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Effect of the Electrochemical Migration of Colloidal Nano-SiO_2 on the Durability Performance of Hardened Cement Mortar

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Colloidal nano-silica was used as a superficial treatment in cement mortar sample by electrochemical migration under an electric field. An electric circuit was configured in order to perform direct current through a hardened mortar sample and to force charged particles of nano-silica move into the pore system of the microstructure and to affect the durability properties of the samples. The behavior of the electric current through the time in the presence of a mortar surface was analyzed. Also, durability tests were carried out by accelerated chloride and CO_2 test. The microstructure was analyzed by Scanning Electron Microscopy and Energy dispersive Spectroscopy coupled. Results show that nano-silica is able to move into the microstructure by migration treatment and affects the chemical composition (Ca/Si, C-S-H ratio) of the mortar sample; thus, affecting the properties of gas and liquid penetration resistance of the cement material.

Keywords: Migration, Colloidal Nano SiO_2, Durability, Electric properties

1. INTRODUCTION

The durability performance of reinforced concrete structures is one the most important topics when discussing about sustainable building industry. A lot of recent studies have been carried out in order to improve the future of construction science[1]. One recent attempt, is the use of colloidal nano-SiO_2 (NS) as an ingredient in the design of cement mixtures in order to improve the properties in cement materials. NS has shown that it can affect properties such as compressive strength and capillary absorption, due to its potential to form a denser matrix, which is obtained by two different mechanisms: a) acting as a promoter of new C-S-H gel from byproducts of the initial hydration process ($Ca(OH)_2$); and b) acting as a filler material due to its particle size, sealing those pores which allow the penetration of deleterious agent from the environment [2-10]. In this research, the use of NS has been investigated as an electrochemical surface treatment with the aim of obtaining a sealing effect in the sample test surface, and therefore increasing the resistance to the entry of aggressive agents which could deteriorate the durability, like chloride ions or CO_2.

The proposed treatment is migration (transport of particles under electric field) of NS through of hardened cement mortar (HCM) sample in a cell arrangement designed for this purpose. The main objective is to study the feasibility of NS particles to be moved due to the electrical nature of their surface and being transported inside the porous system of the cement mortar to obtain a sealing effect. The cell arrangement designed in a configuration of an electric circuit based on HCM sample between two electrodes, was connected to a direct current power supply. The principle is that NS particles are forced to move into de HCM to a later interact in both chemistry and physical way just like when NS is added at fresh stage [11-17].

Once the migration experiment was carried out in the samples and NS surface treatment was performed, HCM samples were analyzed in order to study the effect of the treatment and its durability performance in two accelerate deteriorating test: chloride ion penetration and CO_2 penetration. Also, water absorption tests were carried out in all the samples. The microstructure of samples was studied by Scanning Electron Microscopy with an Energy Dispersive X-ray Spectroscopy (SEM-EDX) and it was found that NS can reach a migration depth distance around of 1.5 mm from the contact surface, according to lower Ca/Si ratios compared with those ones found in reported reference HCM samples [22]. Tests samples were compared after migration, with reference samples (without migration tests) and samples with addition of NS at fresh stage in order to compare the efficiency of the method of sealing effect. Electrical measurements (resistance and direct current evolution) were taken to study the effect of electric current within the cement matrix.

2. MATERIALS AND METHODS

2.1 HCM samples fabrication

Ordinary Portland cement (OPC, clinker 95-100%, chlorides 0.1%, sulphate 4%) was used to fabricate HCM cylindrical samples (height 2.5 cm, diameter 2.5 cm) with a $CaCO_3$ aggregate in a ratio of 3:1 and a water-cement ratio (a/c) of 0.5, according to the standard specification of the ASTM C109 [23]. Samples were demolded after 1 day of curing and stored in a moisture room with a temperature of 22°C ± 2°C and a relative humidity of 95 ± 5% for 7 days, before NS migration treatment. A suspension of colloidal nano-SiO_2 at 30% wt. was used for the experiment, with a particle size of 7 nm, a pH of 8 and a slightly negative charge. Reference samples made to compare the treatment effect were elaborated with the same specification. Additionally, samples with NS added at fresh stage were fabricated.

