PROTECȚIA ELECTROCHIMICĂ, CU PARTICULE DE NANOSILICE, A PASTELOR DE CIMENT PORTLAND ÎNTĂRITE

ELECTROCHEMICAL PROTECTION OF HARDENED PORTLAND CEMENT PASTE USING NANO-SILICA (SiO_2) PARTICLES

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The aim of this work was to study the effect of the interaction of colloidal nano SiO_2 (NS) with a hardened Portland cement paste (PCP). An electric circuit arrangement with two electrodes was used to create an electric field around a PCP sample. NS was used as catholyte and water as anolyte to assure electric conductivity. Results obtained using an optical Microscopy and Scanning Electron Microscopy showed that NS particles reached a distance up to 1.5 mm from the surface in contact with the PCP sample to the interior of the sample. Energy dispersive X-ray Spectroscopy showed an enrichment of Si in the zone where NS migrated. An alteration of the Ca/Si ratios was also observed, with values below of both conventional **anhydrous and hydrated phases*****. Thermo-gravimetric analysis (TG) showed that NS affected the content balance between CSH gel and $Ca(OH)_2$ in a migrated NS sample compared with a reference sample; this could represent an evidence that NS affected the cement matrix with a possible pozzolanic reaction even after the hardened stage of the PCP.***

Keywords: *Electrochemical migration, nano SiO_2, Portland cement paste.*

1. Introduction

One of the most recently investigations focused on nano materials are the nano SiO_2 (NS) particles, which can modify the properties of cementitious material in both fresh and hardened stage. The use of these NS particles in Portland cement based materials (PCM) can modify the rheological properties and workability in the fresh stage of the mixture. According to Erhan et al [1-2], the slump flow diameter is reduced and the flow time is decreased when NS is added to the mix in self-compacting concretes in fresh stage.

Other studies [3] show that NS can interact in the first stages of the cement hydration as elements which can modify the water demand and thus modify the characteristics of the fresh stage. It is well known [4-8] that NS can act as an element which improve the characteristics of hardened cement matrix because NS works as nucleation sites for new CSH phase, beside the normal CSH gel from the cement particles hydration. This new CSH gel has a physical effect (working as a filler material) and a chemical effect [9-14] (working as a pozzolanic reaction promoter) which result in the optimization of compressive and mechanical properties of PCM.

The interaction of NS when it is electrochemically migrated through a Portland cement hardened paste is the main objective of this work. This could lead to the densification of the cement matrix and the refinement of the pore system in order to modify the transport mechanisms involved in the deterioration of PCM. Thus, the risk of decreasing the life time of these materials and structures is reduced when they are exposed to aggressive environments like chloride ions or CO_2 enriched atmospheres [15-20].

Surface treatments have been studied as procedures to protect PCM using some methods such as carbonated precipitation, ethyl silicates, polymer/clay nano composites, epoxy coating and paints, among others. Different performances have been observed, with common drawbacks such as substrate bonding problems or undefined mechanisms [21-24]. With the objective of solving these problems, the use of an electric field to move charged particles into the concrete from the surface through the pore system has been studied by some authors [25-26]. However deeper and wider knowledge about the mechanisms involved in the process is needed. In order to obtain more information about the migration process, this work aims to analyze the interaction of NS and a PCP, without the presence of sand aggregate.

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2. Conditions and experimental procedure

2.1. Portland Cement Paste specimens

In order to fabricate PCP samples, an Ordinary Portland Cement (OPC 42.5, clinker 95-100%, chlorides 0.1%, sulphates 4%) was required. The content of the main calcium phases was: C_3S=57.91%, C_2S=6.28%, C_3A=3.82% and C_4AF=15.44%. The fabrication procedure was according to the ASTM C109 standard [27] but sand was not used because the experiments were focus only in cement paste. It has been observed that certain kind of sands can interfere with the detection of the NS in the microstructure of PCM [25]. A water-cement ratio of 0.485 was used in the mixture. Higher water-cement ratios could be used to obtain a bigger void volume in the microstructure and promote a better migration, but standards were used to obtain similar results to real practice. The fabricated samples were discs with a diameter of 5 cm and a height of 5 mm. After demolded,, the samples were cured under water during 7 days before experimentation to assure water saturation and a better electric behavior.

