Retrofitting and waterproofing of Aged Concrete Using Electromigration of Nanosilica

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Abstract

Reinforced concrete is a common construction material used to support structures around the world. However, the durability of concrete is affected by weathering action, abrasion, and chemical attack and this may lead to reduction in desired material properties necessary to support structures. Electromigration is the transport of material in a conductor under the influence of an applied electric field. All conductors are susceptible to electromigration, therefore it is important to consider the effects the electrical current resulting from the applied field may have on the conductor. The net force exerted on a single metal ion in a conductor has two opposing contributions: a *direct force* and *wind force*. Electrochemical engineering is the branch of chemical engineering dealing with the technological applications of electrochemical phenomena, such as electrosynthesis of chemicals, electrowinning and refining of metals, flow batteries and fuel cells, surface modification by electrodeposition, electrochemical separations and corrosion. This paper presents results of two small-scale tests using electromigration process as a means of transporting nanosilica to recover cement matrix integrity of aged concrete samples extracted from a 40 years old structure. A set up with two vessel was proposed, with electrical font working for 24 hours generating transportation of nanosilica into the aged concrete samples. The success of the electromigration process was verified with electronic microscope (qualitative analysis), scanning electronic microscope, and X ray dispersive energy spectroscopy. The results showed that an electromigration of nanosilica into the cement matrix occurred and resulted in reduction of micro fissures. Additionally, deposition of silica on the sample surface was observed. Reduction of calcium in the matrix was verified with the development of hydrated calcium silicate, providing the recovery of cement matrix in increasing cement mechanical properties like strength and also decreasing the porosity of the concrete matrix.

Introduction

There has been a rise in the development of newer technologies for improving concrete durability. Maintenance and retrofitting of reinforced concrete structures is an expensive operation, but necessary to mitigate premature deterioration of structures. Mehta and Monteiro (1994) showed that repairing or retrofitting structures incur a high cost and sometimes exceed planned budget associated with maintaining structures made from reinforced concrete. The cost of retrofitting and repair has been growing in geometric progression with a rate of five, known as Sitter Rule or Low of the 5. In Europe, costs of retrofit and maintenance are the same as that of the construction of new buildings. For example, 100 billion euros are spent in new buildings annually in Germany with a similar cost for maintenance of the existing buildings. Nano Silica as a retrofitting material has a great advantage, especially when used with active silica (Kara and Durmus 2019). It is a great alternative to develop high strength concrete, or mortar, reducing consumption of cement and increasing lifetime of constructions. Similarly, it is beneficial for structural retrofits due to mitigate exposure to the environment. Recent research found that adding Micro and Nano Silica in cement mortar can increase compressive and flexural strength (Kara and Durmus 2019). 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. Electrochemical engineering is the branch of chemical engineering dealing with the technological applications of electrochemical phenomena, such as electrosynthesis of chemicals, electrowinning and refining of metals, flow batteries and fuel cells, surface modification by electrodeposition, electrochemical separations and corrosion. In analytic chemistry, techniques using electro migration in capillarity are growing in popularity, especially for bioanalysis (Lin et al. 2011). Retrofitting reinforced concrete using electrochemical process has been studied for many decades, especially for steel, and demonstrated the efficiency of the method (Liu and Shi 2009), more recently in cement materials. Technical terms can be found in papers about electrophoresis in clinic chemistry, but mostly cannot be used for capillarity techniques and do not follow definitions of IUPAC. A new technique to retrofit cement or mortar is using electro migration of Nano Silica (Němeček and Xi 2015) that recovers the structure of the cement matrix damaged by environmental action or moisture. Diaz et al. (2015) confirmed the migration of Nano Silica through hardened cement mortar under an electric field, providing a densification of the cement mortar. Nano Silica reacts with calcium hydroxide that is generated after post hydration of cement having mineralogical components close to those developed by cement, which is the Hydrated Calcium Silicate (CSH) gel. This gel is better than CSH of the cement, because of its great mechanical properties. Using of Nano particles have increased significantly in recent years for increasing the development CSH in pozolan reactions with calcium hydroxide in cement matrix formation. Nano materials in the cement induces the agglomeration of Nano particles. This material is also called Nano silica (NS) which are particles of silica in Nano metric size. The result of Nano silica in the formation of cement matrix is a higher densification of the material, what can increase the durability of the mortar. Most of the cement found around the world have about 5% of Gypsum plaster, 12% of slag, limestone and Pozolana and 83% of clinker (Mehta 2010). Due to the substitution of clinker for other materials, clinker concentration is being reduced in the cement and the CO_2 emission in cement manufacturing. Hence, the use of Nanomaterial in this process can contribute for pollution reduction too. Severe weather actions can degrade cement mortar, developing cracks and porosity that reduce the strength of the material. In addition, the steel reinforcement in concrete may corrode due to moisture penetrating through cracks and increased porosity and compromises the structural support capacity. To mitigate this problem, the cement matrix needs to be maintained or retrofitted during the service life of the structure. Nano Silica has the potential to rebuild/heal the damaged cement matrix. However, the process that Nano Silica will be transported into the mortar needs innovation and this paper investigates the use of electromigration to achieve the goal. Electromigration have been used in many researches to verify chemical behavior of substances (Lee et al. 2022; Sprocati and Rolle 2022; Vialich et al. 2022). This is a relatively new technique in concrete retrofitting with scant test results reported in literature (Díaz-Peña et al. 2015; Gaitero, Campillo, and Bustos 2008; Kawashima et al. 2013). The technique needs more verification before its widespread adoption to specific and real situations. In a long term, it could be used to retrofit large structures such as concrete dams that may be subjected to non-stop percolation. This water leach the concrete damaging the cement matrix over time