2.2 Cell assembly and connection

In order to expose the HCM samples to NS under an electric field (migration), cells were designed as shown in Figure 1. These cells consist of an acrylic cylinder attached to the HCM sample by a silicon based adhesive (cold setting) where either the NS solution or deionized water (catholyte) were disposed (50 ml). Inside of the cylinder, a negatively polarized electrode (stainless steel) was installed in the surface of the sample, and a positive one was installed below the HCM sample. Therefore, an electric field configuration could be set through the cell. This configuration allows the NS (negative surface charge) to be transported from top to bottom. The negative electrode was submerged in the NS and the positive electrode in water, in order to assure the electric conductivity in the circuit. HCM samples were exposed a similar treatment using only water instead NS as catholyte in order to evaluate electric field effect on HCM.

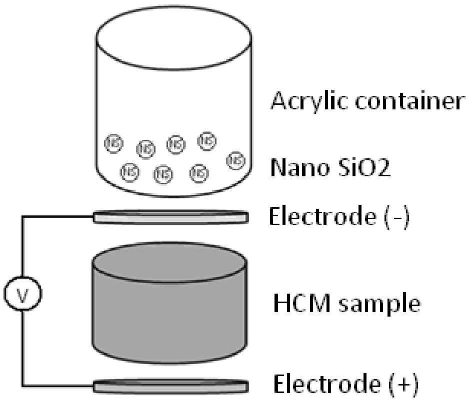

Figure 1. Scheme of the migration cell used to NS treatment containing (from top to bottom) the colloidal NS, negative electrode, HCM sample and positive electrode.

At this point, it is important to noticed that the current limit of the power supply is 5 A, but in a previous test it was proved that each cell do not generate more than 2 mA, so the current limitation is assured. Once the circuit was assembled, the electrodes were connected to the power source and an electrical potential difference of 6 volts was set in the system for 3 and 7 continuous days (Samples A3 and M3; and A7 and M7). The scheme of the circuit arrangement can be seen in Figure 2. The different samples used in this work are listed in Table 1.

Table 1. Conditions of cement mortar samples.

Sample	Description
A3	Migration, H_2O/H_2O (3 days)
A7	Migration, H_2O/H_2O (7 days)
M3	Migration, NS/H_2O (3 days)
M7	Migration, NS/H_2O (7 days)
Reference	Reference sample without migration
NS addition	Sample with NS added in fresh stage

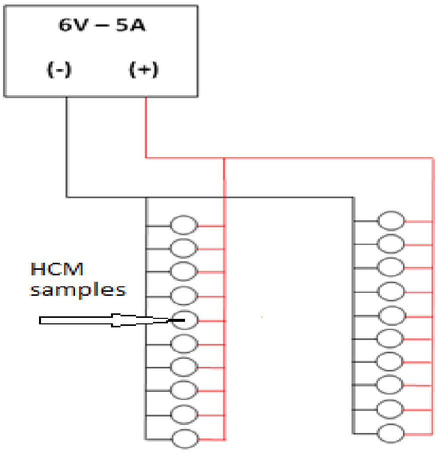

Figure 2. Scheme of the electric circuit connection (parallel) where HCM samples were connected to both positive and negative poles in order to have an electric current passing through the samples.

2.4 NS addition in fresh stage

In order to compare the application of NS as a surface treatment, NS was also added to the mix at fresh stage, and then tested in the same way that references and migrated samples. Colloidal NS was added by 5%wt. of the cement (considering NS as addition) with the same water/cement and aggregate/cement ratio of other samples and cured under the same conditions.

