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Title: Preliminary attempt of hardened mortar sealing by colloidal nanosilica migration

Article Type: Research Paper

Keywords: Colloidal nanosilica, migration, sealing properties, repair techniques.

Corresponding Author: Dr. Mercedes Sanchez Moreno,

Corresponding Author's Institution:

First Author: Mercedes Sanchez Moreno

Order of Authors: Mercedes Sanchez Moreno; Maria Cruz Alonso Alonso, Doctor; Rodrigo Gonzalez Lopez, Doctor

Abstract: An innovative electrochemical treatment for the sealing of hardened mortar by nanosilica migration is proposed. The composition of the colloidal suspension and the electric field power were assessed as significant parameters of the transport efficiency. The interaction between the nano-SiO₂ and the cement matrix was characterized by different techniques: electrical resistivity measurements, DTA-TGA, BS-SEM with EDX microanalysis coupled and MIP. Results showed that the transport of colloidal nano-SiO₂ under the action of the electric field can be achieved. An active interaction with the solid phases of the mortar samples was confirmed from the decrease in the portlandite content of treated mortar and from the smaller C/S ratio found in the solid hydrated phases of the treated mortars. A significant decrease of capillary pores was also identified at the age of 28 days after finishing the treatment. The sealing ability of migrated silica nanoparticles was enhanced with the ageing of the treated sample; smaller amount of micropores was measured with the treated mortar ageing.

Authors acknowledge the comments of reviewers since they have promoted a deeper thinking about the treatment proposed and a qualitative improvement of the result analysis shown in the manuscript. Reviewers' suggestions have been taken into account in the manuscript which includes significant changes in the revised form. Main changes included considering reviewer's comments are highlighted in red colour.

Reviewer #1:

The paper considers the possibility of injecting nanosilica particles into mortar by means of an external applied current. This possibility could be used in the repair of mortar or concrete of existing structures. The topic of the paper is very interesting and deserves investigation: whilst the effect of nanoparticles added to the mix - for new structures - is widely considered in the literature, the possibility of injecting them has received less attention and needs more insights. I think that the Authors should consider the following points.

1. Interpretation of experimental results.

There is no direct correlation between the trend of the electrical resistance measured in the cell during the treatment and the nanosilica transport in the mortar. Hence, the increase of resistance cannot be used "as an indirect measure of the nanoparticle transport inside mortar tested samples". For example, if nanosilica particles completely sealed the mortar surface, the electrical resistance would increase, however this would not indicate penetration of particles into the mortar. The Authors should comment on this point. Furthermore, the methodology is not clear regarding the procedure that was followed to measure resistance. Were "on-off" techniques used? Were polarisation contributions at the electrodes included? Is there any contribution of the nanosilica suspension at the cathode compartment? Reporting actual values of resistance instead of just their ratio would have been helpful in understanding.

Authors agree with reviewer's comment and they have modified the manuscript and included a more detailed description of the treatment and the measurements performed. The figure with the absolute values of resistance has been represented.

2. Methodology

The results of characterisation of mortar indicate sealing ability of the treatment but do not confirm penetration since only average or bulk values were reported by the Authors. To assess nanosilica penetration, results of characterisation should have been reported in terms of variation as a function of the depth in the sample. Moreover, no details are given regarding the sampling procedure used for MIP and thermal analyses, so it is not clear whether results refer to average of the sample, or localised at a certain distance from the surface.

Penetration is analysed through SEM backscattering with EDX using transversal samples from the surface of penetration and the C/S profile is obtained. The MIP analysis and the thermal analysis have not been developed at different depths, although authors agree that will be interesting and should be considered in further investigations.

It seems that SEM observation was carried out in several locations over the thickness of the specimen, however only results "in the mortar surface nearest the negative side" are reported. C/S ratio is a qualitative parameter, and it is the only parameter that the Authors consider to support nanosilica penetration. Performing MIP, DTA and SEM observations at varying depths from the cathode surface could have supported nanosilica penetration. Otherwise, nanosilica may be localised on a very thin layer close to the surface, and this may even occur without any applied current, i.e. by simple contact with the suspension.

Authors thank reviewer's comments and agree that there is much research to do concerning the nanosilica penetrability. Further studies are being carried out concerning the nanosilica penetrability and also the influence of the electric field; present paper mainly deals with migration capacity and interaction of nanosilica with hardened mortar. Authors are confident that results concerning the penetration capacity will be part of their further publications in this research issue.

Moreover, the Authors attribute nanosilica injection (and subsequent reduction of porosity and pozzolanic activity) to the applied current. However they do not detect any effect of applied electric field. This discrepancy could have been better clarified considering a reference case for comparison. i.e. a cell with the same solutions and specimens, but no current applied. In the present paper, based on their results, the Authors can only hypothesise, but not demonstrate, that "The penetration of colloidal nanosilica can be accelerated by electrochemical techniques based on the nanoparticles migration under the action of the electric field" (as stated in the Conclusions, lines 48-50).

In the manuscript, any attribution of the nanosilica injection to the current applied has been avoided. The interest of the paper lays on the possibility of transporting nanosilica through the hardened mortar and its ability to react with solid cementitious phases. In this paper, the transport has been reached by migration; however, other transport mechanisms are being considered in further studies to analyse the possibilities of the different alternatives.

3. Practical relevance

The Authors investigate the possibility of injecting slightly negatively charged nanosilica particles. Up to now, the few literature contributions available had considered slightly positively charged nanosilica particles: in real applications, the reinforcement can be used as cathode. Conversely, this is not possible with negatively charged nanoparticles, since the reinforcement should work as anode. The Authors do not mention this aspect. In the Introduction section they mention "conventional" electrochemical methods such as ECE and ERA, and their "promising alternatives for non-invasive repair of reinforced concrete". What kind of configuration have the Authors in mind with respect to real reinforced concrete structures? If the aim of paper was to characterize the nanoparticle transport inside mortar, a literature review should be considered in the introduction.

These comments have been now taken into account in the revised version.

Authors should also check abstract length and reference style.

It has been changed in the reviewed manuscript.

Reviewer #2:

Migration of nano-silica dispersion in mortar, and its influences on the electrical resistivity and the microstructure are investigated in this manuscript. The technique is promising in repair works. However, a number of problems, including general and technical issues, exist. Comments from the reviewer are shown as follow.

General Comments:

(1) The title needs to be revised to cover the main research content.

It has been taken into account in the new version.

(2) The authors are suggested to make the abstract briefer, and summarize the contents in one paragraph.

It has been taken into account in the new version.

(3) Many sentences are too long. I suggest to replace them by shorter ones, or use commas to separate them to make understanding easier. Examples of the long sentences include: lines 22-28 on page 3 "Cylindrical mortar samples.....in Table 1"; lines 17-23 on page 4 "Migration tests were schemed in Figure 1".