(Gaitero, Campillo, and Bustos 2008). Nano technologies can improve some properties of cement materials, such as workability, water loss cracking, cohesion, mechanical properties, ductility, porosity and corrosion of rebars in reinforced concrete structures as reported in Topçu and Uzunomeroglu (2019). Current research in Nano Silica or carbon nanotubes addition in mortar or concrete includes evaluation of cement properties such as rheology, pozolanicity, compressive and flexural strength, durability of cement products using Nano and microstructures in the cement matrix (Kara and Durmus 2019). Nano silica reactions with calcium hydroxide have been reported (Lin et al. 2011; Rodrigues 2011) and can develop hydrated calcium silicate (C-S-H) which is the mainly responsible for the concrete compressive strength. The benefits of this reaction can be measured by the reduction of Ca in the chemical reaction (Björnström et al. 2004). This paper presents results developed in laboratory using a new process involving nanoparticle to retrofit cement or mortar using electro migration of Nano Silica, recovering the cement matrix. This article aims to provide proof that the electromigration process works to protect concrete and improve performance of damaged cement mortar using Nano Silica. It is worth to note that improving concrete performance with electromigration seems to be economic and environmental advantage.

Material and Methods

A laboratory scale test was designed to validate the electromigration of Nano Silica for retrofitting damaged or aged concrete. Two similar tests were made: Test 1 was conducted at Flowtest in Brazil and Test 2 was conducted at George Mason University – USA. Electromigration in capillaries have been used as a method of separations through reduced diameter capillaries and a high value electric field. Different principles of separation can occur, such as electrophoretic capillaries and chromatographic capillaries, which use electric field to pump fluid. Electromigration in capillaries has showed high efficiency in separations of small ions, both organic and inorganic, explosives, drugs, dyes, polymers, proteins and peptides, DNA and RNA, cells, particles, etc. In the same way, ions conduction is the process with Nano Silica used in this test to retrofit cement matrix, taking advantage of porosity and capillarity of the cement matrix. The layout for the tests has an electrical font, with voltage regulator, and the concrete provides the ionic means of conduction. The circuit worked for 24 hours. It is a low-cost electrochemical laboratory, shown in Fig. 1.

The concrete samples were extracted from an aged concrete structure, made in 1980. These samples were exposed to environmental factors for 40 years, such as pollution and contaminants including chlorides and sulfides. A circular saw was used to extract the samples from the existing aged concrete structure, as shown in Fig. 2. Samples were screwed to reach the dimensions of 10 cm in height, 15 cm in length and 8 cm in width, as shown in Fig. 3.

The concrete sample was then broken by mechanical shear after the electromigration process, to ensure cement matrix preservation (Fig. 4). Qualitative analysis was made using an electronic microscope to verify Nano Silica deposition inside the cement matrix of samples. The analysis allowed validation of the electromigration process with deposition of Nano Silica inside and outside of the surface of the sample.

Test 1 samples were analyzed with X ray dispersive energy spectroscopy probe to verify chemical identification and with Field Emission Gun (FEG) Scanning Electron Microscopy (SEM) to verify material morphology, crystalline structure and chemical composition. For these analyses, the samples were cut preserving the samples surfaces. Figure 5 shows samples cut for these analyses. The equipment parameters include 15 kV and 20 kV of electron beam voltage, 18.0 nm of spot size, 15 mm of work distance and scan resolution mode. Representative areas of the material, with no pretreatment to increase conductivity, were used for microanalysis. Qualitative analysis for verifying the presence of chemical elements was conducted using spectroscopy detector of X-ray.

Results and Discussion

Test 1

It was found out that there was a buildup of silica on the specimen faces that were exposed to the fumed silica, with a buildup also occurring on the upper face of the aged concrete sample as shown in Fig. 6. The Nano Silica migrated to positive electrode due to its negative charge and electric field forces.

Furthermore, it was verified that electroextraction process occurred coupled with electromigration. Figure 7 shows the setup after the test. In part A of the vessel there was deionized saturated Nano Silica water and the negative electrode. In part B, before starting the test, there was only deionized water, positive electrode and a sensor to measure pH. It is possible to see that during the process of electromigration, contaminants of the aged concrete were extracted, and migrated to part B, going through the solution to positive electrode. The brownish color indicates the probable presence of iron in the sample with other contaminants. This fact confirms the electroextraction process occurring concurrently with the electromigration of Nano Silica to the concrete sample.

