual individual healing mechanism and its conditions. It is well-known that as concrete hydrates its permeability decreases. Continued hydration, however, is not the only mechanism which causes such reduction. Autogenous healing refers to carbonation of dissolved $Ca(OH)_2$ from concrete, with narrower cracks sealing faster than wider ones; and the self-healing mechanism, which is largely attributed to the dissolution and redeposition of hydrates, which can also significantly reduce the flow.

In order to provide a systematic design of robust healing abilities to even aged high performance concrete, optimization methods can be applied, such as (a) partial cement replacement by high volumes of pozzolanic materials like fly ash, silica fume and/or blast-furnace slag, which can be related to the progressive filling of the internal cracks by newly formed C-S-H gels due to the pozzolanic reaction for continued hydration healing mechanism; (b) addition of ductile-type fibers for reinforcing cementitious matrix and incorporating shrinkage compensation additives, which aids the formation of autogenous healing products due to the tight space between fibers: the formation of calcium carbonate crystal leads to reducing water permeability and recovery of tensile strength; and (c) use of mineral geo-materials and carbonate-based chemical agents, acting as a crystalline catalyst to supply the effect of cementitious recrystallization in voids of cracked concrete, in order to improve chemical stability and self-healing time.

2 EXPERIMENTAL PROGRAM

2.1 *High Performance concrete (HPC)*

A standard mix design was prepared having a constant water/cement ratio of 0.50 and using two types of blended cement: a Type IS (MS) blast-furnace slag cement (slag content < 70%) and a Type I (SM) slag-modified Portland cement (slag content < 25%) according to ASTM C595, with and without addition of crystalline catalysts at the rate of 2.5% by weight of cement content. Altogether, four different mixtures of HPC with addition of AR glass fibers were produced for the test program. The composition of the concrete is given in Table 1 and properties are summarized in Table 2 which was optimized under the aspects of impermeability, workability and costs.

Table 1. Standard composition of the concrete mixture used

w/c ratio	Cement (kg/m^3)	Aggregate (kg/m^3)	Additions and Admixtures (kg/m^3)
0.5	392	1749	4.0 PCE, 2.4 FM, 2.0 VMA, 10.0 XA, 0.9 GF

Slag cement	Type IS (MS)	CPIII 40RS
Slag modified cement	Type I (SM)	CPII E 40

PCE	Polycarboxylate ether superplasticizers (1.0%)
FM	Water reducing superplasticizers (0,6%)
VMA	Viscosity modifier admixture (0.5%)
XA	Crystalline catalyst (2.5% of cement content)
GF	Alkali-Resistant Glass Fiber (12 mm).

Table 2. Properties of the concrete mixture used

Mix	Compressive strength 28d (MPa)	Air content (%)	Slump flow (mm)	0.7 MPa water penetration (mm)
1	53.3	0.7	700	20
2	51.2	0.8	760	22.5
3	53.4	0.7	730	20
4	47.2	0.7	780	25

Mix 1	Slag cement + crystalline catalyst
Mix 2	Slag cement
Mix 3	Slag-modified cement + crystalline catalyst
Mix 4	Slag-modified cement

2.2 *Compressive strength recovery*

After a 28 days curing, a uniaxial compression load up to 90% of the ultimate compressive strength, determined at 28 days, was applied to generate microcracks in cylindrical concrete specimens for 2 minutes. Immediately after the release of pre-loading, the samples were tested to determine the loss in mechanical properties by determining compressive strength. After pre-loading, the concrete specimens were stored in water, and tested after 28 and 56 days, during a period necessary for self-healing of these microcracks, to determine the compressive strength recovery in mechanical properties, as presented in Figure 1.