2.2. Colloidal Nano SiO_2

The NS used for the experiments was a colloidal nano SiO_2 at 30%wt with a particle size of 7 nm, a pH value of 8 and a negative electric charge. A test was carried out to analyze the mass loss (water content) in the colloidal NS and to observe the mass corresponding to the NS. This test was a comparison between two containers with NS: one of them in a muffle at 100°C and the other in a lab desk at room conditions (24-26°C). The mass loss test was used to observe the behavior of the NS when water is removed and SiO_2 particles are forced to bond.

2.3. Electric field circuit connection

The arrangement used for the experiment consisted in a set of electrodes located in both sides of a PCP sample inside of a container (as shown in Figure 1). Once the electrodes were located, the upper electrode was connected to the negative pole and the other was connected to the positive pole. Then, NS was poured in the container in contact with the negative electrode and positive electrode was immersed in water to assure a better electric conductivity. The experiment was carried out with a potential difference of 12V during 7 days and direct current (mA) was measured during all the days to analyze the electric response of the PCP.

2.4. Thermo gravimetric and X-Ray Diffraction analysis

Thermo-gravimetric analysis were used in NS samples and references samples in order to study the expected pozzolanic reaction between Portlandite ($Ca(OH)_2$) and migrated NS. These TG experiments are used to determine the mass loss associated to each phase (Portlandite and C-S-H gel) because they have different characteristic intervals of temperature related with their decomposition. The TG experiment was carried out from 0°C to 1000 °C with a heat rate of 10°C/min. For Porlandite, the temperature interval is 100°C to 350°C and for C-S-H gel is 350-450°C. Once the TG equipment finish the experiment, percentages (%) are determined according to results.

The mass loss test experiment also allowed to obtain a solid phase of the NS which was used for X-Ray diffraction analysis to determine the crystallinity or the structural order of the NS nano particles.

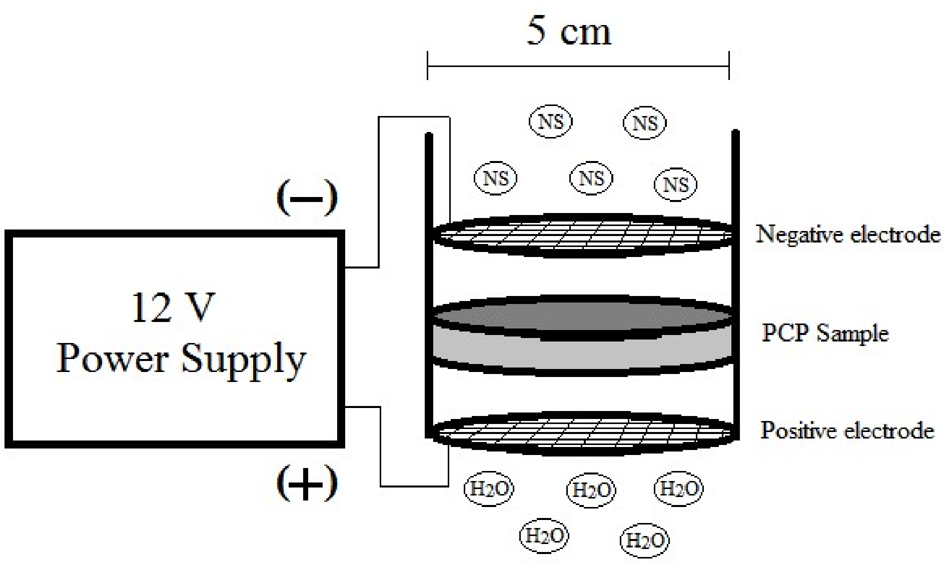

Fig. 1 - Circuit connection of the power supply and the electrodes with a PCP sample.