Results of SEM can be seen in Fig. 8(a) with no electrochemical process and (b) after electrochemical process, both 280x magnified. Morphological and texture analysis validates the presence of silica on the sample. Additionally, mineralogical maps can be seen in Fig. 9. These results point to reduction of Ca due to electromigration of Nano Silica during the process. The exothermic process between silica and calcium hydroxide explains these results with decomposition of Si-O-Si. Calcium ions (Ca^{+2}) compensate the charge imbalance, linking to silanols group (Si-OH), and to $Si\text{-}O^{+}$, developing hydrated calcium silicate gel (C-S-H). This gel is the mainly responsible for the compressive strength of concrete. Nano silica reactivity with $Ca(OH)_2$ depends on Nano silica Q^3 percentage, that is the molecular structure of silicates in function of molar ratio. This percentage influences the reaction kinetics. The reduction of calcium indicates the capacity of cement matrix retrofit, once more concentration of C-S-H increases the compressive strength of concrete.

The reduction of calcium after electromigration process was verified with higher magnified view as well. For instance, with 580x and 800x magnification, the same behavior was noted. The presence of micro fissures was easily observed on the samples with no silica treatment. Analysis of SEM, for samples after electromigration process, found micro fissures on the cement matrix only for higher magnified views (580x and 800x). Samples after process showed denser matrix comparing to samples with no process. These results points to a retrofit of aged concrete cement matrix, increasing the strength by filling the matrix with silica.

Test 2

Electronic microscope was used to qualitative analyze the inside part of the sample. To verify the electromigration process of the fumed silica, after the natural drying time, the concrete sample was broken by shear and analyzed using an electronic microscope. Figure 10 shows the inside part after the break process for visual analysis.

It was noticed that the silica entered more easily and in greater quantity in the cracks of the sample. With the aid of the same electron microscope, it was possible to see the surface of the part inside the crack regions in detail in Fig. 11.

Regarding the central part of the sample, a significant lower amount of silica accumulation was observed in the sample of Test 2, comparing to the samples of Test 1. It should be noted that the silica was dispersed in the central region of the sample, instead of in the crystallized form. The reasons for these differences mentioned are still being explored. The plausible explanation for the cause is the different force fields that were formed due to the electrodes and differences in electric potentials generated by the local power networks in Brazil (test 1) and in USA (test 2). Figure 12 shows the 1600x magnified microscopic images where the pulverized silica is in the central region of the tested concrete sample from test 2. In general, it appears that silica was accumulated on the external faces of the concrete sample and, although it has permeated the sample, there was no significant concentration in the central region. As mentioned earlier, one possible cause of the difference between the results observed in Test 1 and those in Test 2 is the type of silica used in the two tests. Nanosilica is industrially produced with purity near 100%. It can be manufactured with various desired specific surfaces areas ranging from 60 to over 600 m^2 /g (0.012 to 0.123 ft^2 /lb). Nanosilica was found to be much more efficient than microsilica for improving the durability, strength, and permeability of cement-based materials in literature (Kara and Durmus 2019). Considering that all the boundary conditions of the tests were the same, it can be inferred that the physicochemical characteristics of the Nano silica of North American supply exhibits different characteristics from that of Brazilian supply. Apparently, the current density passing through the Nano silica solution had its value decreased in relation to the Test 1. It seems that there was not electroextraction in Test 2 process. However, there was electromigration. The migration of Nano silica inside the sample was attenuated which corroborates the influence of the decrease of current density in the case of Test 2.

Conclusion

Aged concrete samples were subjected to electromigration and electroextraction processes. The samples were extracted from a concrete structure with approximately 40 years. Electrochemical process showed the migration of Nano Silica to the sample surface and interior part. Additionally, was possible to verify the migration of contaminants presents in the sample to the electrolytic solution. The proposed test set up with coupled vessels was efficient to provide Nano Silica transportation into concrete samples. Analysis using X ray diffraction (XRD) and Scanning Electron Microscopy (SEM) verified the migration process of Nano Silica into the concrete samples and cement matrix recovering with $Ca(OH)_2$ reaction as well. Other tests are being carried out to ensure the appropriate saturation of the Nano Silica in the solution and the contaminants that this process can extract from aged concrete.

Declarations

Competing interests

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Financial interests

Any undeclared financial interest that could embarrass the author were it to become publicly known after the work was published. The authors have no relevant financial or non-financial interests to disclose.

Author Contributions

Dr. Fausto Batista Mendonça: His contribution to the current study includes conceptualization, methodology, test preparation and full paper writing and editing. Dr. Girum Solomon Urgessa: He has contributed to the field test, paper review and analysis of results. Marcela Galizia Domingues: She has contributed to the investigation, methodology, test preparation and formal analysis of test results. Bruno Rocco: His contribution for the current study includes full test preparation and resource providing. Dr. Leopoldo Junior: He has contributed to the field test preparation and conduction. Dr. José Atilio Fritz Fidel Rocco: His contribution includes project administration, methodology, supervision in the field test and acquisitions. All authors have read and agreed to the published version of the manuscript.