It has been modified in revised document.

(4) Would the authors suggest, in a proper position of the manuscript, how the technique can be transferred to practice? E.g. to use an external metallic cathode, and the rebar network as the anode?

This point has been detailed in the revised manuscript. Authors have an invention patent in which the arrangement to transport anionic compounds by electromigration into reinforced concrete is proposed.

(5) The highlights need to be shortened to fulfil the journal's requirement, i.e. shorter than 85 characters.

It has been modified in the new version.

(6) The "ATD" in highlight 3 and line 7 on page 8 should be changed to "DTA".

It has been corrected in the reviewed highlights.

Technical Comments:

(1) Line 4 on page 4 "...modified by silane...": How the silane treatment was conducted to negatively charge the nano-silica particles should be introduced briefly, or at least be supported by relevant references.

For this study authors have employed commercial colloidal nanosilica. It is described in the product data sheet: The silica dispersion is sterically stabilized and the amorphous silica particles carry a negative surface charge. The data sheets have been included as references in the reviewed manuscript.

- (2) As in MIP, DTA and BS-SEM (section 2.4) ages after treatment are mentioned, it has to be clarified in section 2.3 how the specimens were placed after the 8-hour treatment, in ambient environment or wet cured again?

After the 8 days treatment the specimens were placed in wet cured again until reaching the age of characterization. It has been detailed in the revised manuscript.

- (3) The authors should give an evaluation of the influenced range in the slice sample. After the treatment, to what an extent over the 1 cm thickness was the specimen influenced by the nano-silica? As shown in Figure 7, the influence is strong on the nano-silica side, but weak on the water side. Then how can the authors make sure that the samples taken for MIP, DTA or BS-SEM are representative to reflect the influence of nano-silica on the microstructure? This should be clarified in section 2.

It has been clarified in the reviewed manuscript.

- (4) In section 2.4.3, please give details of the sample used for DTA/TGA. Is it powder, how is it dried, is sand eliminated, etc.? Or add references to note according to whose method the powder samples were prepared for DTA/TGA, e.g. ([http://dx.doi.org/10.1061/\(asce\)mt.1943-5533.0000302](http://dx.doi.org/10.1061/(asce)mt.1943-5533.0000302))

It has been better detailed in the reviewed manuscript.

- (5) The "after 28 days of treatment" in line 27 of page 5, line 36 of page 5, and line 27 of page 7, may lead to misunderstanding as "after a treatment of 28 days long". Is it better to be revised as "at the age of 28 days after finishing the treatment"? or other forms of revision to avoid misunderstanding.

It has been taken into account in the reviewed manuscript.

- (6) Figure 4, Figure 8 and relevant text: the division between gel pore and capillary pore is normally 10 nm. When 50 nm is used to divide pores into smaller and larger pores, the terms gel pore and capillary pore should be used carefully.

It has been taken into account in the reviewed manuscript.

To express the pore structure, MIP results in the form of cumulative pore volume curve or logarithmic differential pore volume curve are more favored, as they can give more information.

Graphs with cumulative pore volume curve and logarithmic differential pore volume curve have been included in reviewed manuscript. Total porosity and % capillary pores have been included in table 3.

- (7) Line 18 on page 6: should the "lesser particle size" be "smaller particle size"? Line 23 on page 6: should the "higher particle size" be "larger particle size"?

It has been modified in reviewed manuscript.

- (8) In Figures 4 and 8, the "Left" and "Right" can be denoted by (a) and (b).

It has been changed in new version.

- (9) Line 5 on page 8: the "reactive ability" is normally written as "reactivity".

It has been changed in new version.

- (10) To provide more information, the DTA or TGA curves are suggested to be added.

TGA curve has been added in revised manuscript and the estimation of the composition has been resumed in a table (table 4).

- (11) References [14] and [16] are the same one, thus [16] should be eliminated.

It has been corrected in new manuscript.

*Highlights

- Efficient superficial sealing of mortar by colloidal nanosilica migration.
- Significant parameters in treatment: nanosilica composition and electric field power.
- Consolidation of treated mortar due to the decrease of capillary pores.
- Nanosilica and cementitious matrix interaction: pozzolanic activity and C-S-H gels formation.

Preliminary attempt of hardened mortar sealing by colloidal nanosilica migration

M. Sánchez^{1,*}, M. C. Alonso¹, R. González²

¹ Instituto “Eduardo Torroja” de Ciencias de la Construcción (IETCC – CSIC), C/ Serrano Galvache 4, 28033 (Madrid).

² Universidad Autónoma de Nuevo León, Facultad de Ingeniería Civil, Pedro de Alba s/n, San Nicolás de los Garza, Nuevo León (México).

* Corresponding author: mercesanc@ietcc.csic.es (M. Sánchez). Tfn: +34 913020440 – Ext. 870304

Abstract.

An innovative electrochemical treatment for the sealing of hardened mortar by nanosilica migration is proposed. The composition of the colloidal suspension and the electric field power were assessed as significant parameters of the transport efficiency. The interaction between the nano-SiO₂ and the cement matrix was characterized by different techniques: electrical resistivity measurements, DTA-TGA, BS-SEM with EDX microanalysis coupled and MIP. Results showed that the transport of colloidal nano-SiO₂ under the action of the electric field can be achieved. An active interaction with the solid phases of the mortar samples was confirmed from the decrease in the portlandite content of treated mortar and from the smaller C/S ratio found in the solid hydrated phases of the treated mortars. A significant decrease of capillary pores was also identified at the age of 28 days after finishing the treatment. The sealing ability of migrated silica nanoparticles was enhanced with the ageing of the treated sample; smaller amount of micropores was measured with the treated mortar ageing.

Keywords: Colloidal nanosilica, migration, sealing properties, repair techniques.

