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https://doi.org/10.1590/2317-4889202220210061

BJGEO
Brazilian Journal of Geology

Inhibition of swelling clays and consolidation of Itararé Sandstone using diaminoalkanes (DAA) and ethyl silicate (TEOS)

Danielle Grossi[1], Eliane Aparecida Del Lama[2*]

Abstract

The conservation of stones containing swelling clay minerals such as montmorillonites is a challenging task. In this context, swelling inhibitors (DAA) were tested and a treatment based on consolidation with TEOS (ethyl silicate) was carried out on a sandstone containing swelling clay minerals: the Itararé Sandstone (commercial name). In this laboratory experiment, the inhibition of swelling, pore size and distribution, capillarity, colorimetric alteration, durability of treatments against the action of water, effectiveness of consolidation, and penetration depth were evaluated. Swelling inhibitors were effective in inhibiting the clay minerals from swelling. The consolidant, despite its effectiveness, altered the pore size and distribution and water absorption significantly, forming a very cracked gel, darkening the stone, reducing resistance to the action of water and presenting small penetration depth. When swelling inhibitors were applied before the consolidant, swelling inhibition also occurred, the porosity was less altered, the consolidant was less cracked, there was less chromatic modification and the sample became more resistant to the action of water. Therefore, this treatment proved to be more effective with fewer changes to the physical characteristics of the stone than the sole application of the consolidant.

KEYWORDS: ethyl silicate; swelling clays; diaminoalkanes; sandstone; consolidation; stone conservation.

INTRODUCTION

Deterioration processes occur due to the interaction of the physical (e.g. porosity), petrographic (e.g. mineralogy and size of grains/crystals) and mechanical (e.g. anisotropy) characteristics of the stone with the environment where it is found, be it in nature or in buildings and monuments.

Some sedimentary stones present swelling clay minerals in their composition. In areas exposed to moisture, these minerals expand, resulting in internal pressures that deteriorate and affect the durability of these stones used in buildings (Wendler *et al.* 1990, Delgado Rodrigues 2001, Jiménez González and Scherer 2004, Sebastián *et al.* 2008, Wedekind *et al.* 2013). In addition to the expansion, these stones exhibit viscoelastic behavior, likely due to the sliding of the clay mineral sheets (Scherer and Jiménez González 2005).

There are several examples of the sedimentary stones with the presence of swelling clay minerals used in the heritage and their deterioration is the subject of study of many researchers (Wüst and McLane 2000, Jiménez González and Scherer 2004, Weiss *et al.* 2004, Scherer and Jiménez González 2005, 2006, Jiménez González and Scherer 2006, Sebastián *et al.* 2008, Wangler and Scherer 2008, 2009, Ruedrich *et al.* 2011, Asku *et al.* 2015, Tiennot *et al.* 2020). Wheeler (2005 and references therein) discusses the consolidation of stones with clay minerals with the use of alkoxysilane, such as TEOS.

Identifying the type of expansion is the key step for understanding and preventing damage. Two main types of expansion in clay minerals have been identified: short-range, with increased volume in intracrystalline spaces, and long-range, with continuous osmotic expansion. The first one happens due to the hydration of the counterbalancing cations, which generates a sudden and fixed augmentation of the spacing between the layers. In the second case, the spacing between the layers increases continuously as the interaction with the water also increases (Wangler and Scherer 2008). One way to differentiate the two types of expansion is to compare XRD analyses from untreated and surfactant-pretreated samples exposed to organic solvents. Another way is to carry out mechanical tests that progressively measure the swelling.

For stones that present swelling clays and show a certain degree of degradation, the necessity of consolidation should be evaluated. When consolidation is necessary and advisable, a possible treatment is the application of a consolidant (ethyl silicate — TEOS), preceded by the use of a swelling inhibitor (diaminoalkane — DAA). DAA reduces the swelling of clay minerals and prolongs stone durability, and TEOS increases the strength and restores its physical properties.

[1]Programa de Pós-Graduação em Geociências (Mineralogia e Petrologia), Instituto de Geociências, Universidade de São Paulo – São Paulo (SP), Brazil. E-mail: dannigrossi@gmail.com

[2]Instituto de Geociências, Universidade de São Paulo – São Paulo (SP), Brazil. E-mail: edellama@usp.br

*Corresponding author.