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Figures

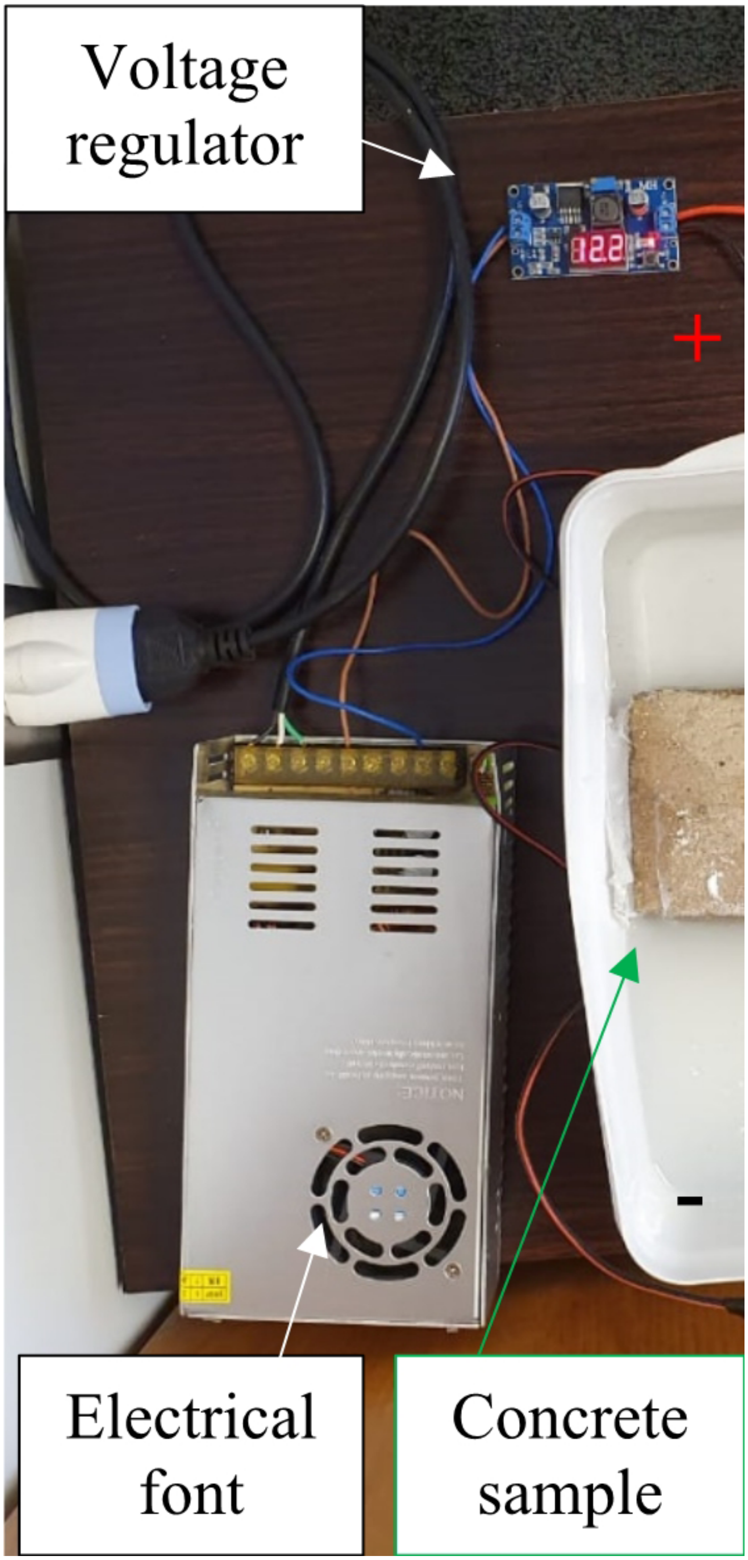

Figure 1

Set up of the electrochemical test

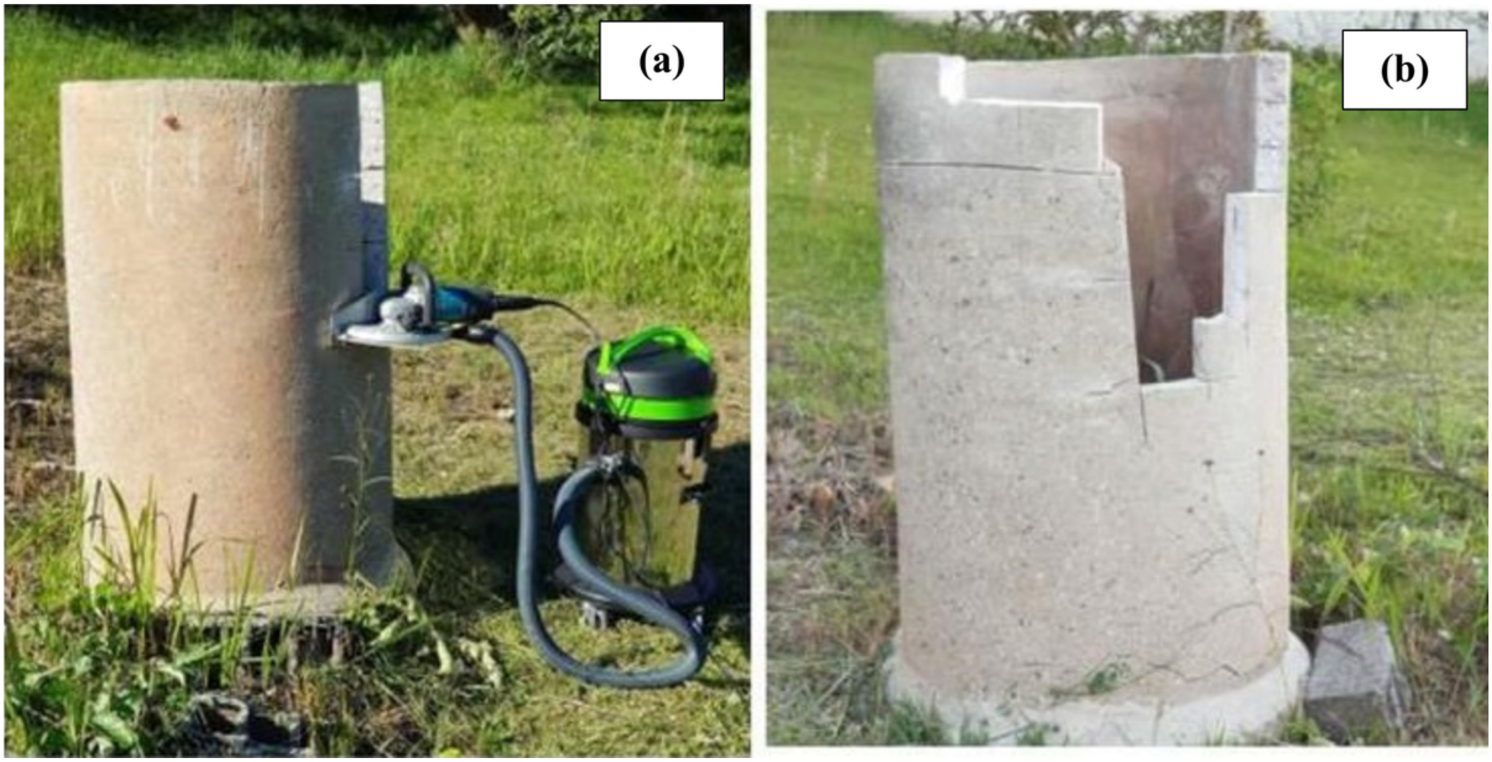