3. Results and discussion

3.1. Mass loss and XRD analysis

Figure 2 shows the preliminary test of mass loss carried out in two containers with NS. In the chart, it can be observed that colloidal NS lost 72.2% of its initial mass in the first 6 hours at 100°C. After this time, no significant changes were observed despite the test lasted 700 hours. On the other hand, the container at room conditions showed that the rate of mass loss was proportional to the time variation. At the end of the test, the container at room conditions displayed a mass loss of 63.7%. It can be inferred that the remaining mass in the containers (27.8% and 36.3%, respectively), correspond to the agglomerated NS particles. Those particles were expected to move into the PCP microstructure.

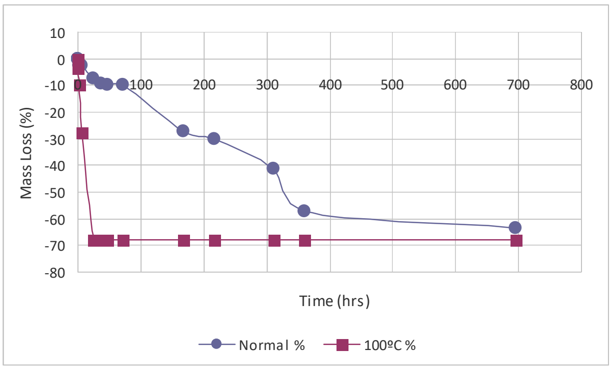

Fig. 2 - Mass loss test between NS at 100°C (squares) and NS at room conditions (circles).

Once the NS solid phase was obtained (after the mass loss), it was grinded until reach a proper size for XRD analysis. Figure 3 shows the XRD analysis where it can be noticed the amorphous nature of the NS, necessary to promote the pozzolanic reaction [28-29] in PCM's.

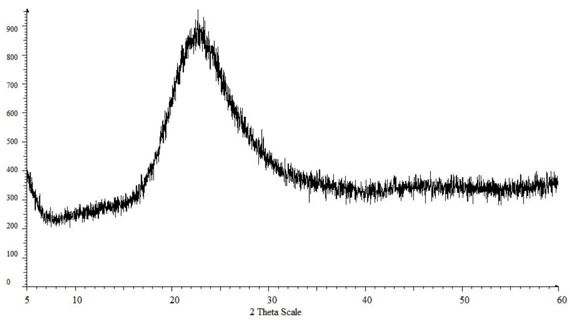

Fig. 3 - XRD analysis of dried and grinded colloidal NS, showing amorphous characteristic.

3.2. Electric connection of the PCP

As a background, in a previous work [30], two cement mortar samples were connected to a power supply (6V, similar arrangement to that described above) to observe the effect of having NS as catholyte (the side in contact with the negative electrode). The results were compared with treatments having water instead of NS. The electric behavior of these samples was analyzed using the electric resistance (Ω).The sample with NS reached an increment of 260% of its initial electric resistance value, meanwhile the sample with water exhibited an increase below 50% of its initial value until the end of the experiment. From this experiment, it can be inferred that NS affected the electric properties of cement mortar samples. As the electric conductivity is related with the pore system of the cement matrix [31,32], is feasible to imply that migrated NS affected the pore system at least by a filler effect in the outer zone (interface colloidal NS/PCP).

The pore system is responsible for most of the transport mechanisms in PCM and represents the entrance for fluids, gases, particles and ions to the interior of the cement materials and structures. Once the PCP sample was connected to the power supply (as shown in Figure 1), direct current passed through the circuit during 7 days. The measurements are shown in Figure 4. The chart shows an initial value of 47 mA, which significantly decreased during the first 24 hours to a value of 16 mA. After that, the values decreased to a final value of 8 mA. It is important to notice that a high variation of current was shown during the first 24 hours; this could be attributed to the applied potential difference (12V), which is enough to generate 47 mA at the beginning but then the NS rapidly starts to move into the PCP sample (first 24 hours), sealing the pores and reducing the space where charged particles can move. At the end, NS agglomerated in the surface of the sample and a NS solid phase was generated.