Clay minerals have many OH groups, which are receptive to alkoxysilanes, for instance TEOS. However, sandstones with clay cementation present half of the increment of strength in comparison to sandstones with silicate cementation (Sattler and Snethlage 1988). Stones with clay minerals show preferential deposition of TEOS between their layers, compared to stones that do not present these minerals (Felix and Furlan 1994 *apud* Wheeler 2005). Snethlage and Wendler (1990) warn of the dangers of treating clay cemented sandstones since treatment with alkoxysilanes increases the expansion that occurs in clays when in the presence of water, hence the importance of pretreatment with inhibition of swelling.

The treatments are individualized, and each stone needs to be studied to verify which is the best treatment product and the best application technique in addition to other variables, since what works well in one case scenario may not present good behavior in another (Ferreira Pinto and Delgado Rodrigues 2008). Thus, there are no ready-made recipes and no product should be used indiscriminately without previous laboratory and field tests. When applying a product to the stone, it is important to check if it changes and if its properties are above acceptable limits, especially in relation to strength, sorptivity, water absorption, and appearance. It is always necessary to evaluate both the changes in these properties and the effectiveness of the product versus the extent of damage.

In this context, the Itararé Sandstone was studied. It covers the front facade of the Municipal Theater in the city of São Paulo, Brazil, presenting swelling clay minerals (montmorillonite) in its composition and showing an advanced state of degradation and loss of grout between the sandstone blocks. The consolidation product that was applied in the last restoration work completed in 2011 obstructed the pores, not allowing the water infiltrated by the joints to evaporate, therefore generating an increase in the internal pressure behind the treated layer and causing spalling (Fig. 1). Thus, studies that can help the conservation of the Itararé Sandstone are important for the preservation of this iconic building in the city of São Paulo. The goal of this paper was to evaluate the performance of three swelling inhibitors (DAA) and one consolidant (TEOS) applied to this stone aiming its conservation.

MATERIALS AND METHODS

The studied stone was characterized by petrography. In order to inhibit the swelling of montmorillonite and possibly improve the performance of the consolidant, the pretreatments were tested. To verify the effectiveness and behavior of the products, the following tests were performed: X-ray diffraction (XRD), cation exchange capacity (CEC), mercury porosimetry, capillarity, scanning electron microscopy (SEM), spectrophotometry, saturation and drying cycles (with evaluation of the P-wave velocity) and penetration depth.

Stone

The material studied, the Itararé Sandstone, is a stone containing swelling clay minerals from the group of montmorillonite, which cause great damage to the buildings these minerals constitute due to the spalling caused by its expansion and contraction.

The color of the Itararé Sandstone is beige to pale yellow (Fig. 2), with plane-parallel and cross stratification. The granulometry ranges from fine (0.11-0.36 mm) to coarse sand (0.18-1.1 mm) (Fig. 3A), and the grains are sub-rounded to sub-angular. It is composed predominantly of quartz, as well as feldspars, muscovite, biotite and matrix consisting of clay minerals (Fig. 3B). Titanite, tourmaline and zircon appear as accessory minerals. The detailed petrographic description can be found in Del Lama *et al.* (2008) and Grossi (2016).

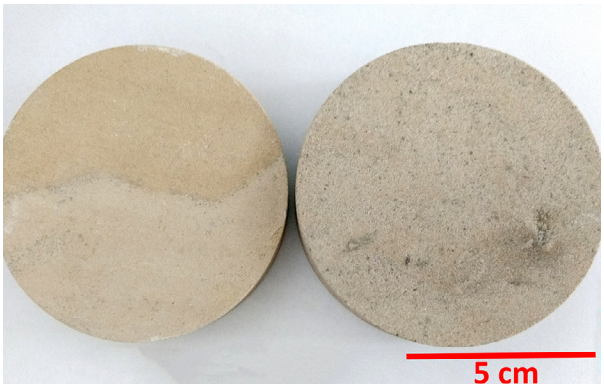

Figure 2. Itararé Sandstone, untreated sample.

Figure 1. Degradation of the Itararé Sandstone in the front facade of the Municipal Theater of São Paulo.