Figure 2

(a) Circular saw coupled to a dust control. (b) Structure after extraction

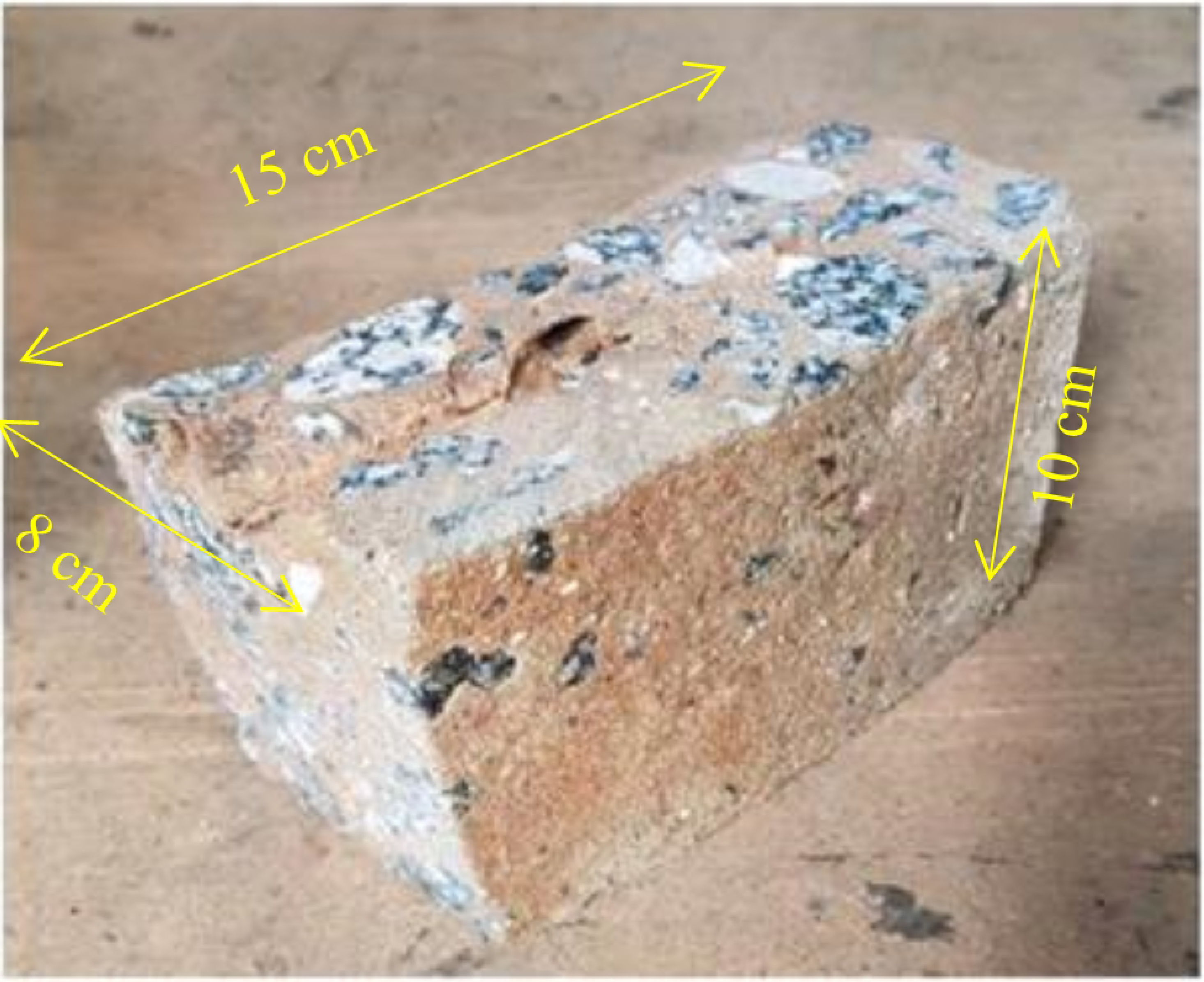

Figure 3

Sample dimensions after screw process

Figure 4