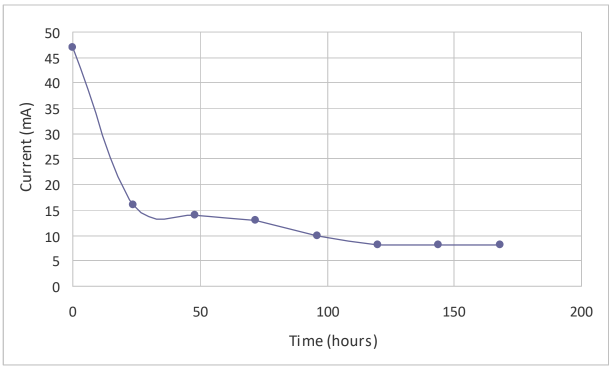

Fig. 4 - Direct current behavior in a PCP sample with NS as catholyte at 12V during 7 days.

3.3. Visual inspection by optical microscopy

Once the experiment ended, the PCP sample was extracted from the power supply and it was cleaned for visual inspection. It was observed a solid phase of the NS in the surface of the sample which was strongly bound to the interface. To obtain a better view, the sample was fractured in half and a cross section view could be observed (Figure 5). It can be noticed a significant alteration in the appearance of the paste, where the zone in contact with the NS (upper) shows a light grey coloration, different from the dark grey zone below. This light grey zone has a distance between 1.2 mm and 1.5 mm from the surface to the inner of the sample. The color difference could be appreciated with naked eyes.

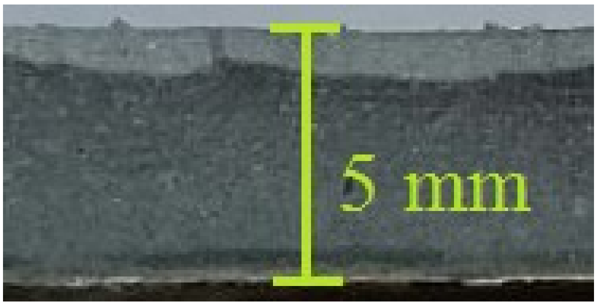

Fig. 5 - Image by optical microscopy of a cross section of the PCP after NS migration.

3.4. SEM-EDS analysis

Backscattering electrons (BE) detector mode was used to analyze the sample in both zones observed by optical microscopy (light and dark grey). The analysis consisted in the observation of the microstructure from the surface in contact with the NS (Figure 6a), passing through the interface between light and dark grey zones (Figure 6b), to the inner of the sample (Figure 6c). It can be observed a significant difference between the two zones in the composition of their microstructures; dark grey paste showed a considerable amount of *anhydrous phase* (white signals). Then, EDS was used to identify the chemical composition of some points in the microstructure to determinate the Ca/Si ratio along the cross section.

As can be observed in Figure 7, the relation between the content of Ca and Si varied according to the distance from the surface. C_3S and C_2S had a Ca/Si ratio of 3 and 2 respectively and a conventional C-S-H gel usually has a Ca/Si ratio between 1.5 and 1.7. Figure 7 shows values of Ca/Si below of the conventional anhydrous and hydrated products, which mean that an enrichment of Si occurred from the surface up to 1.5 mm to the inner of the sample. Below the interface, normal values of Ca/Si corresponding to a conventional PCP were found.

In order to validate that the values of Ca/Si corresponding to an enrichment of Si and do not involve a Ca loss, a mapping by EDS was carried out in the interface zone and it is shown in the Figure 8. The Figure 8(a) corresponds to the mapping of Si and the Figure 8(b) to the mapping of Ca. As it can be observed, the mapping of Si showed a higher number of Si signals in the upper half; this means that the presence of this element was concentrated in the light grey zone. In the case of the mapping for Ca, the signals were distributed homogeneously.