1. Introduction

Nowadays, nano-technology is a real aspect of the daily life and is present in almost every developed industrial field, although its intrusion is being slower in the construction industry. The use of nano-materials with cementitious functions coupled with the application of modern technologies is in continuous evolution, promoting important performance improvements in the construction industry. These aspects are getting more demanded every day in order to increase the lifetime not only of new

1 concrete structures to be built but also in the case of the existing ones. In this sense, the
2 addition of colloidal nano-silica to fresh concrete has been proposed as a promising
3 technology to improve significantly the mechanical and durable properties in hardened
4 state [1-4]. The technology for improving the performance of existing structures in a
5 non-invasive way is still in an incipient state, even though of the emerging industrial
6 interest in developing sustainable technology in the field of rehabilitation and
7 retrofitting of damaged concrete structures.
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13 Conventional electrochemical repair methods, such as electrochemical chloride
14 extraction (ECE) or electrochemical realkalization (ERA), are already standardized [5-
15 6], although reticence concerning their long-term efficiency [7-9] and total regeneration
16 of the passive layer still exists [10]. Then, improvements of these techniques to
17 overcome those limitations arise as promising alternatives for non-invasive repair of
18 reinforced concrete. The simultaneous application of corrosion inhibitors during the
19 electrochemical repair treatment has been reported to significantly improved the
20 repassivation of the rebar after finishing the treatment [11-14]. Applying a superficial
21 treatment to seal the concrete surface has been also proposed to increase the efficiency
22 of electrochemical repair methods by limiting the further access of aggressive chemical
23 species in the structure [15-16].
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34 Electrochemical repair methods are based on the accelerated transport of charged
35 particles into the pore structure by migration mechanism under the action of an electric
36 field. In this sense, the electric field can be used not only to extract chloride ions from
37 the porous system of the cement matrix connecting the reinforcement as cathode [5-6],
38 but also to introduce positive charged particles to the concrete bulk. **Cathodic inhibitors,**
39 **such as organic based mixed inhibitors, have been effectively migrated using**
40 **conventional arrangement of ECE or ERA treatments by connecting the reinforcement**
41 **to the cathode [13-14].** Electrokinetic transport of positively charged nanoparticles
42 using similar arrangements has been also performed; alumina coated silica nanoparticles
43 have been penetrated into concrete specimens to promote the efficient reduction of the
44 hardened concrete permeability [15]. The interaction of these particles with the cement
45 matrix has been reported to promote the formation of a denser material, reducing the
46 chloride induced corrosion of reinforced concrete [17-18].
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However, this arrangement cannot be directly employed for negatively charged compounds and an appropriate modification of the procedure has been performed to favour the migration of anodic inhibitors, as demonstrated in [11-12]. Furthermore, the migration of colloidal nano-SiO₂ under the action of an electric field has been also considered [19]. The practical implementation of such technology implies the use of the modified arrangement described in [11-12] to promote silica nanoparticles, negatively charged.

The interaction of colloidal nanosilica with the cement grains when added in fresh state has been analysed in literature [20]. A physical effect of nanosilica acting as filler by filling up the pores to give a cement paste with larger packing density and smaller porosity has been observed [21]. Furthermore, the chemical interaction of nanosilica with portlandite forming additional C-S-H gel that implies a pozzolanic reaction has been reported elsewhere [22-23]. Nanosilica has also showed ability to accelerate the cement hydration by acting as nucleating sites [24] on the anhydrous cement grains. However, in the case of nanosilica penetration through hardened concrete, scarce information can be found concerning the interaction between the transported silica nanoparticles and the cementitious matrix. Thus, in the present work a migration treatment of silica nanoparticles on hardened mortar has been performed and the effect of nano-SiO₂ on the cement matrix after the migration process has been assessed. The effect of significant variables such as the electric field power and the size and concentration of nanoparticles in interaction with the hardened cement mortar has been analysed. The ageing of the treated mortar has been also considered to evaluate the long-term behaviour of this type of sealing treatments.

2. Materials and method

2.1 Cement mortar samples

Cylindrical mortar samples with 7.5 cm of diameter and 15 cm of height were prepared with an Ordinary Portland Cement (OPC 52.5 R) sulphate resistant with low C₃A content (3.4 %) and low alkali content (Na₂O_{eq} 0.7 %). The cement chemical composition is detailed in Table 1. The sample preparation was carried out using siliceous aggregates with a chemical composition of $\geq 98\%$ SiO₂ and a moisture content $< 0.2\%$. Deionised water was used in order to avoid the intrusion of other ions in the mix that could interfere with the analysis. A water/cement ratio of 0.5 and a proportion

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of cement/aggregate of 1:3 were used in the preparation of the mortar samples. An automatic mortar mixer was used to prepare the materials following UNE-EN 196-1:2005 standard. Once prepared the mortar samples, they were cured under controlled conditions (98 ± 2 % relative humidity and 21 ± 2 °C) for 7 days.

<Table 1>

After curing, the mortar samples were cut in slices of 1 cm, removing the top and bottom sides. The 1 cm mortar slices thickness were saturated in water under vacuum conditions and were maintained immersed in water for storage until testing.

2.2 Colloidal Nano-SiO₂

Two different **commercial** colloidal nano-SiO₂ aqueous dispersions were used, as resumed in Table 2. **As indicated by the product data-sheet [25-26]**, the amorphous silica particles are discrete, spherical and monodispersed and modified with a reactive epoxy silane to have a slight superficial negative charge.

<Table 2>

2.3. Migration cell assembly

Migration tests were carried out in a two compartments cylindrical cell. The compartment acting as catholyte (cathode connection) was filled with the colloidal nano-SiO₂ solution and the anolyte compartment (anode connection) with distilled water. The mortar slice was located between both compartments. The scheme of cell is detailed in Figure 1. The electric field was connected between two steel rebars (diameter of 6 mm) located at both compartments acting as external electrodes. Two different constant voltages (6 V and 12 V) were applied during 8 days of treatment.

<Figure 1>

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5 During testing, periodical electrical measurements, such as the current passed through
6 the system and the real voltage between both sides of the mortar sample, were carried
7 out with an Autoranging Microvolt DMM multimeter from Keithley. The effective
8 voltage was measured between two stainless steel meshes located close to the mortar
9 surfaces, as observed in Figure 1, in order to avoid the polarization contributions at the
10 electrodes and to minimize the electrolyte contribution. Current passing through the
11 system was also periodically measured. The evolution of the mortar electrical resistance
12 was estimated by Ohm's Law.
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21 **2.4. Characterization of the nanosilica/mortar interaction**

22 *2.4.1. Electrical resistivity measurements*

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26 The resistivity of the mortar sample was measured before and after the treatment by a
27 direct measurement using two electrodes attached to both sides of the treated sample
28 according to UNE 83988-1:2008. This parameter was utilized as an indirect indicator of
29 the mortar consolidation due to the migration nanosilica treatment.
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33 *2.4.2. Mercury Intrusion Porosimetry (MIP)*

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37 After nano-SiO₂ treatment, mortar samples taken from the surface directly exposed to
38 the nanosilica compartment during the migration treatment (4-5 mm depth) were
39 analysed in an AutoPore IV 9500 V1.05 equipment from Micromeritics Instrument
40 Corporation. The total porosity values and the pore size distribution were determined.
41 Before the analysis, the samples were dried at 40°C during 48 hours. Two different ages
42 after the treatment were considered: 28, and 90 days.
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49 *2.4.3. Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA)*