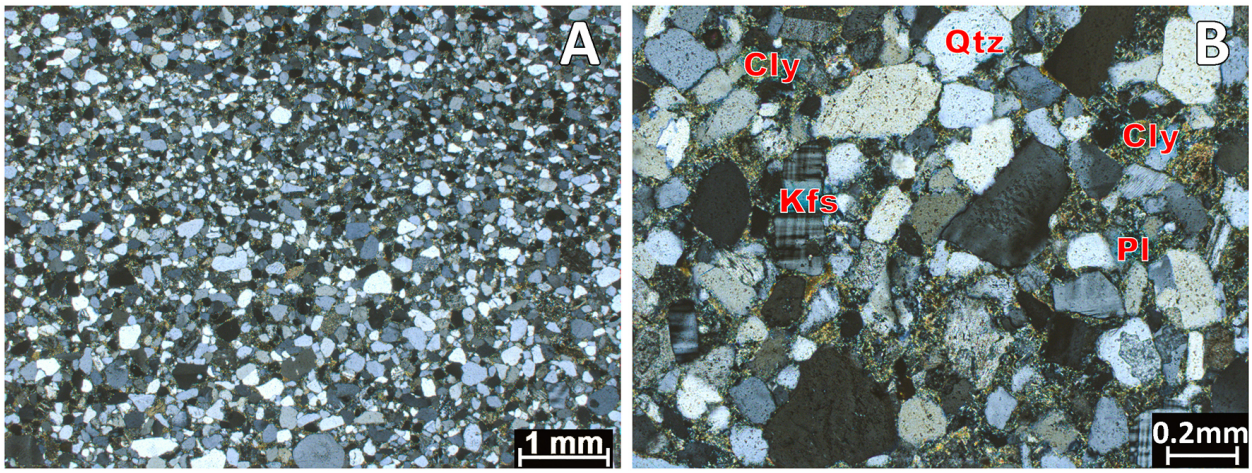

Figure 3. Photomicrographs of the Itararé Sandstone. (A) Gradual passage of the thinnest and thickest quartz grains — crossed nicols. (B) Itararé Sandstone mineralogy: quartz (Qtz), potassium feldspar (Kfs), plagioclase (Pl) and clay minerals (Cly) — crossed nicols.

Treatments and products used

The products used in this study were DAA and TEOS.

DAA, whose general formula is $NH_2(CH_2)_nNH_2$, is a straight chain alkane, with amine groups at each end. These surfactants are believed to replace the alkali cations between the layers of clay minerals, binding them and preventing clay expansion. Another benefit of using these products is the performance improvement and durability of silicate consolidants in the presence of specific substrate conditions, i.e., swelling clays (Wangler and Scherer 2009). The solubility of these products decreases as the number of carbon atoms increases. The DAAn notation is used to indicate the number, n, of carbon atoms. The concentration indicated for $n \leq 10$ is 0.31 mol/L, according to Wangler and Scherer (2009). These products had already been used previously (Snethlage and Wendler 1990, Jiménez González and Scherer 2004), demonstrating that DAA can reduce the swelling of clay minerals. This product will be referred to as **A** in this paper.

TEOS, also known as ethyl silicate, is one of the most used products for consolidating stones, mainly sandstones and granites due to its high compatibility and efficiency. However, it has been used on a wide range of substrates, like limestones (Sassoni *et al.* 2013, Rodrigues *et al.* 2021), Portland cement mortar (Barberena-Fernández *et al.* 2015), bricks and terracotta decorations (Franzoni *et al.* 2014), as well as masonry construction materials (Muñoz *et al.* 2015). The deposition of silica gel by the application of TEOS occurs by two reactions that take place simultaneously. The first one refers to the hydrolysis of the alkoxy group, separating the ethanol molecules. This reaction can be improved by acid or alkaline catalysis, which is done in most products sold on the market. The second step is the condensation of unstable silanols (2 -Si-OH → -Si-O-Si- + H_2O) to form an amorphous gel. TEOS is found on the market in monomer and oligomer forms, which have the same reaction to form silica gel. The only difference is the presence of oligomers in the latter (Snethlage and Sterflinger 2011). An advantage of TEOS is that the by-products formed in the reaction result in ethanol, which is evaporated and does not cause damage to the stone (Wheeler 2005, Snethlage and Sterflinger 2011). However, stone consolidation is still a challenging task and TEOS, as many other products, has limitations and consequences resulting from the product-substrate interaction (Wheeler 2005, Siegesmund and Snethlage 2014). This product will be referred to as **TW** in this paper.

The studied samples were separated into groups in which different products (**A**, **TW**, **ATW**) or product sequences (**A2**, **A3**, **A6** — application of A2 and drying, application of A3 and drying, and finally application of A6 and drying) were done so that it was possible to better understand the action of each product individually and its action when used sequentially, that is, in consecutive and unmixed treatments. Consecutive treatments have also been carried out in other articles (Wangler *et al.* 2006, Wangler and Scherer 2009).