3. RESULTS AND DISCUSSION

3.1 Electrical test of HCM

Before testing cells with electrical field, an exploratory test was performed to observe the direct current (mA) evolution in NS and water as a catholyte, where both negative and positive electrodes were placed in contact with a container with water and another with NS during 5 days. Figure 3 shows the evolution of the current in each test. As it can be seen, water has a very stable behavior between 4 and 6 mA through the test time and just small variations of ± 1 mA were registered at the end. Evolutions of gas and corrosion signs were also observed in the electrodes, because of the normal process of redox reaction. In the case of NS, a very high value of conductivity was observed at the beginning of the test (compared with water) with 38 mA, but a strong tendency to decrease through the test, until a final value of 3 mA. Also, gas evolution and corrosion signs were present, but a significant agglomeration of NS was found in the positive electrode, where NS seems to flocculate around the electrode and form a solid material. This precipitation process could be the main cause of the decreasing current evolution measured in the equipment, because the ions (charged particles) hardly pass this solid barrier.

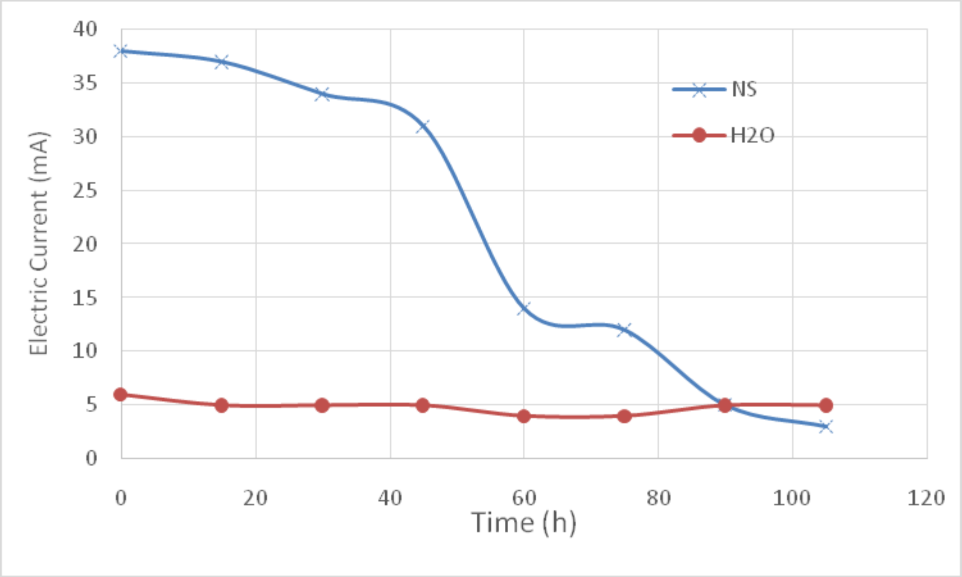

Figure 3. Direct current (mA) evolution passing through a) colloidal NS suspension (cross) and b) ordinary water used in the cells (circles) during 5 days to compare their capacity conduct electric charged particles.

After testing the conductivity of water and NS, the electrical resistance measurements of the cells were analyzed, this value indicates the connectivity grade of the porous system and its capacity to conduct electric charge (a denser microstructure means a highest electric resistance).They are shown in Figure 4 for a migration test during 3 continuous days; and Figure 5 for the cells during 7 continuous days.