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51 The DTA/TGA analysis was conducted on a TA Instruments SATQ600 thermal
52 analyser in a dynamic nitrogen atmosphere. The samples were heated at a rate of 4
53 °C/min from 25 to 1000 °C. Small pieces of mortar were taken from the surface that had
54 been exposed to nanosilica compartment during the migration treatment (negative side).
55 Mortar samples were powdered for the analysis by grinding at the ambient air. The
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1 powdered samples were not previously dried before the thermal analysis. Platinum and
2 aluminium crucibles were used as references. The weight loss associated to the
3 dehydration of cement products such as C-S-H gel and portlandite were estimated for
4 mortar samples at the age of 28 days after finishing the treatment. A non-treated mortar
5 with the same age was taken as reference.
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8 9 10 *2.4.4. Back-Scattering Microscopy with X-Ray Microanalysis (BSE/EDX)*

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12 The nanosilica interaction and reactivity with the cement matrix were also evaluated by
13 characterizing the microstructure and chemical composition of mortars at the age of 28
14 days after finishing the treatment by BSE/EDX with a JEOL JSM-6360LV with an
15 EDX detector coupled for elemental chemical analysis. The C/S ratio of C-S-H gel
16 phases was estimated as a qualitative indicator of the chemical interaction between the
17 silica nanoparticle and the cement solid matrix.
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24 **3. Results and discussion**

25 26 27 *3.1. Nanosilica transport characterization*

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29 The mortar electrical resistance, estimated during the connection of the electric field, is
30 represented in Figure 2. A clearly different behaviour was observed for both colloidal
31 suspensions studied, B-30 and B-40. An increase of the mortar electrical resistance was
32 registered from the beginning of the treatment migrating the less concentrated
33 suspension with smaller nanoparticles size, B-30. In the case of B-40 suspension, the
34 electrical resistance of mortar only increased after a certain induction t time of the
35 electrical fields running, that varies with the level of the voltage used. Thus, the increase
36 of the resistance against the ions movement through mortar sample was progressively
37 detected during the nanosilica migration treatment. The ionic transport seemed to be
38 more hindered for the migration of the smaller nanoparticles (B-30 suspension) through
39 the mortar pores.
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53 <Figure 2>
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59 *3.2. Nanosilica/mortar interaction* 60 61 62 63 64 65

1 The sealing ability of the colloidal nanosilica was characterized on mortar samples at
2 the age of 28 days after finishing the treatment by the relative resistivity of the treated
3 mortar, taken as a qualitative indirect indicator. The relative resistivity values, defined
4 as the ratio between the final and the initial resistivity, are included in Figure 3 for the
5 different studied situations.
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12 <Figure 3>
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18 An increase on the resistivity was measured after the treatment of sealing with the
19 colloidal nanosilica, independently on the experimental conditions. While a non-
20 significant influence of the electric field power was deduced, the effect of the product
21 composition seemed to be more relevant. The larger increase on the resistivity values
22 obtained after the treatment with B-30 suspension should be related to an improved
23 sealing ability of this product with smaller nanoparticle size. A more significant mortar
24 densification and consolidation could be expected in this case. .
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31 MIP measurements were carried out to obtain additional information about the sealing
32 ability of the penetrated nanosilica. The MIP characterization was carried out on mortar
33 samples at the age of 28 days after finishing the treatment, taken from the surface
34 directly exposed to the nanosilica during the treatment. A non-treated mortar with the
35 same age was taken as reference. In Figure 4(a) the cumulative pore volume curve is
36 represented for each case.
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46 <Figure 4>
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51 Smaller cumulative porosity was found for the treated mortars confirming the sealing
52 ability of nanosilica after the migration treatment. However, not significant effect
53 neither of the electric field nor of the nature of the nanosilica dispersion could be
54 deduced, Figure 4(a). In table 3 the total porosity values are resumed and the slight
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1 porosity decrease in the treated mortar at the age of 28 days after finishing the treatment
2 can be perceived.
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11 For a more detailed analysis, the differential pore size distribution is represented in
12 Figure 4(b). Treated mortars showed similar porosity distribution, with two marked
13 peaks at around 0.5 and 0.07 μm , independently of the electric power applied and the
14 suspension composition. However, for the reference case, the pore size distribution
15 appeared slighted displaced to larger pore diameters. The sealing effect of nanosilica
16 treatment seems to affect mainly the capillary pores ($< 0.1 \mu\text{m}$). Similar behaviour was
17 observed in cement pastes with nanosilica addition [21] where the filler effect of
18 nanosilica by filling up the voids between the cement grains was reported to promote a
19 reduced capillary porosity of the cement paste. The estimated capillary pore content for
20 the different samples is resumed in Table 3, where the clear decrease is registered for
21 the treated mortars in comparison to the reference mortar. Neither the applied voltage
22 nor the nature of the nanosilica suspension used for the treatment showed a crucial
23 influence in porosity results.
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37 MIP results do not inform the type of sealing obtained after the nanosilica migration
38 treatment; both a physical effect due to the filler action of nanosilica and a chemical
39 effect associated to the nanosilica reactivity can be expected [22-24]. To confirm if the
40 nanosilica is able to react even when applied on a hardened cementitious matrix,
41 DTA/TGA analyses were carried out. In Figure 5, the TGA curve is included for the
42 mortars at the age of 28 days after finishing the treatment with 12 V electrical
43 connection and also for a reference mortar, without treatment. The same region than the
44 studied with MIP was analysed.
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<Figure 5>

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No significant differences between treated and non-treated mortars were detected from the DTA curve, although larger portlandite content in the reference sample could be deduced from the peak at 450 °C. For a more quantitative analysis, the content of the main solid phases of the cement matrix was estimated from the weight losses data, as shown in Table 4. The different characteristic intervals of temperature considered were the related to water from C-S-H gel (100-350°C) and water from portlandite (350-450°C).

<Table 4>

Smaller weight losses were registered for the treated mortar samples than for the reference one. A significant decrease of the portlandite content was registered in both treated mortars confirming that the nanosilica particles are able to promote the pozzolanic reaction even when applied to hardened mortar. However, certain effect of the electric field should not be neglected neither; in fact, the enhancement of the portlandite dissolution due to the electric field connection was already reported elsewhere [27].

Even though similar pozzolanic activity is expected for both colloidal nanosilica suspensions, the weight loss associated to C-S-H gels was different in each case; when using the more concentrated solution with larger nanoparticle size (B-40), a more significant decrease in this parameter was detected, while this diminution was not so evident for the solution with less concentration of smaller silica nanoparticles (B-30). The decrease of the weight loss associated to the C-S-H gel content could be explained by a different composition of these calcium silicate hydrates in the treated mortars. However, a certain accelerated leaching of C-S-H due to the application of electrical field could also being contributing [28], mainly during the treatment with B-40 where smaller efficiency of the nanosilica penetration is expected. Nevertheless, further studies are in way to identify the real contribution of the electric field.