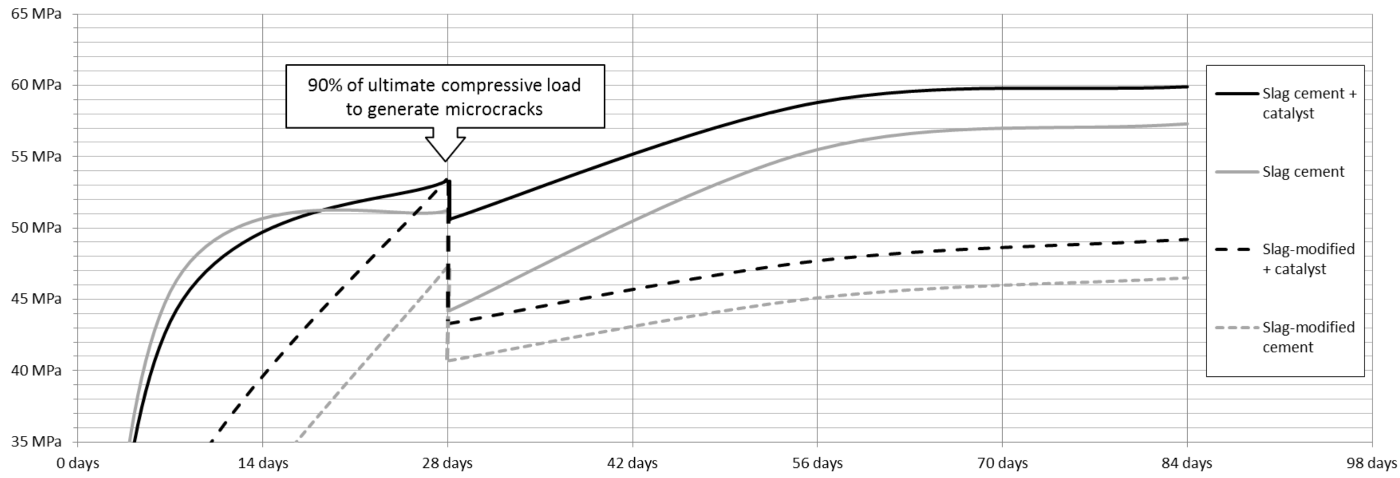

Figure 1 - Loss of compressive strength and recovery due to self-healing of microcracks

The results of the recovery of compressive strength can be attributed to the self-healing of these pre-existing microcracks, due to hydration of anhydrous particles of cement and especially by the activating effect of the crystalline catalyst, on the surfaces of these microcracks, this is determined as a percentage of gain of mechanical properties, Table 3 presents the mechanical properties of concrete specimens at 14 days, 28 days before preloading, and 28 days immediately after preloading, 28 days (56 days) and 56 days (84 days) after preloading.

Table 3. Compressive strength properties of concrete (MPa)

Mix	14 d	28 d before	28d after	56 d	84 d	loss (%)	recovery (%)
1	43.5	53.3	50.6	58.8	59.9	5.1	17.4
2	45.6	51.2	44.2	55.5	57.3	13.7	25.6
3	30.2	53.4	43.3	47.7	49.2	18.9	11.0
4	22.9	47.2	40.7	45.1	46.5	13.8	12.3

Mix 1 Slag cement + crystalline catalyst
Mix 2 Slag cement
Mix 3 Slag-modified cement + crystalline catalyst
Mix 4 Slag-modified cement

2.3 *Water absorption rate of concrete specimens*

Based on ASTM C1585, the registered increase in mass of cracked and healed concrete specimens at given intervals of time, when permitted to absorb water by capillary suction, is presented in Table 4. The specimens were dried in an oven at 50 °C for three days, and one surface of the specimens was allowed to be in contact with a 3 to 5 mm of water. The rate of absorption (mm^3/mm^2), defined as the change in mass (g) by cross section of the specimen (mm^2) and density of water, against square root of time ($sec^{1/2}$). The slope lines obtained defines the rates of water absorption during the initial 6 hours of the virgin specimens and the cracked/ healed specimens in Figure 2.

Table 4. Water absorption rate test of concrete specimens

Specimen	Slag cement +catalyst		Slag-modified +catalyst	
Virgin	Mix1	Mix 2	Mix 3	Mix 4
60	0.158	0.209	0.171	0.170
120	0.193	0.276	0.214	0.206
180	0.214	0.311	0.236	0.241
240	0.232	0.343	0.259	0.266
360	0.245	0.366	0.274	0.294
480	0.253	0.389	0.284	0.309
720	0.274	0.389	0.298	0.330
960	0.291	0.412	0.317	0.351
1200	0.301	0.437	0.337	0.366
1500	0.313	0.461	0.361	0.406
2160	0.361	0.501	0.398	0.454
2940	0.393	0.531	0.433	0.481
3840	0.421	0.571	0.455	0.512
4860	0.446	0.613	0.487	0.544
7200	0.485	0.642	0.546	0.608
21600	0.609	0.807	0.667	0.778
Healed	Mix1	Mix 2	Mix 3	Mix 4
60	0.120	0.141	0.142	0.202
120	0.163	0.185	0.180	0.250
180	0.184	0.209	0.200	0.290
240	0.222	0.229	0.219	0.316
360	0.240	0.244	0.236	0.342
480	0.254	0.258	0.242	0.358
720	0.262	0.269	0.261	0.388
960	0.270	0.292	0.277	0.422
1200	0.279	0.303	0.303	0.437
1500	0.293	0.319	0.323	0.472
2160	0.309	0.354	0.362	0.518
2940	0.323	0.365	0.400	0.572
3840	0.350	0.384	0.427	0.611
4860	0.363	0.405	0.456	0.666
7200	0.412	0.467	0.494	0.719
21600	0.455	0.485	0.667	1.010

Mix 1 Slag cement + crystalline catalyst
Mix 2 Slag cement
Mix 3 Slag-modified cement + crystalline catalyst
Mix 4 Slag-modified cement