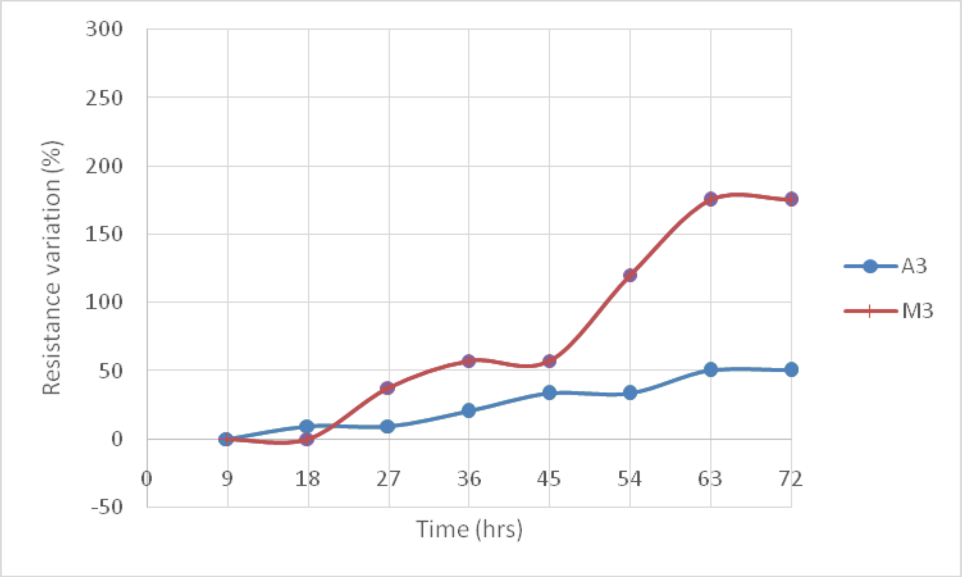

Figure 4. Electric Resistance behavior during 3 days under electric field for HCM samples with NS (M3) and water (A3).

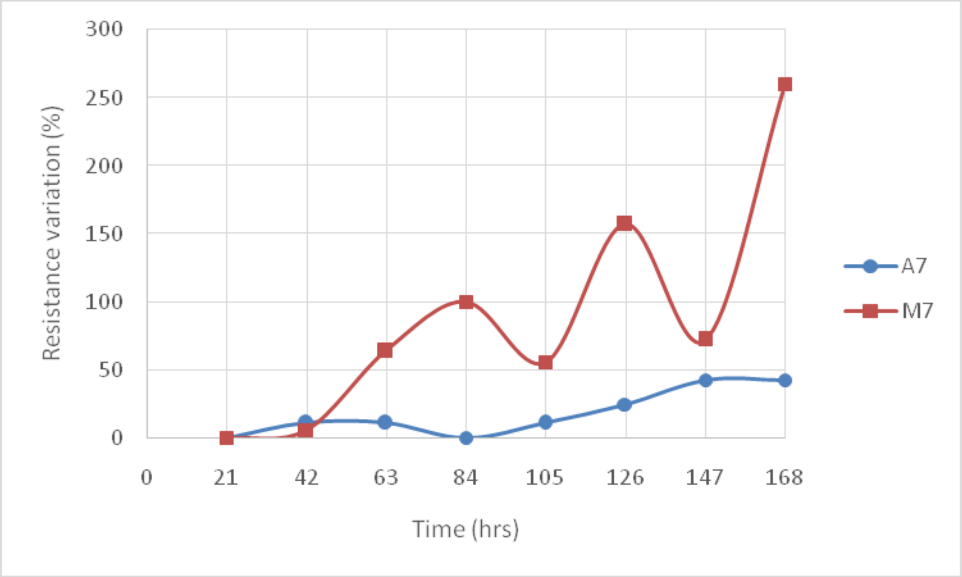

Figure 5. Electric Resistance behavior during 7 days under electric field for HCM samples with NS (M7) and water (A7).

This electric resistance was calculated from measured values of voltage and current from the power supply and a multimeter, according to the Ohm's law. An HCM sample was tested under electric field without NS (water in both positive and negative electrodes) in order to observe the effect of the DC on the HCM. In the case of 3 days, the resistance of the water/water HCM test sample (A3) has a tendency to slightly increase through the time with a maximum variation of 50%, whereas the migration sample (M3) shows a tendency to significantly increase until a final increment of 175%.

In the case of the samples under electric field after 7 days, the cell with water in the two sides follows the same behavior that A3, which means that probably its electric resistance will remain stable through the time. For the migration sample after 7 days (M7), again a tendency to increase is followed and a final variation reaches the 260% of the original value. This increment of electric resistance was also found in the studies of Sanchez et al [2], where a progressively increment of the resistance of ion movement during a NS treatment in HCM samples is mentioned. They applied different levels of voltages and particle size, but all with the same tendency to obstruct the pass of charged particles into the microstructure. The increment of the electric resistance can be related to the penetration of the NS in the porous system and its deposition, causing the reduction of the space for ions to be moved through the HCM microstructure.