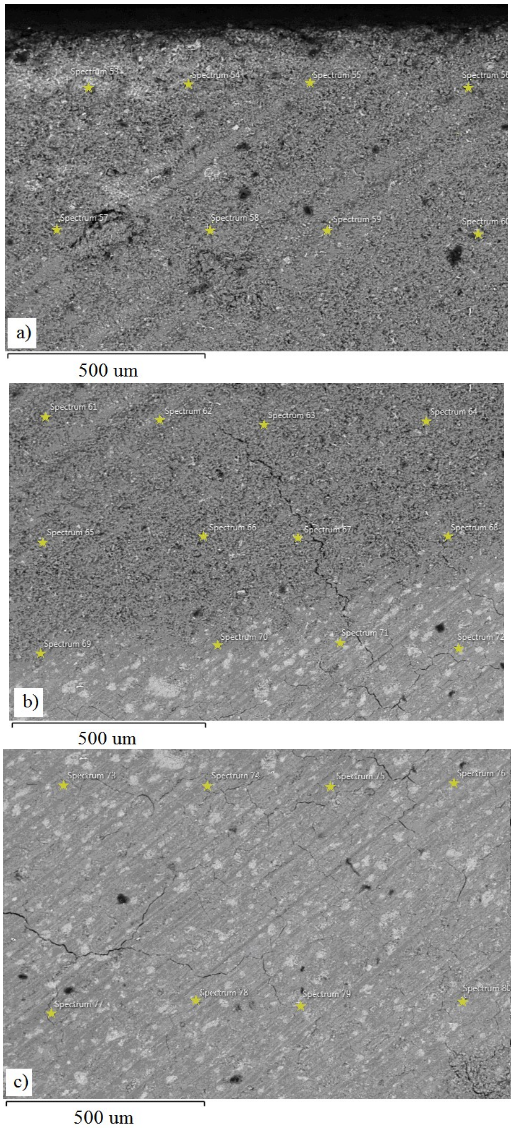

Fig. 6 - SEM-BE images of the cross section of the PCP sample after NS migration. EDS point analysis are indicated (scale 500 μm). Surface in contact with NS (a), interface zone (b) and dark grey zone (c).

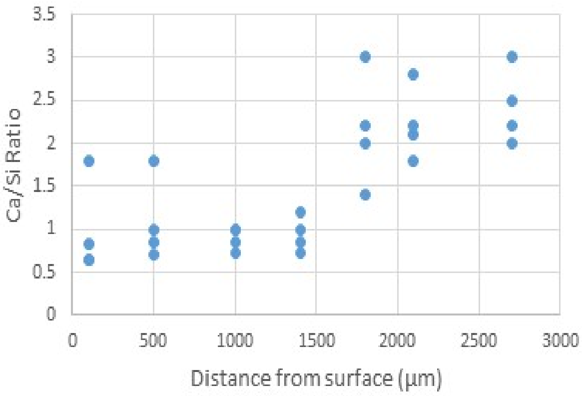

Fig. 7 - EDS analysis for Ca/Si ratio calculation from the surface of the PCP sample to the inner.