Mechanical shear fracture process of test 1 sample

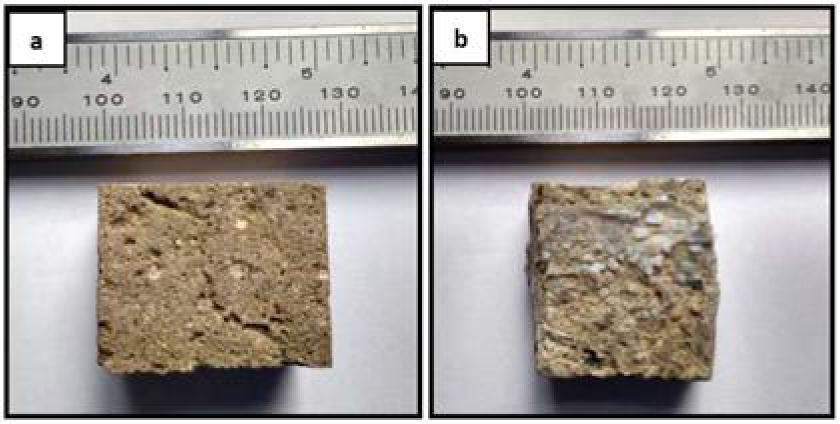

Figure 5

Samples (a) with no electrochemical process, and (b) after electrochemical process