3.2 Microscopy Analysis

A polished surface of a cross section of a mortar sample after NS migration treatment was analyzed by microscopy. The image corresponds to the surface in contact with the colloidal NS. The samples were polished using silicon carbide sandpaper in order to obtain a more detailed surface and to identify the effect of the NS penetration. In Figure 6, the way of the cross fracture of the sample to be analyzed can be observed. Images of the sample showed a modified section in the side in contact with the NS, which presents a different appearance from the rest of the mortar surface with an approximate depth distance of 2.2 mm, which was further analyzed with SEM.

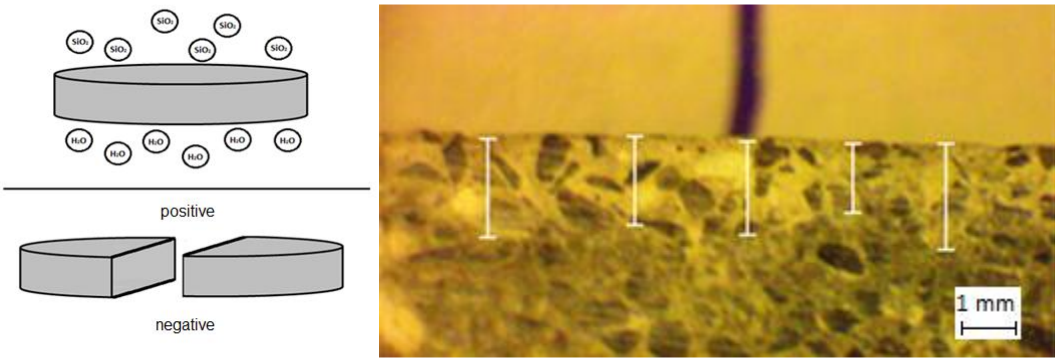

Figure 6. Cross fracture for optical analysis of a sample after NS migration. The two sides (NS surface and water surface) of the samples were identified to be compared in optical and electronic microscopy.

3.3 SEM analysis

Samples were analyzed after NS migration by SEM, using backscattering electrons and an EDS coupled detector. A voltage of 20 kV and a work distance of 16 mm was used. The image in Figure 7 shows a zone where Ca/Si content ratios were measured, which values are lower than cement hydration conventional products for a cement paste in a depth around 1 mm from the surface in contact with NS. Ca/Si between 0.5 and 1.1 do not correspond to the normal C-S-H gel values and it can be inferred that and enrichment of silicon could be carried out after the NS treatment. Also, normal values between 1.5 and 1.7 were found around the particles with the modified Ca/Si ratio, thus it can be inferred that the NS interaction is non uniform through the sample matrix.

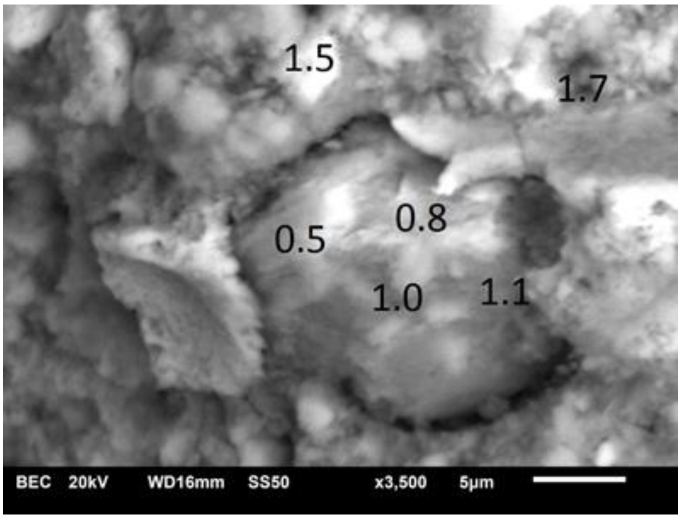

Figure 7. SEM analysis (backscattering electrons and EDX detector) of a sample after migration with Ca/Si ratios shown in a zone with silicon enrichment in a depth of 1 mm, surrounded by ordinary C-S-H gel.