It should be remarked that the mortar densification was detected by MIP measurements at the age of 28 days after finishing the treatment (Figure 4), and thus, an effective reactivity of nanosilica particles can be deduced. A different reactivity of both solutions

1 can be expected probably due to the different size of the nanoparticles that may have
2 different nucleating capacities and even promote the formation of C-S-H gel with
3 different compositions (that is, lower C/S ratio, larger polymerization degree, etc).
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6 The nanosilica penetration through the mortar due to the treatment was confirmed by
7 BS-SEM coupled with EDX microanalysis, as represented in Figure 6 for the case of
8 treatment with B-40 at 12 V.
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11 <Figure 6>
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18 Spherical particles with high silica content were clearly observed in the first mm beyond
19 of the mortar surface connected during the treatment to the negative side of the
20 electrochemical cell. The nanoparticle flocculation was expected to occur since the
21 diameter was significantly larger (5 μm) than their initial mean diameter (7 nm). **The**
22 **chemical EDX microanalysis of these spherical particles is included in Figure 7 and**
23 **compared with the analysis of a region with C-S-H gel in the centre of the treated**
24 **sample. The presence of such flocculated nanosilica particles found beyond the treated**
25 **mortar surface was the evidence confirming that nanoparticles had certain penetrability**
26 **into the treated sample and not only the superficial deposition occurred. Besides it has**
27 **to point out that the use of silica aggregate could masked the identification nanosilica**
28 **particle.**
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41 <Figure 7>
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47 The interaction of the nanosilica particles with the cement matrix was **qualitatively**
48 **evaluated with the C/S ratio of the C-S-H gel zone at different regions of the transversal**
49 **section of the treated sample at the age of 28 days after finishing the treatment. The C/S**
50 **ratio of the C-S-H gel was also analysed in a 28 days reference mortar (R0). In Figure 8**
51 **the C/S ratio profile through the mortar transversal section is represented for treated**
52 **samples as well as the mean value obtained for the reference case.**
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<Figure 8>

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5 The C/S profile in the transversal section of the treated samples showed an increasing
6 tendency from the negative side (in contact with the colloidal nanosilica) to the positive
7 side (in contact with water during the treatment); similar C/S ratios were found
8 independently of the applied suspension (B-30 or B-40). The smaller C/S measured in
9 the negative mortar surface should be related to the formation of a Si enriched C-S-H
10 gel probably due to the reaction of the additional silica particles with the C-S-H gel
11 structure or even with the present portlandite forming C-S-H gels with lower C/S ratio
12 by following a pozzolanic reaction. This could be a similar phenomenon than those
13 detected in cement pastes with colloidal nanosilica additions [23] or even, when using
14 mineral additions with high silica content as silica fume or fly ash [29]. This effect was
15 only detected until 1.5 – 2 mm from the mortar surface exposed to the colloidal
16 nanosilica and must be indicative of the nanoparticle migration capacity. From the
17 middle of the sample (around 5mm depth) the typical ratio of a conventional mortar (1.5
18 – 1.8) was measured.
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31 **3.3. Treated mortar ageing**

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34 The evolution of the interaction between the nanoparticle and the cement matrix due to
35 the colloidal nanosilica reactivity was assessed by MIP and the changes registered in the
36 capillary pores are represented in Figure 9, where different sealing ability of both
37 treatments can be deduced. Using B-30 treatment the main reduction in capillary pores
38 was detected after 28 days of treatment; in the case of the most concentrated solution
39 (B-40), a gradual decrease of this capillary pores was observed, and an increased
40 efficiency could be deduced after 90 days of finishing the treatment. Then, a faster
41 reactivity was expected for the most diluted solution containing smaller particles (B-
42 30). However, the activity of the most concentrated solution could neither be neglected,
43 as its evolution with time was more significant even reaching higher long-term
44 efficiencies.
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<Figure 9>

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3 Although the paper is a preliminary attempt on migration of colloidal nanosilica, the
4 results are promising and show clear evidences about the viability of drive the
5 nanoparticles through the pores of a hardened cement matrix under an electrical field.
6 Furthermore, the chemical interaction with the substrate is confirmed that allow a
7 sealing phenomenon to occur in the matrix of the mortar.
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15 **Conclusions**

- 16 – Colloidal nanosilica particles were successfully infiltrated in hardened mortar
17 forced by migration under the action of an electric field.
- 18 – The nanoparticle size and the concentration were found to be significant variables
19 affecting the transport and sealing ability of the treatment. However, no significant
20 effect of the electric field can be deduced.
- 21 – The decrease of the capillary pore volume confirmed the sealing ability of the
22 treatment which evolves to larger efficiencies with ageing. A chemical interaction
23 of the nanosilica with the cement matrix was found; nanosilica maintained its
24 pozzolanic activity even when applied to hardened concrete. The supplementary
25 silica incorporated by the treatment seems to react with the C-S-H gel of the matrix
26 reducing the C/S silica ratio of these gels.
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43
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Table 1. Chemical composition of the employed OPC cement (%).

Na ₂ O	K ₂ O	Al ₂ O ₃	CaO	Fe ₂ O ₃	SiO ₂	MgO	SO ₃	Loss Ign.
0.33	0.59	4.16	67.48	4.57	19.68	0.83	3.25	---

Table 2. Properties of the studied colloidal nanosilica suspensions.

ID	Average particle size, nm	Silica, wt%	Density, g/cm ³	pH
B-30	7	29	1.2	8
B-40	12	37	1.3	8

Table 3. Total porosity and capillary pores content at the age of 28 days after finishing the treatment.

Sample	Total porosity, %	Capillary pores (< 1 μm), %
R0_28d	16.76	88.05
B30_6V_28d	15.41	78.81
B40_6V_28d	14.35	82.10
B30_12V_28d	14.34	81.57
B40_12V_28d	15.06	83.56

Table 4. Composition of the main solid phases of treated mortars at the age of 28 days after finishing the treatment compared the reference mortar estimated from TGA results.

Sample	% Mass loss	
	C-S-H gel (100-350°C)	Portlandite (350-450°C)
R0_28d	1.95	1.43
B30_12V_28d	1.89	1.09
B40_12V_28d	1.66	1.00

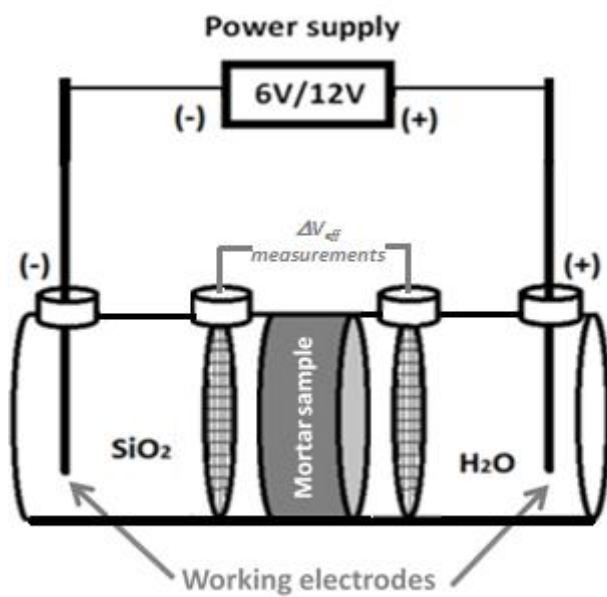


Figure 1. Scheme of the migration cell set-up.