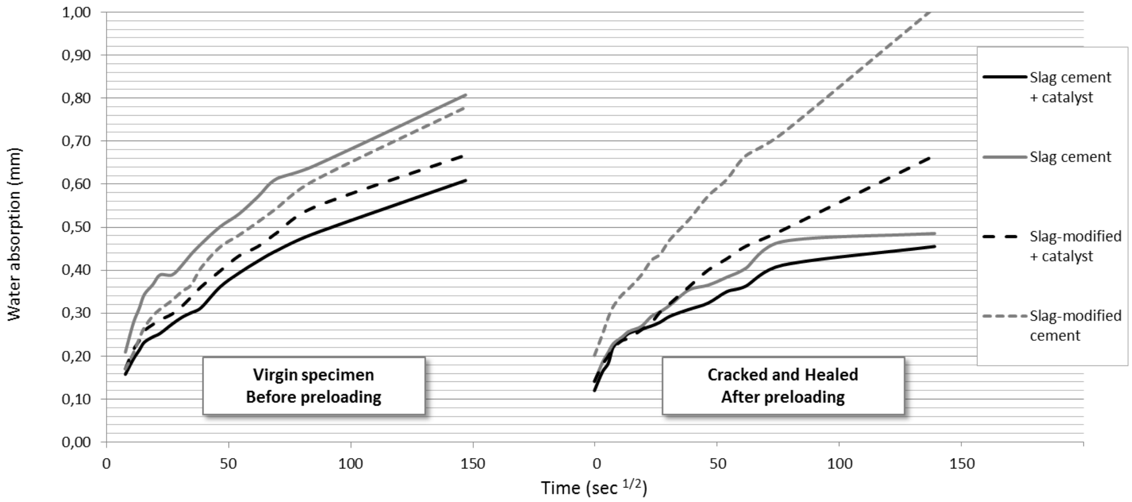

Figure 2: Comparison of Water absorption rate of virgin specimen and cracked/healed concrete specimen

2.4 *Results and discussion*

A permanent solution for repairing cracked reinforced concrete elements caused mainly by water penetration through cracks, resulting from cyclic mechanical loading has been desired for a long time. The conventional repair method that has been adopted in the past is to physically block off water by applying a waterproofing material with crack-bridging abilities, or injection into the crack of low viscosity resins consisting mainly of an organic substance on the concrete. In contrast, there is another method which waterproofs the whole concrete structure as well as the cracks by the application of a crystalline waterproofing catalyst, which multiplies the cement gel inside the concrete matrix, as well as on the cracked surface of the concrete, even on a dynamic moving structure (Mori, Kuramoto, Takagi, Horie, & Tanimoto, 1996).

Pre-loading the concrete caused an increase in its total porosity and a loss in its ultimate compressive strength. As microcracks developed inside the concrete structure, the pore structure was modified and the continuity of the cracks was increased. Internal cracking due to the mechanical loading, initially reduced the compressive strength by about 5.1 ~ 18.9 %, when preloaded up to 90% of their ultimate compressive strength, and after 56 days the recovery by about 11.0 ~ 25.6%. It was observed that there was an improvement in the compressive strength at 56 days due to healing of slag-modified cement with addition of crystalline catalyst of some 99% with respect to virgin specimens at 28 days, with the specimen without catalyst showing 92%. Similar observations were also made on the blast furnace slag cement, there was a compressive strength improvement at 56 days due to healing of the specimen with addition of crystalline catalyst of 112% with respect to virgin specimens at 28 days.

This was explained to due to the fact that high volumes of pozzolanic materials, have an important amount of unhydrated particles available in their microstructures, and these observations are attributed to the self-healing effect of the pre-existing cracks activated by crystalline catalysts. The recovery of compressive strength and permeation properties can be related to the progressive filling of cracks by newly formed C-S-H gels due to the self-healing effects. The crystalline catalyst modified slag cement and slag-modified concretes have benefited from prolonged limewater curing and show more significant reductions in water absorption rate than the control mixes. Ongoing chemical reactions between crystalline catalyst and cement by-products could be promoted by such curing conditions, which have resulted in reduced volumes of permeable voids (Sahmaran, Keskin, Ozerkan, & Yaman, 2008).

2.5 *Conclusions*

From this experimental research, it was clear that the crystalline catalyst was effective in improving the durability of the high performance concrete stressed by continuous and repeated mechanical loading. It was confirmed that C-S-H cement crystals are increased in the cracks of the concrete and hence an improved compressive strength and waterproofing which also contributed to understanding the self-healing phenomenon study.

In order to systematically design a robust self-healing technology for concrete structures subjected to continuous exposure to water, the use of a Type IS (MS) blast-furnace slag blended cement (25% < slag content < 70%) with addition of crystalline catalyst and ductile-type fibers is highly recommended.

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