IMPROVEMENT OF HARDENED CONCRETE DURABILITY BY NANOSILICA ELECTROMIGRATION

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ABSTRACT

Application of nanotechnology in construction industry is a quite new field with many interesting and promising possibilities. Nanosilica self healing properties, based on the high reactivity of these particles with the calcium components of cement, are of great interest in rehabilitation treatments of hardened concrete. In present work, the application of nanosilica to hardened concrete is proposed as innovative technology to improve the effectiveness of electrochemical repair methods and to increase the durability of rehabilitated structures by sealing the concrete pores.

An accelerated methodology, compatible with the electrochemical repair treatments of concrete, is proposed to introduce nanosilica in hardened concrete by connecting an external electric field. Two different commercial products with SiO_2 of 7 nm and 12 nm in diameter have been analysed. Silica nanoparticles have been transported through a mortar sample under a 12 V electric field. The interaction between the SiO_2 nanoparticles and the concrete have been characterised by different techniques: resistivity measurements, mercury intrusion porosity, scanning electron microscopy.

The results show that the interaction concrete/nanosilica takes place in the first centimetre of concrete cover from the surface of the nanosilica application. A denser microstructure with higher content of capillary pores is obtained after the nanosilica penetration. Also the resistivity of the mortar increases due to the treatment with nanosilica.

1. INTRODUCTION

Nowadays application of nanotechnology to construction industry is one of the research areas with higher possibilities. Nanotechnology can be applied in several circumstances in the construction field, from the fresh state, added as additives to the concrete mix, to the hardened concrete, applied on the surface. Several studies reported with nanoparticles are based on the nano-silica (nano-SiO_2) addition to the fresh mix to improve the performance of concrete. Nano-SiO_2 is highly reactive with calcium hydroxide [1] and is able to act not only as a filler [2], blocking the concrete pores, but also as an activator to promote pozzolanic reaction [3]. In this sense, nano-SiO_2 is expected to be an active sealing with self-healing properties based on the high reactivity of these nanoparticles with the calcium hydroxide of solid phases of concrete, blocking the transport of aggressive ions or refurbishing damaged or cracked concrete.

Nano-SiO_2 can also be considered in repair treatments in order to improve the performance of the repaired concrete structure The application of nano-SiO_2 as a sealing in hardened concrete appears as an interesting option to block the pores in hardened concrete decreasing its permeability [4]. Repair of existing structures is nowadays one of the mayor concerns in construction. The trend is to minimize the amount of damaged concrete to be replaced during the reparation by developing more economic solutions, such as electrochemical repair methods, aiming on the removal of the aggressive agent (realkalisation or chloride removal) [5]. These techniques are based in the connection of an electric field between the reinforcement, acting as a cathode, and an external anode. Although the application of these electrochemical repair methodologies has already been standardized, several uncertainties concerning the long-term efficiency of the treatment remain.

Nowadays, new developments are emerging to improve the long-term performance of electrochemical repair treatments by modifying the procedure of application. The transport of nanoparticles, more particularly nano-SiO_2, through the concrete pores as the final stage of the electrochemical repair treatment is one of the most promising actuations [4, 6-7] hindering the further penetration of aggressive agents. The self-healing properties of the nano-SiO_2, as for instance by reacting with the calcium hydroxide of the cement paste like in a pozzolanic process, will promote the sealing of pores reducing the porosity of the concrete surface.

In this paper, the ability of colloidal silica nanoparticles to transport by electromigration through the concrete is analysed. The migration mechanism and the interaction between the concrete and the nano-SiO_2 have been assessed for two different commercial products.

2. MATERIALS

The study was carried out with mortar samples manufactured with Ordinary Portland Cement (OPC), normalized sand and deionized water. Cylindrical mortar samples of 7.5 cm were manufactured with a 0.5 w/c ratio and a 1:3 cement sand ratio. After 7 days of curing in chamber at 98±2% relative humidity and 21±2 ºC of temperature, samples of 1 cm thickness were cut for migration tests. Before testing, mortar samples were saturated by immersion in water for 24 hours under vacuum conditions. Two different commercial colloidal silica suspensions lightly negatively charged were studied: the first one at 30% and the second one at 40% concentration by weight, with a particle size of 7 nm and 12 nm respectively.

3. METHODS

The cell employed in the migration tests is shown in Figure 1. The cell consists of two carbon steel electrodes, each one located to each side of the cell, and connected to a 12 V voltage supply. The mortar sample is located at the centre. The nano-SiO_2 suspension was placed in the compartment connected as cathode (catholyte) in order to promote its behaviour to the anode (anolyte), filled with distilled water. Samples were identified as 30% and 40%. To evaluate the effect of the electric field on the mortar, a migration test using distilled water in both sides of the cell (sample named RH2O) was also carried out. Migration tests were carried out in 8 days approximately.