Figure 6

Silica accumulation points on the upper surface of the sample

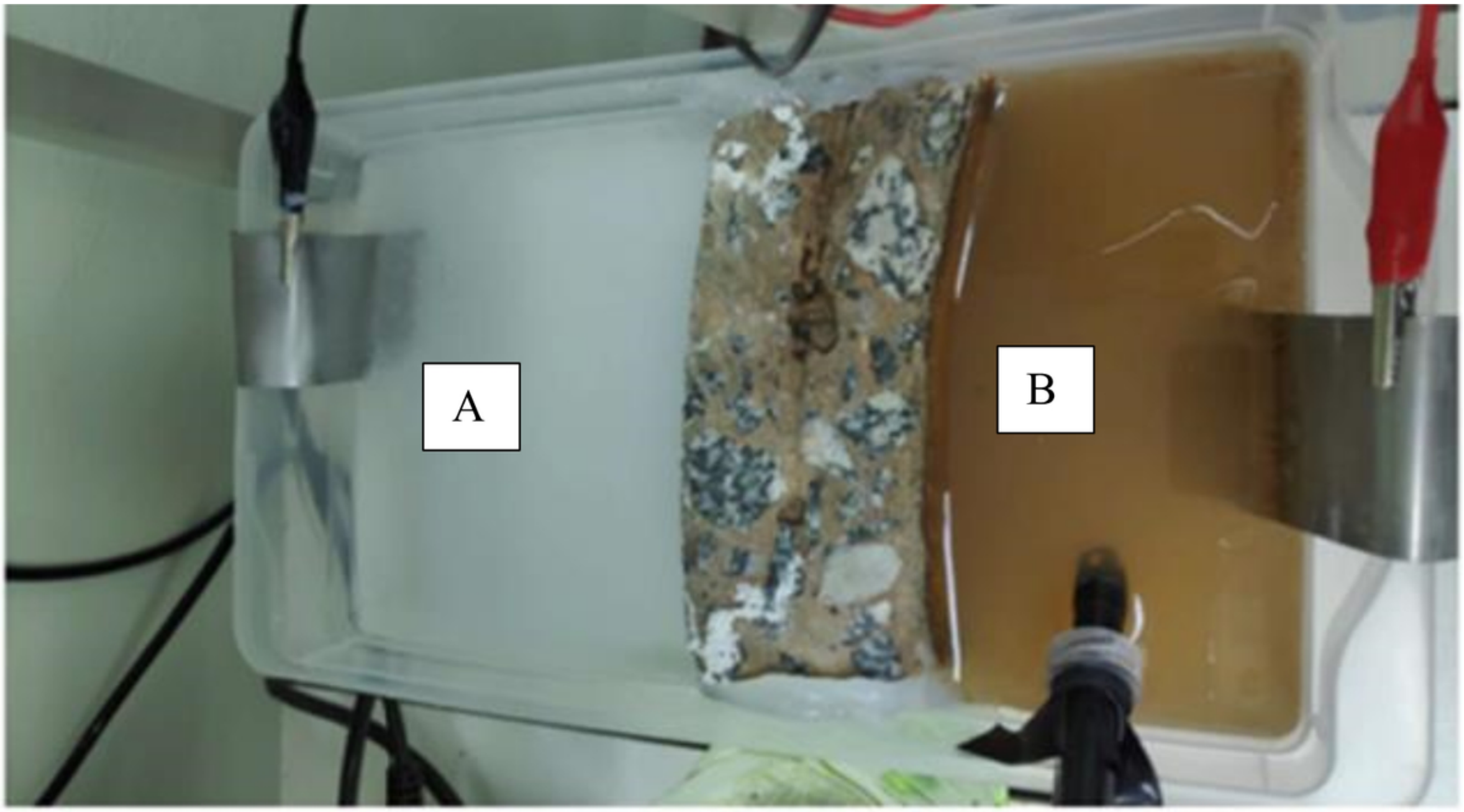

Figure 7

Electromigration and electroextraction verification after Test 1

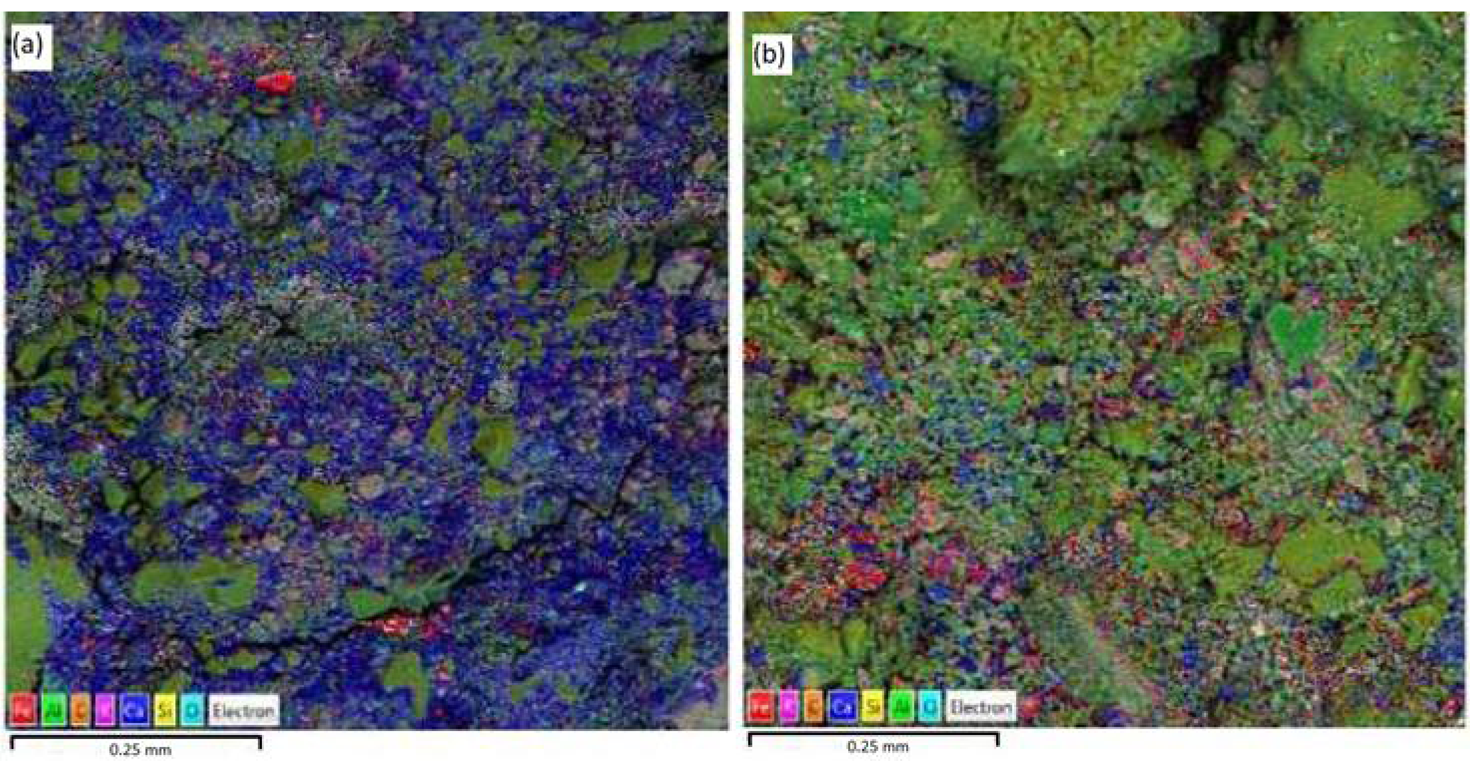

Figure 8

Sample (a) with no silica treatment and (b) after silica treatment