The reason of these lower Ca/Si values is the moving of NS particles from the surface through the porous in the microstructure because of the electric field. And according to similar results of Sanchez et al. [2], where Ca/Si ratios were found (NS treated samples≈ 1, control samples= >1.5), these particles move into the mortar sample and fill up the space available in the microstructure and then start to act as a source of silicon in the surrounding phases. Reductions of Ca/Si ratios present in this SEM analysis agree with the phenomenon found by Hou et al. [3] as well, where samples treated with NS promote the obtaining of lower average Ca/Si ratios compared to control and also Ca/Si values below of their standard deviation (up to Ca/Si:1).

3.4 Chloride ion diffusion and accelerated carbonation test

For chloride ion diffusion evaluation, the samples were cracked in the middle and the test was performed by image analysis of a color change when a solution of silver nitrate (AgNO3) is applied on crack surface. A color change is presented when there is not chloride in the cement surface and the distance, in the case of change, was image analysis measured and registered. A solution of NaCl at 3% was used for the test and samples were immersed in the solution during the test time. For carbonation test, the samples were stored in an accelerated carbonation chamber with a temperature of 30 °C, a relative humidity of 52% and a CO_2 concentration of 5%. Once the samples have the required time under carbonation, they were fractured and, in the same way that chloride test, phenolphthalein is applied in the surface; again, the zone with no carbonation presents a color change and the affected zone is measured with an image analysis software according to the reduction of the pH and the color change from this.

For both tests, samples were prepared with a cover of epoxy paint in all its faces except one, where the chloride and CO_2 have contact. The exposed face to NS in the samples with migration was that without epoxy coating.

As it can be seen in Table 2, the reference (without treatment) samples have the higher values of penetration in both CO_2 and Cl^- test, showing that NS could have a positive effect when is applied to the mortar samples even after hardened state. Samples with NS addition at fresh stage show penetration distance (Cl- and CO_2) values higher than samples after migration. NS can modify the requirements for cement mortar fabrication, but in this work, the same conditions (aggregate and water ratios) were taken for all samples. Even with these results, NS addition shows a better behavior than reference samples, but lower than samples after migration, showing that NS can be acting in the surface of the treated samples as a densifier material. Addition of NS at fresh stage could have a better behavior if proper conditions are taken into account when the fabrication is being carried out, as found by Hongjian Du et al. [24] and their studies, where samples with NS additions were tested in their durability performance according to chloride ion diffusion at 28 and 90 days. They found that NS can reduce up to 31% the diffusion coefficient in concrete. The addition of NS has been demonstrated to be an important factor to improve the durability [25-26]. Nevertheless, it is important to point that they and other authors found slightly decrements of performance when the content of NS is increased, probably due to its property of agglomeration and the consequent lack of homogenization or excessive amount of silica which cannot reach more $Ca(OH)_2$ to react [27-29].

Table 2. Distance of penetration of Cl- and CO_2 test for reference and NS addition samples compared with migration at 3 and 7 days

CO_2, (d)	Reference (mm ± 0.3 mm)	NS addition (mm ± 0.3 mm)	M3 (mm ± 0.3 mm)	M7 (mm ± 0.3 mm)
30	2.5	1.9	*0.0	*0.0
60	4.9	3.9	2.7	2.9
90	6.9	6.3	3.5	3.6
Cl^-, (d)				
30	4.0	2.5	*0.0	*0.0
60	6.5	2.7	1.0	1.3
90	9.0	3.1	1.4	1.6

*No apparent penetration

3.5 Water absorption test

Water absorption test, DIN 52617, was performed to samples after NS migration at 3 (M3) and 7 (M7) days of treatment, reference samples (Reference) and samples with NS addition at fresh stage (A3 and A7). It can be observed in Figure 8 that the reference and NS addition samples show an increment in their weight in the first hours of the test; both of them reach a variation around 6% and then they keep gaining weight until 7.5%. After that, reference and NS addition follow a tendency which could be related to the saturation of the sample. The samples after migration in both cases (3 and 7 days of treatment), show a similar slope that reference and NS addition samples at the beginning, but they stop that tendency to increment at a value between 2 and 3%, then they keep gaining weight until 3 and 4%. After 6 hours, values show a tendency to slowly increment and reach the saturation of the samples. The results of this test indicate a reduction of the water absorption of both of the treated samples; 60% of reduction of the sample M3 compared with control and 54% for M7. These results from the water absorption test can be compared with the results of Hou at al. [3], where percentages of water absorption reductions of 19.7% at 40 min and 9% at 24 hours were found. In both cases, the application of NS seems to be a significant element to obtain that water absorption reduction. But using an electric field could help obtain a better performance in the process of NS penetration. As the CO_2 and Cl^- penetration test, migrated NS seems to be acting as a sealing material in the surface of the treated samples, resulting in the modification of the outer microstructure and the increment of the resistance to the entry of water from the exterior. The results of the water absorption test can be compared to results from other studies [24-25] of addition of NS, where silica nano particles can reduce the water absorption even at early ages (28 and 60 days).