For swelling inhibitors, three DAA with 2, 3 and 6 carbon atoms were applied successively: anhydrous ethylenediamine (**A2**), 1.3 diaminopropane 99% (**A3**), 1.6 diaminohexane 60% (**A6**); respectively. Wangler and Scherer (2009) demonstrated that these molecules act between the clay layers replacing the amine groups with counterbalancing cations, although they leave residual tension after the application. These products were prepared at 0.25 mol/L based on the results found by Wangler and Scherer (2009), who used the 0.31 mol/L dilution. Three swelling inhibitors were used consecutively since, in a previous study, Wangler *et al.* (2006) found that the application of smaller molecules of the swelling inhibitors before the larger ones presented better results.

For consolidation, the ready-to-use TEOS from Wacker Chemie AG — Silres® BS OH 100 (**TW**) was applied, without the need for a solvent (pure) as indicated by the manufacturer.

Three different procedures were carried out:

- assessment of the performance of swelling inhibitors by means of only a pretreatment with consecutive application of three swelling inhibitors, waiting for the drying of one swelling inhibitor before application of the next one (hereinafter referred to as **A**);
- only consolidation with application of TEOS (hereinafter referred to as **TW**), without the prior application of swelling inhibitors;

- application of swelling inhibitors (as mentioned above), followed by the consolidant (hereinafter referred to as **ATW**).

Application method

All products were applied by capillarity and subsequent immersion. The largest side of the samples was immersed in 0.5 mm of the product (Fig. 4A). After the product reached the top, the samples were completely covered in the solution and remained in a capped container for 24 hours (Fig. 4B). After this period, they were left to dry at room temperature until their weight stabilized, which means that the volatiles were eliminated and the liquid evaporated.

Capillarity application cannot be carried out in large proportions, such as the facade of a building. Thus, techniques adapted for use in the field (in situ) were evaluated. The penetration depth was evaluated according with the procedure performed by Franzoni *et al*. (2015), in three application techniques: brush, spray and pulp (cellulose and bentonite). For the spray and brush techniques, 3 layers with a 5-minute interval between them were applied. This technique was used so that there would be enough product available for the stone to absorb it at its greatest potential. The cellulose pulp was applied for 5 minutes. After this, the samples were split in half and the wet area was measured visually with the aid of a ruler and caliper. All products were tested at this stage.

The size of each sample was 2.5 × 2.5 × 8.5 cm, with the following exceptions: 1.0 × 1.0 × 0.5 cm for the SEM analysis, 5.0 × 5.0 × 5.0 cm for the capillarity and depth of penetration test, and 1.0 × 1.0 × 1.5 cm for the mercury porosimetry analysis.

The results refer to 36 samples.

To facilitate the reading of the results, product abbreviations and respective treatments are listed in Table 1.

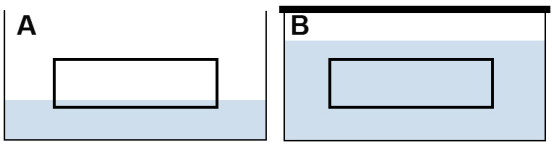

Figure 4. Application method of the products. (A) Initially, only the base of the sample was in contact with the product. (B) After the product reached the top by capillarity, the sample was completely immersed in the product.

Table1. List of abbreviations and products used in the treatments.

Abbreviation	Treatment
A2	DAA2: anhydrous ethylenediamine
A3	DAA3: 1.3 diaminopropane 99%
A6	DAA6: 1.6 diaminohexane 60%
A23	A2 → A3
A236	A2 → A3 → A6
TW	TEOS or Ethyl silicate
ATW	A2 → A3 → A6 → TW

→ consecutive treatments.

Tests

The tests performed are described below.

A X-Ray Diffraction (XRD): the Bruker's D8 Advance diffractometer with copper tube (Cu Kα) and nickel filter was used. The analysis were performed using the DIFRAC.EVA 4.1 program. The stones were ground and only the clay fraction was separated to be tested by the powder method. The same fraction was treated with each product and glycolated. XRD is important to identify the clay minerals;

B Cation Exchange Capacity (CEC): it was determined by the Hesse method (Hesse 1971) for untreated and treated samples. The stone was ground and the clay fraction was separated. This fraction was stirred for two hours with sodium acetate in a Falcon tube. After this period, the samples were centrifuged and the supernatant was discarded. To the rest, deionized water was added. The samples were manually stirred, centrifuged for 10 minutes, and the supernatant excluded. This procedure was repeated three times to remove all sodium acetate, then ethanol was added to the tube. The samples were centrifuged for 10 minutes and the supernatant was excluded. Subsequently, ammonium acetate was added and stirred for 2 hours at room temperature. The solution was centrifuged to separate all ammonium acetate, the supernatant was separated, and the sodium was measured. The reading was done on the flame photometer. The test was carried out on two untreated and two treated samples. This analysis was performed to measure the variation in the cation exchange capacity of clay minerals after application of the swelling inhibitor;