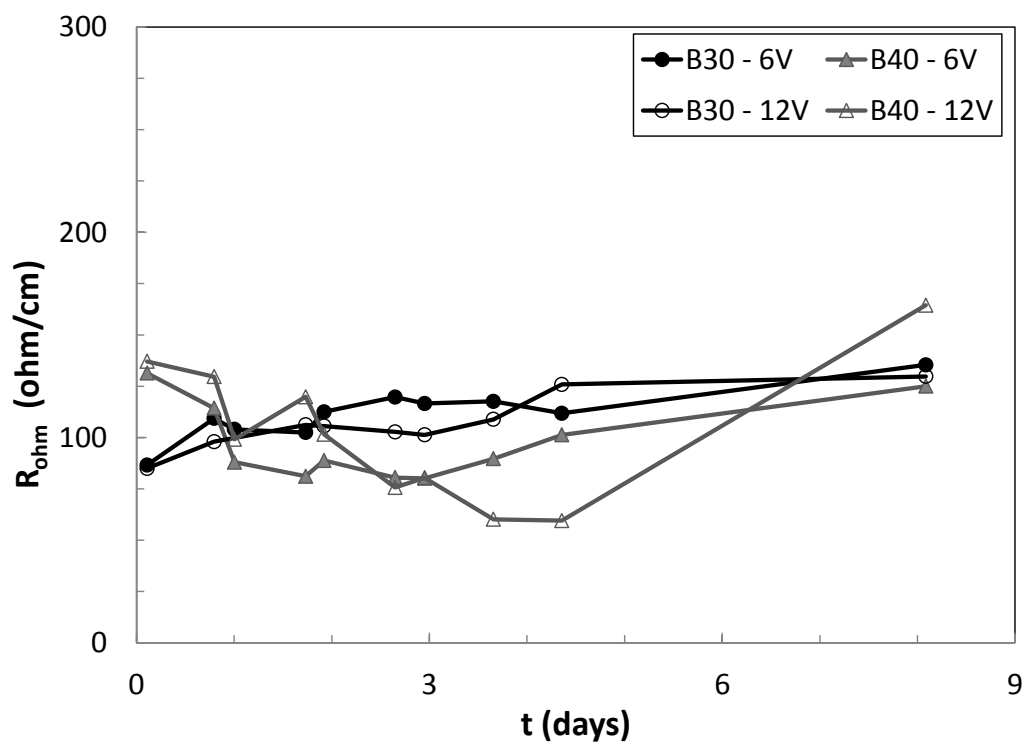


Figure 2. Evolution of the electrical resistance through mortar sample during the electric field connection.

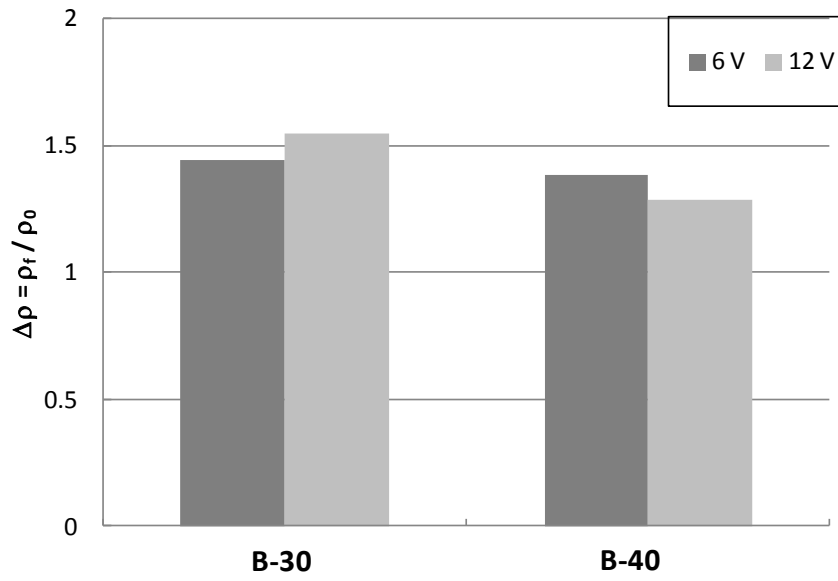


Figure 3. Relative resistivity increase of treated mortar at the age of 28 days after finishing the treatment.