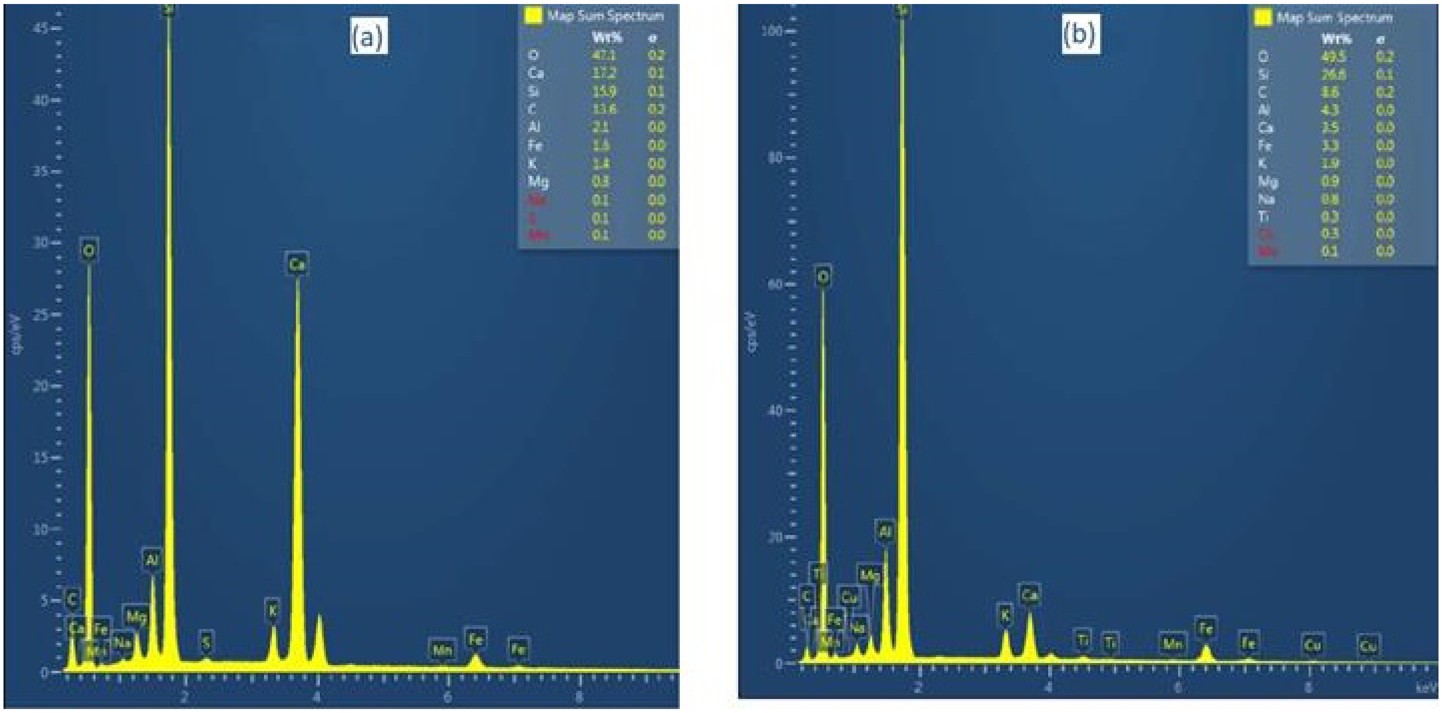

Figure 9

Mineralogical map (a) with no electrochemical process and (b) after electrochemical process

Figure 10

Inside of sample after test

Figure 11

Fumed silica accumulation on the sample surface (1800 x magnified)

Figure 12

Internal accumulation of no crystalized silica fumed (1600 x magnified)