C Mercury porosimetry: the Micrometrics Pore Sizer 9320 porosimeter was used. One sample of each treatment and three untreated samples were tested, where the stone porosity was determined;

D Capillarity test: this test was performed in accordance with the BS EN 1925 (1999) standard. Weight was measured in intervals of 0, 15, 30, 60, 120, 180, 200, 300, 360, 420, 480 and 1440 minutes. One sample of each treatment was tested to determine the amount of water absorbed by the sample and it was used to verify if there was a change in this property of the stone after the treatment;

E Scanning Electron Microscopy (SEM): two instruments were used. The first, LEO 400I, equipped with an Oxford X-ray dispersive energy spectrometer (EDS), for which the samples were covered with carbon. The second, a Quanta FEG 600 — FEI, equipped with a microanalysis system by EDS Quantax-Bruker, (Detector 4030) and with a silicon drift detector. The samples were covered with platinum, approximately 15 nm thick. In this case, carbon could be analyzed in the samples. SEM was used to study the behaviour of the applied products and their morphology;

F Colorimetry: a Konica Minolta CM 2500d spectrophotometer was used. It was configured with D65 illuminant (spectral range of 350 – 750 nm), specular component included (SCI) and excluded (SCE), observer at an angle of

10º, and 8 mm opening. For the data analysis, the software On Color version 5.4.5.1 was used. Random readings were taken at five locations on the same side on three treated and three untreated samples, and the average results were expressed as L* (lightness), a* (red positive/green negative) and b* (yellow positive/blue negative) values. The number of measurement was based on Kuzmickas (2013), which establishes, through the accumulated average, the minimum number of measurement required in order to achieve a stable average in a stone of great colorimetric variability. This test was used to measure the chromatic variation after treatment;

G Saturation and drying test: a home-made device (Jiménez González and Scherer 2006) was used and configured so that the sample remained immersed in water for 20 minutes and 40 minutes emersed in the air, drying with the help of a fan. This time corresponds to 1 cycle and 550 cycles were tested in total. Before the test, the samples were submitted to heating at 300°C for 24 hours, as suggested by Sassoni *et al.* (2011), to magnify thermal stress in the samples and accelerate their weathering, since the samples used in the tests were obtained in the original quarry with no alteration;

H Ultrasound test: the P-wave velocity was obtained before and after the saturation and drying test to check the durability of the consolidants to the action of water. For the ultrasound test, the Mark III V-Meter (NDT James Instruments Inc.) was used, by the direct method, with 54 kHz transducers. For coupling, grease covered with plastic film was used. The orientation of the bedding was perpendicular to the propagation of the ultrasonic waves. For P-wave velocity measurements, the samples were dried at 60°C in an oven until they exhibited constant weight. Three samples of each treatment were tested.