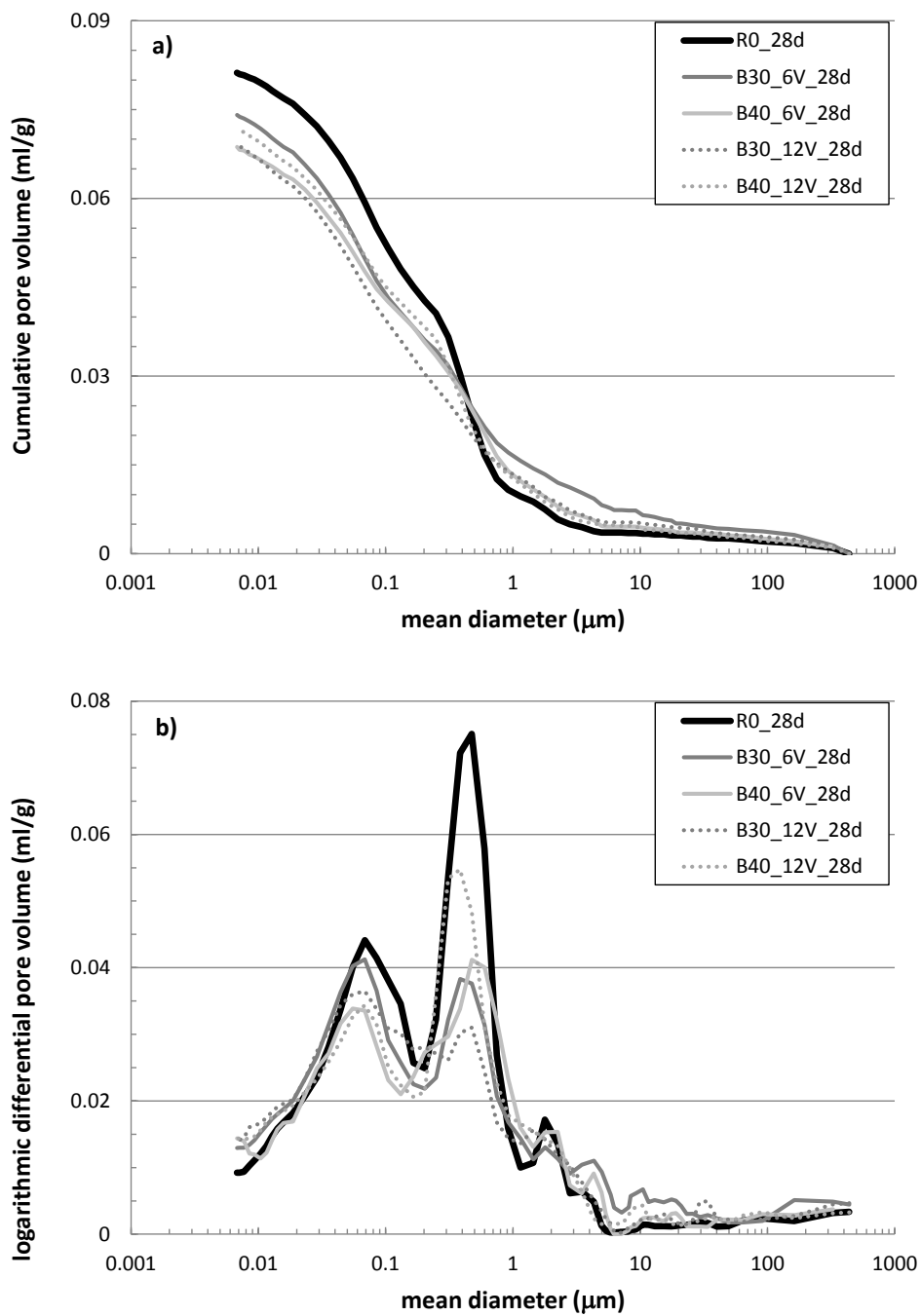


Figure 4. MIP at 28 days after the treatment finished. (a) Cumulative pore volume curve. (b) Logarithmic differential pore volume curve.

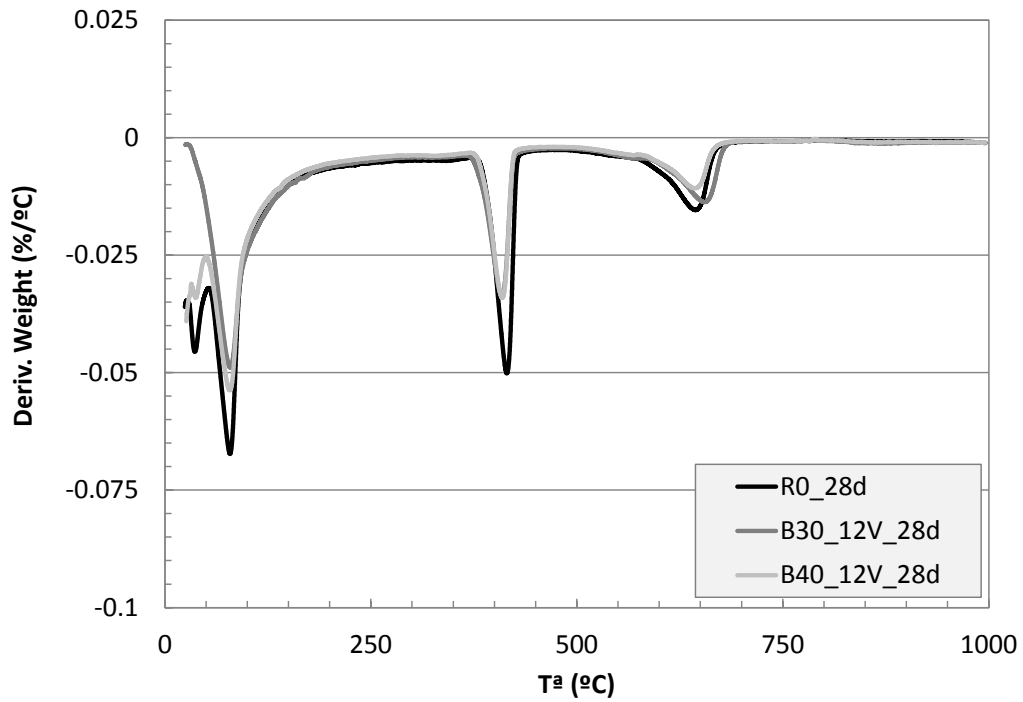


Figure 5. TGA of reference and treated mortars at the age of 28 days after finishing treatment.

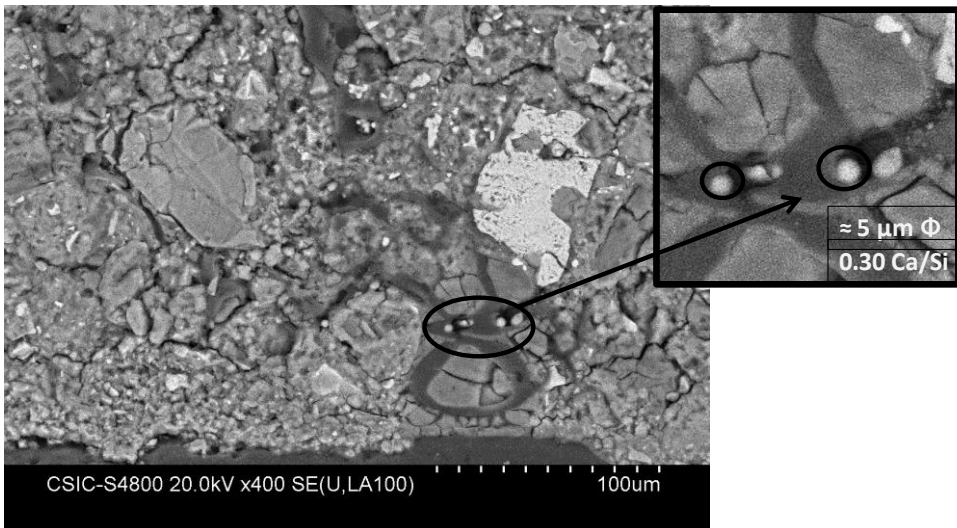


Figure 6. Micrograph of treated sample at the age of 28 days after finishing the treatment (B-40 at 12 V). Mortar exposed to the cathode (0.1 mm from surface).