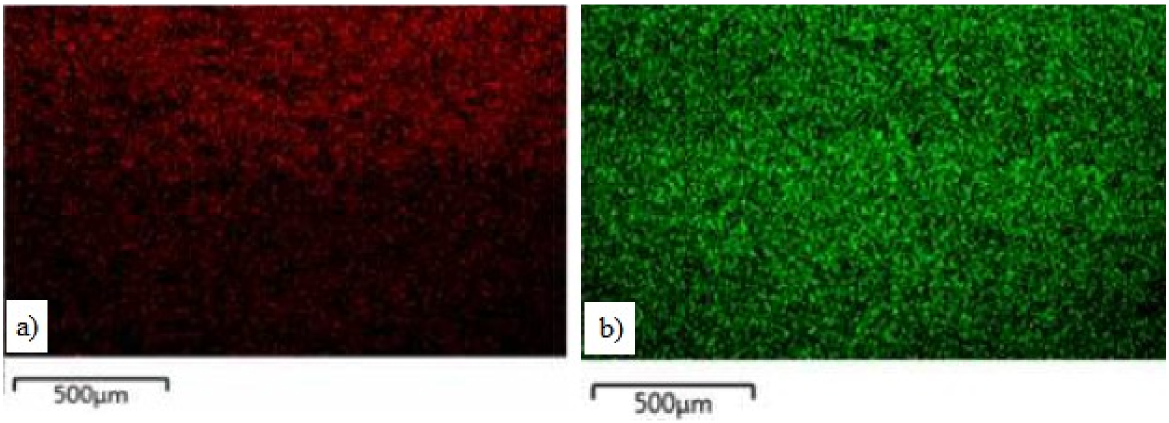

Fig. 8 - Mapping for Si (a) and Ca (b) in the interface zone of a PCP sample after NS migration.

3.5. Thermo-gravimetric analysis

To study the possible pozzolanic effect of the migrated NS in the cement matrix, Thermo-gravimetric analysis (TGA) were carried out to measure the mass loss in the characteristic temperature ranges for C-S-H gel (100-350°C) and Portlandite ($Ca(OH)_2$, 350-450°C). In Table 1 the mass loss percent for each of those intervals for TGA samples are shkwn: one sample was taken in the light grey zone (migrated zone) and other was a reference PCP sample. According to the results obtained, the migrated sample showed a higher mass loss than the reference sample in the range of 100-350°C.This means that a higher content of this phase was found because of NS migration. In consequence, if new C-S-H gel is stimulated, a consumption of Portlandite should be present in the migrated sample. This hypothesis was demonstrated at the range of 350-450°C, where a higher mass loss was observed in reference sample. Therefore, this phase presented a higher content than reference sample.

Table 1

TGA analysis of an enriched Si paste and a reference paste

Sample	Mass loss % (100-350°C)	Mass loss % (350-450°C)
Migrated sample	8.67	2.65
Reference	8.1	3.77

4. Conclusions

According to the results from this study, it can be concluded that:

1. The applied voltage (12V) could generate an electric current to pass through a PCP sample. The behavior of this current was affected by the presence of colloidal NS, which significantly decreased due to a phenomenon where the colloidal NS charged particles moved towards the direction of the PCP sample and agglomerated it in the surface, creating a solid phase which starts to seal the porous system.

2. According to the results of optical and electron microscopy, NS particles could penetrate a distance of 1.5 mm into the cement paste microstructure and change its appearance. The presence of the migrated NS was demonstrated by SEM-EDS analysis, where Si enrichment was observed and it caused the alteration of the Ca/Si ratio of the microstructure. Below the affected zone (1.5 mm), the evaluated Ca/Si ratios were found in the values corresponding to a conventional PCP in both anhydrous and hydrated phases. The mappings in the interface zone showed a high presence of Si in the affected zone, without a significant effect in the content of Ca in the entire matrix.

3. Thermo-gravimetric analysis showed that the migrated NS had an effect in the content balance of C-S-H gel and Portlandite. Based on the results obtained, NS increased the content of the C-S-H gel and decreased the Portlandite phase, compared with a reference PCP sample. This could be related to a pozzolanic reaction when the NS interacts with a hardened PCP.

4. The permeability of the PCP is highly related with its porosity and that depends on the grade of hydration in the PCP microstructure. It can be said that the porosity is a result of the normal process of hydration of cement particles, because there is always a space where C-S-H gel (and other hydration products) can not reach and thus, a system of interconnected pores is created inside the microstructure. This pore system is responsible of a lot of harmful process which affect and deteriorate the PCM's because is the entrance of all kind of aggressive particles like chlorides ions, CO_2, sulfates, among others. Migrated NS can help to seal the surface due its filler and pozzolanic effect when interact with a PCP matrix and reduce the effect of the transport mechanism of aggressive particles to the interior of the materials.

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