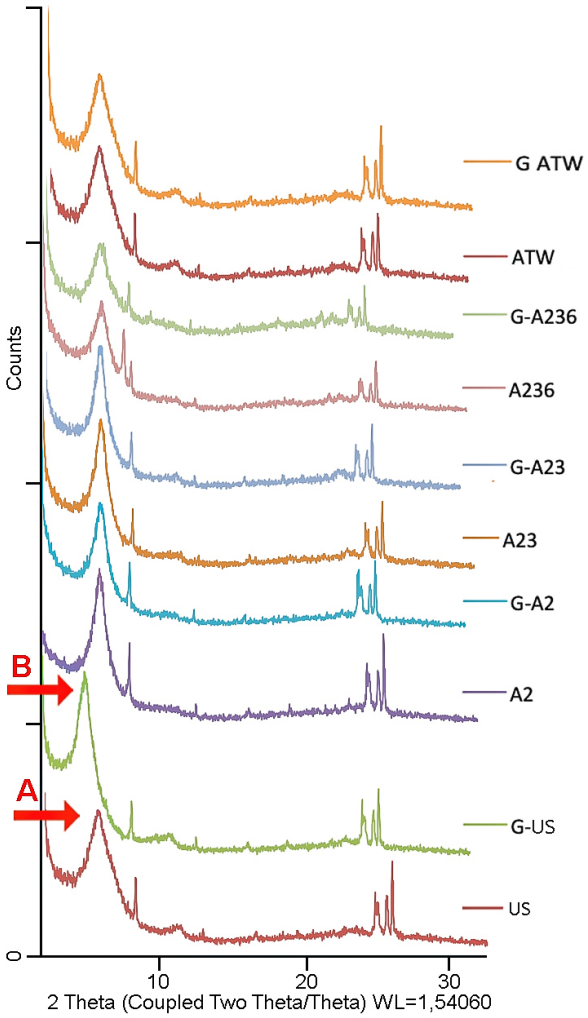

Figure 5. X-ray diffractogram of the clay fraction of Itararé Sandstone. From bottom to top: Untreated sandstone (US), glycolate untreated sandstone (G-US), treated with DAA2 (A2), treated with DAA2 and glycolate (G-A2), treated with DAA2 and DAA3 (A23), treated with DAA2, DAA3 and glycolate (G-A23), treated with DAA2, DAA3 and DAA6 (A236), treated with DAA2, DAA3, DAA6 and glycolate (G-A236), treated with DAA2, DAA3, DAA6 and TW (ATW), treated with DAA2, DAA3, DAA6, TW and glycolate (G-ATW).

RESULTS AND DISCUSSION

The clay fraction of the Itararé Sandstone was analyzed via X-ray diffraction (Fig. 5), checking the peak of 14 Å (arrow A) of interplanar distance, which after saturation in ethylene glycol changed to 16 Å (arrow B), guaranteeing the presence of swelling clay minerals from the montmorillonite group. These data corroborate results reported by Bocardi *et al.* (2006), Morenghi (2007) and Del Lama *et al.* (2008). Only the clay fraction was separated and treated with each of the three DAA (**A2**, **A3** and **A6**) to verify if the swelling behavior remained after glycolating. There was no expansion of clay minerals (Fig. 5), even using a product with a lower amount of carbons (**A2**). Regardless of the application of the **TW** consolidant, the swelling inhibitor behavior of the pretreatments (**A236**) remained. The analysis of the swelling clay minerals using the XRD was successfully performed by Wangler and Scherer (2008).

The clay fraction was analyzed by CEC. Before treatment, the value obtained was 61.14 cmolc/kg, and after treatment (**A**), it was 34.57 cmolc/kg, attesting to a decrease in the cation exchange capacity and the efficiency of DAA as an inhibitor in the expansion of the montmorillonite, confirming the analyzes performed by X-ray diffraction presented in Figure 5.

The celulose pulp proved to be the most efficient technique to apply the swelling inhibitors, as it penetrated in greater depth (Fig. 6). The second method that caused the products to penetrate in greater depth was the spray and, lastly, the brush. Even though the application of the products with the pulp caused better penetration, the depth was still low. These techniques were used in order to make laboratory tests more feasible for the field work, as the immersion technique is not likely to be used in large-scale conservation projects.

The swelling inhibitors (**A2**, **A23** and **A236**) managed to penetrate more compared with the consolidant, likely due to their low viscosity (close to that of water), reaching almost 3 cm in the case of **A23**. Cellulose pulp was the

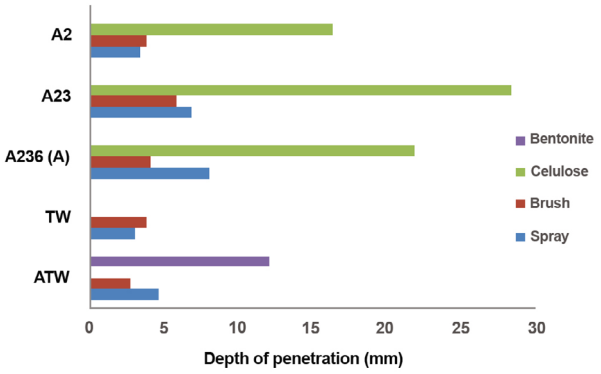

Figure 6. Penetration depth test with different techniques.

application method that caused the product to penetrate to the greatest depth.

The cellulose pulp technique was not suitable for **TW**, as it did not adhere well to the vertical surface. The bentonite was then tested in the sample pretreated with **A** (**ATW**), which showed greater adherence, but left residues. Due to this fact, **TW** bentonite pulp was not applied, as it is not a treatment that can be used, therefore the pulp is not an effective method to apply **TW**. The swelling inhibitors do not seem to have affected the penetration of **TW**, when applications with brush and spray are compared. **TW** and **ATW** penetrated very little and there was no substantial difference between them.