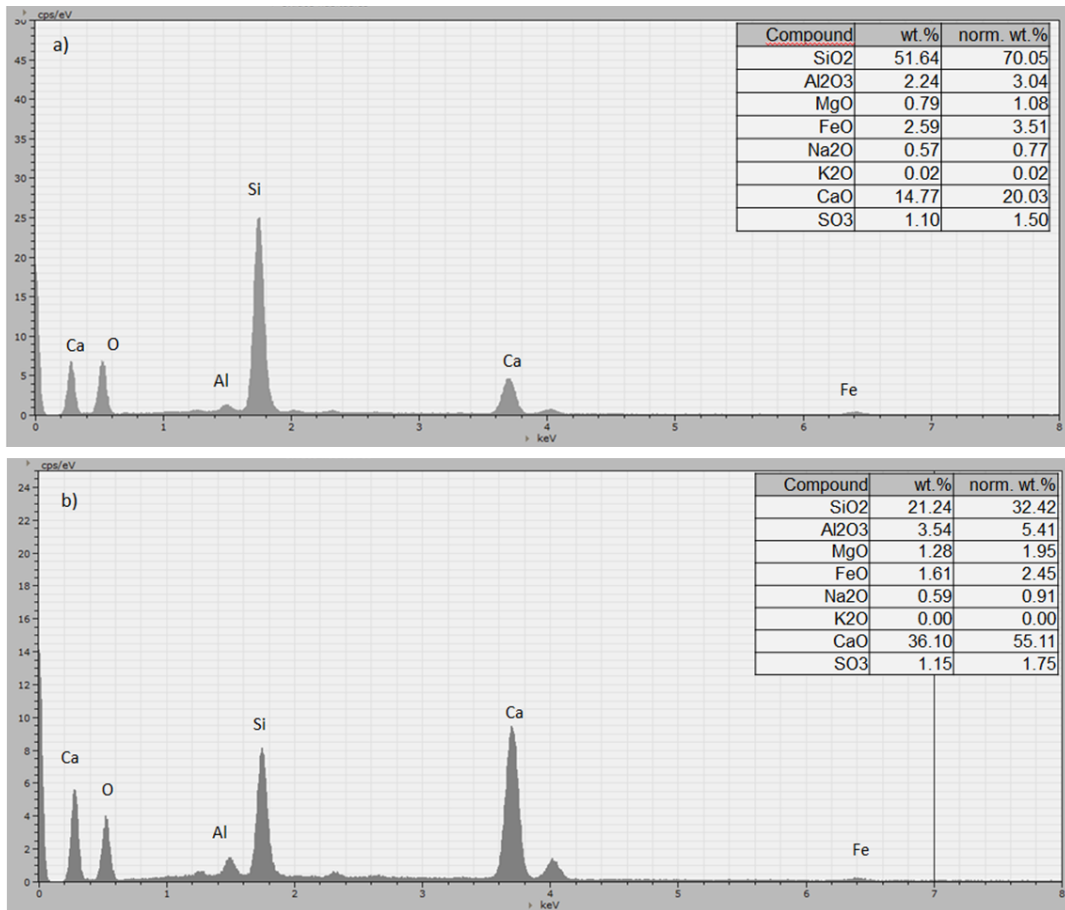


Figure 7. EDX microanalysis in treated mortar at the age of 28 days after finishing the treatment (B-40 at 12 V). (a) Flocculated nanoparticles observed in Figure 6, (b) gel C-S-H in the central region of the treated mortar.

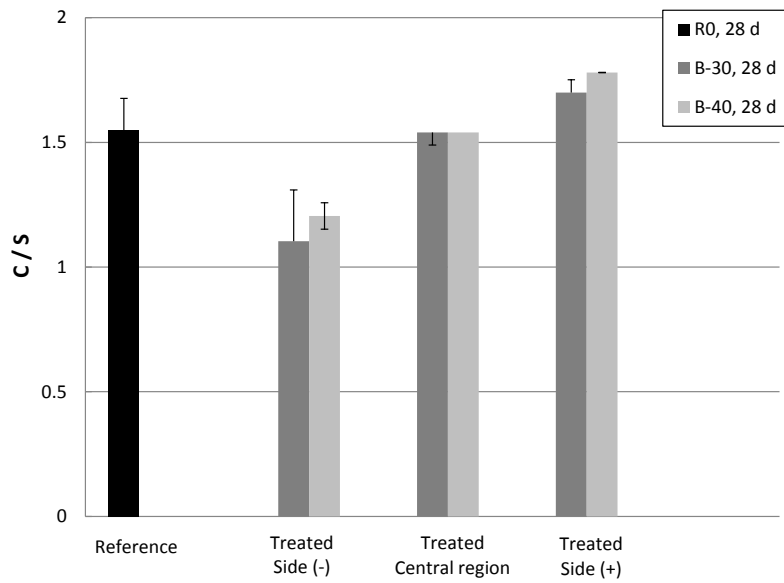


Figure 8. C/S ratio of reference mortar and profile at different regions of the treated samples (28 days after finishing the treatment at 12 V).

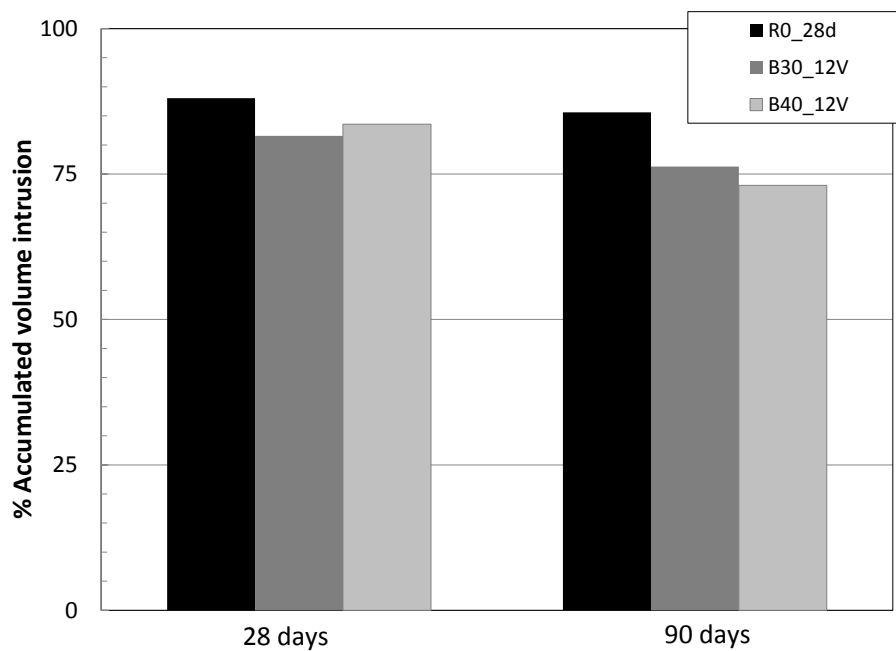


Figure 9. Evolution of capillary pore content at the ages of 28 and 90 after finishing the treatment.