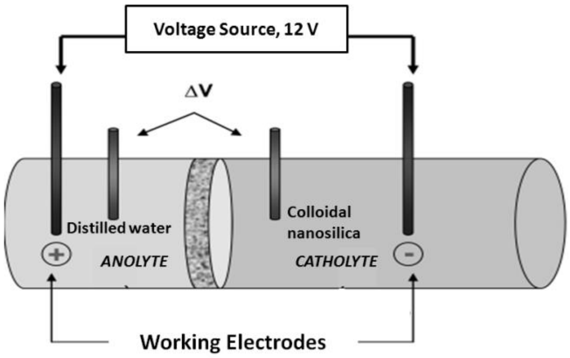
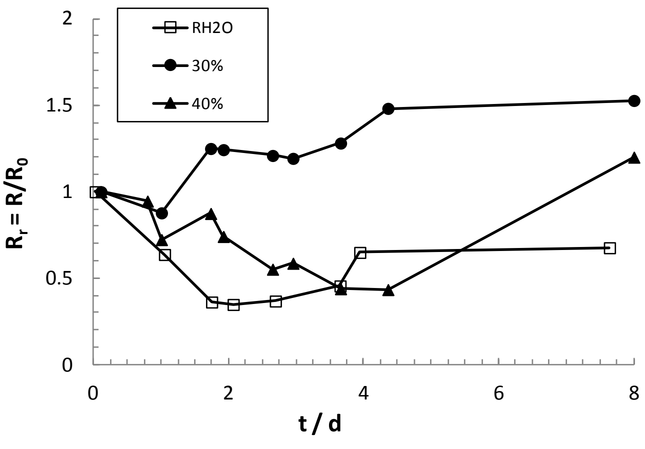


Figure 1: General scheme of the migration cell configuration.

Electrical and chemical measurements were periodically taken during the testing and at the end. Initial and post-treatment resistivity measurements were conducted in the mortar tested samples. After treatment, samples were dried at 40ºC and mercury intrusion porosimetry tests, SEM observation and EDX analysis were carried out after 28 days.

4. RESULTS

The migration of colloidal silica nanoparticles to the interior of hardened mortar under the application of an external electric field shall be enhanced from the catholyte (negative pole) to the anolyte (positive pole) due to the negative charge of nanoparticle suspension employed. The mobility of the monodispersed colloidal silica particles may be affected both by the variables of the experimental process and by the electrochemical nature of the solution [8]. During the testing the electric response of the system was monitored by registering the voltage between both sides of the mortar sample and the current in order to estimate the evolution of the resistance values. In Figure 2 the evolution of the relative electric resistance (R_r), referred to the initial value (R_0) has been included. The influence of the type of nano-SiO_2 suspension can be deduced from these results.



Sample	***Relative resistivity ($\rho_{final}/\rho_{initial}$)***
30%	2.1
40%	2.0

Figure 2: Left - Evolution of the relative electric resistance (R_r) during the treatment at 12 V. Rigth – Relative resistivity in samples after the treatment at 12 V.

The application of the electric field without nano-SiO_2 (RH2O sample) promotes the decrease of the mortar relative resistance probably due to the extraction of different ions to the anolyte and to the catholyte depending of the ionic charge. In the case of nano-SiO_2 penetration, even though the decrease of the relative resistance also occurs during the first days of testing, after a certain period of time an increase of this parameter is registered: after two days of testing in the case of 30% and after 4 days of testing in the case of 40%. This increase of resistance could be associated with a reduction of the porosity in the mortar hindering the transport of ionic species. In this sense, also a significant increase on the mortar resistivity after the treatment with nano-SiO_2 was registered (table of Figure 2-Rigth) if comparing with the initial value of resistivity measured before the migration test.

The mercury intrusion porosimetry results also confirmed the efficiency of the nano-SiO2 in sealing the mortar pores after an electromigration treatment, as can be deduced from Table 1, where the total porosity values as well as the percentage of pores of different size are resumed for the untreated mortar (R0) and the mortar samples after the different treatments.

Sample	***% <0.1***	***% change***	***% 0.1-1***	***% change***	***% 1-10***	***% change***	***% >10***	***% change***	***Total poros.***
R0	40.89		47.29		7.76		4.19		16.76
RH2O	38.62	-2.26	50.55	+3.26	4.55	-3.21	6.40	+2.21	16.64
30%	47.90	+7.01	33.82	***-13.47***	11.03	+3.27	7.40	+3.21	14.34
40%	38.02	-2.86	43.59	***-3.70***	12.81	+5.05	5.71	+1.52	15.06

If the total porosity is considered, only a minor decrease is measured after the treatment with the nano-SiO_2, slightly higher in the 30% sample. Furthermore, a significant decrease of the pores with size between 0.1 – 1 μm is observed when the nano-SiO_2 is transported through the mortar pores, and thus, it is expected that the nano-SiO2 has been able to enter into the mortar matrix and to flocculate and react with the cement paste matrix.

EDX analysis conducted in cross-section of the study samples shows the reduction of the Ca/Si ration in the negative border of the sample when treated with nano-SiO_2 (values between 1.50 and 1.10 have been measured while a mean value of 1.80 can be considered for a conventional cement paste). Thus, the reaction of nano-SiO_2 with portlandite can be expected, in similar way than reported for studies with addition of nano-SiO_2 in fresh conditions [9], and self-healing properties of nano-SiO_2 added to hardened mortar by electromigration are confirmed.

5. CONCLUSIONS

Electromigration of colloidal silica nanoparticles to the interior of hardened mortar is possible under the action of an electrical field. The composition and nature of the nano-SiO2 suspension influences the transport of the nanoparticles: it seems to be faster in the case of 30% with smaller size (7nm vs 12 nm). The sealing of capillary pores is expected to occur by reaction of nano-SiO_2 with calcium compounds of the cement paste.

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