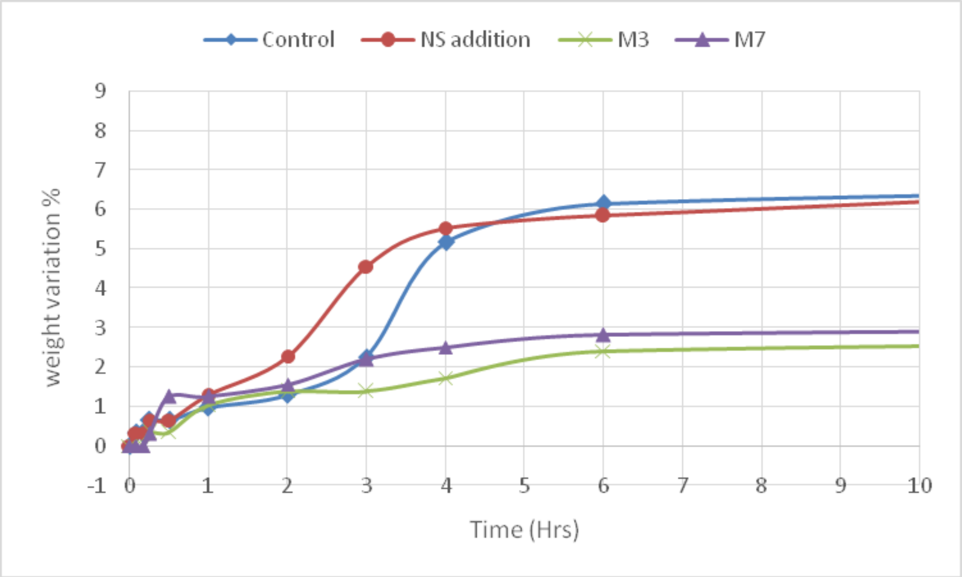

Figure 8. Weight variation percentage from water absorption test for samples after migration (cross and triangle), reference samples (rhomb) and samples with NS addition (circle) until 10 hours of test.

4. CONCLUSIONS

The following conclusions can be drawn for this study:

1. After migration of colloidal nanoparticles of SiO_2, optical microscopy analysis shows a slightly variation in the appearance of the mortar samples. A small variation of color and texture can be observed from the surface in contact with NS until a depth around 1.5 to 2 mm. According to the SEM-EDS analysis, this area presents Ca/Si ratios with values lower than the conventional for cement paste, due to a SiO_2 enrichment from the migration process, which means that nano particles move into the microstructure through the porous, fill up the available space and agglomerate there; after that, the silicon starts to chemically affect the phases surrounding these agglomerations.

2. It has been found that NS can affect the electric properties (resistance) of the hardened cement mortar samples when is added by migration under an electric field. The microstructure of a HCM is affected by NS when migration is carried out. NS particles could come into the porous system and reduce the diameter of the pores, and thus external particles will find a harder way to penetrate.

3. External mortar detrimental agents like CO_2, Cl^- and water will have a more difficult way to come through the surface of treated samples, because NS can act as a pore blocker material. Results from the penetration tests lead to infer that NS can improve the microstructure of HCM when is used in both addition at fresh stage and migration treatment.

In future work, the effect of the relation of the NS with the cement materials microstructure after hardened stage should be studied by other advanced techniques in order to determine the grade of progress of the pozzolanic reaction. Some works with cement paste are being carried out to study other aspects like micro hardness and NS depth distance.

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