Although the use of cellulose and bentonite pulp improved the penetration depth of **A** and **ATW**, the penetration of the products was still short, no more than 28 mm at best. The penetration depth could be improved by leaving the pulp on the surface longer.

To check whether the products were present in the moist area, thin sections in the profile of the samples were made and observed with SEM. The purpose of this step was to rule out that the swelling inhibitors had been absorbed by the first layers of stone and only water had seeped into the stone. **TW** could not be observed since its composition is essentially silica, which is the same as that of stone. However, product **A** has calcium in its composition, an element that is not present in the stone, thus serving as a marker and allowing the **ATW** sample to be analyzed. The analysis indicated that the product was able to penetrate around 5 mm in depth (Fig. 7). This suggests that the penetration depth of 28 mm is only for the solvent.

The sample of the untreated Itararé Sandstone was submitted to the mercury porosimetry test and it was observed that the pores concentrated in the range of 0.4 to 2.5 µm, 6 µm and 100 µm (Fig. 8). Porosity was 17.6%, and absorption was 0.08 mL/g of mercury (Tab. 2).

In all the treated samples, the pores of 100 µm were eliminated, possibly by partial filling, as the pores of 6 µm had their quantity increased. Swelling inhibitor **A** greatly increased the pores of 6 µm, which is larger than that of the untreated samples, therefore, treated samples should have pores slightly larger than those presented by the untreated samples. They have an average pore concentration of 0.5 to

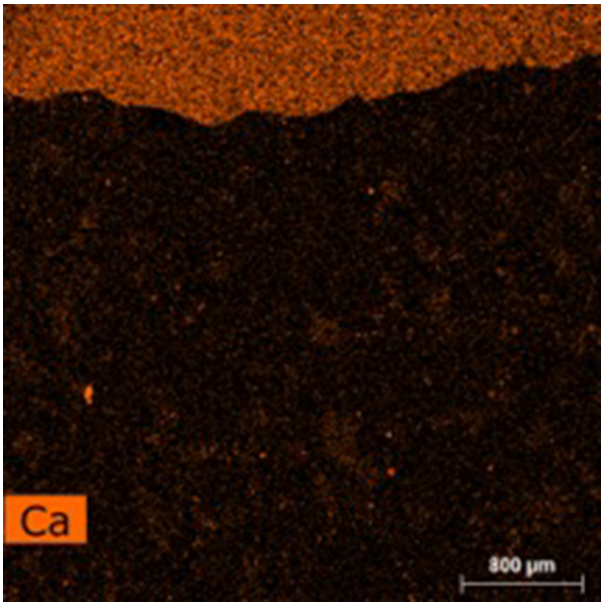

Figure 7. Sample profile treated with ATW observed with SEM, showing the presence of calcium inside the stone.

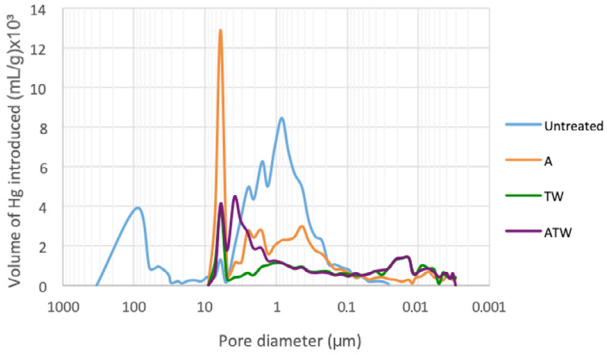

Figure 8. Pore size distribution in mercury porosimetry test in untreated and treated samples A (all the three consecutive treatments), TW e ATW.

Table 2. Results of porosity and cummulative intrusion with the mercury porosimetry test.

Samples	Porosity (%)	Total volume intrusion (mL/g)
US	17.6	0.08
A	13.0	0.06
TW	7.6	0.03
ATW	10.7	0.05

2.5 µm, slightly decreased porosity (13.0%) and total volume of mercury absorbed of 0.06 mL/g. **TW** showed only a smaller peak at 6 µm, which could also be inferred by the reduction of porosity (7.6%), and by the total volume of mercury absorbed (0.03 mL/g). **ATW** showed peaks at 4 and 6 µm, causing lower change of porosity (10.7%) and less absorbed mercury (0.05 mL/g). However, the porosity was still much lower than that observed in the untreated sample. All products decrease the porosity, however, treatment with **A** modified it less. **TW** markedly decreased porosity and pore size distribution, but when **A** was first applied (**ATW**), these properties approximated those of the untreated

sample. Therefore, the application of swelling inhibitors (**A**) benefits the porosity maintenance, helping the consolidant (**TW**) not to clog pores as much.

Treatment with the swelling inhibitors (**A**) did not alter the water absorption by capillarity when compared to the untreated stone (Fig. 9), indicating that there was no obstruction of the pores and no change in the capillary dynamics of the stone, although the porosity changed slightly. The samples treated with **TW** and **ATW** showed a great reduction in water absorption (overlapping lines in the lower part of the graph) due to the hydrophobic behavior of the consolidant, as previously pointed out by other authors (Sassoni *et al.* 2013, Cai *et al*. 2016, Martinez *et al.* 2016). Ratifying literature data, after 3 years, the samples kept in the laboratory have not yet lost their hydrophobic behavior.

The treated samples were observed with SEM and it was verified that when applying the **A**, flower-shaped structures made of carbon appeared (Figs. 10A, 10B, 10C and 10D). The samples were cut perpendicularly to the application of the product to check if these structures were formed inside the stone, but they were not found, having only formed superficially. The formation of these structures is not clear and as far as the authors know, these features have not been described in other papers. Spheroidal structures made of calcium were also identified (Figs. 10E and 10F). They were observed in all samples pretreated with these products. X-ray fluorescence analysis pointed out that the calcium comes from the swelling inhibitor applied to the stone, despite not being included in the composition according to information from the producer. As the stone has no calcium in its composition, it was used as a marker of the penetration depth of this product.

After treatment with **TW**, the following features were observed: clay minerals covered (Figs. 11A and 11B) and formation of a cracked, thick gel after drying, indicative of over-consolidation (Figs. 11C and 11D). Cracking is commonly seen after consolidation with TEOS (Wheeler 2005). Although the producer indicates that the product should be applied without dilution, over-consolidation and obstruction of the pores were observed.

When **A** was applied before **TW** (**ATW**), the product showed spheroidal structures made of calcium from **A** (Figs. 11E and 11F) and fewer fractures (Fig. 11G). The presence of carbon in the sample treated with **ATW** was detected (Fig. 11H), which suggests that the swelling inhibitor delays the polymerization of **TW**. Nevertheless, it also resulted in over-consolidation.

The chromatic parameters were analyzed before and after the treatments (Fig. 12). **TW** darkened the stone and increased the parameters a* and b*. When applying **A** before **TW** (**ATW**), the luminosity did not change and the average of parameters a* and b* remained very close to the untreated sample, despite presenting greater dispersion. Swelling inhibitors (**A**) made the stone slightly whitish and reduced the intensity of the red (a*) and yellow (b*) tones, while helping to keep the color closer to the untreated stone when applied before **TW**.

The total color variation (ΔE*) was calculated and the values obtained for treatments with **A**, **TW** and **ATW** were 2.0, 6.1 and 4.9, respectively. In other words, **A** changed the color of the stone the least and **TW** changed it the most. According to parameters proposed by Sasse and Snethlage (1996) for restoration work, ΔE* must be less than 3. Therefore, **A** was within the acceptable limits for restoration. **TW** and **ATW** had values above this limit, but **ATW** had less chromatic variation than **TW**.

Before the saturation and drying cycles test, the samples were heated at 300°C for 12 hours (adapted from Sassoni *et al.* 2011, who used this procedure in limestones) to simulate altered sample conditions, which caused a decrease in the P-wave velocity due to the decreased cohesion of the stone (Fig. 13). Another consequence of the heating of the samples was the chromatic alteration, showing to be reddish and slightly grayish in some samples. Despite the small amount of iron in the stone, the chromatic alteration is likely linked to the oxidation of this element. This color change was also found in other works, such as Sena da Fonseca *et al.* (2017). Currently, lower temperatures are being tested on the sandstone, which is presenting better results in the ongoing research. It was checked via XRD whether the heating would have altered the minerals (Fig. 14). The diffractogram showed an amorphization of the material, denoted by the replacement of the 14 Å peak by bulging in this region of the graph, observed in the green curve. Therefore, heating at 300°C is not suitable for this stone, as this temperature is much higher than that found in natural conditions. However, the stone heated at this temperature showed the P-wave velocity similar to that found in naturally-altered stones.

After the treatment, the P-wave velocity increased, mainly after the application of the consolidant (**TW** and **ATW**). In the samples treated only with the swelling inhibitor (**A**), the velocity increased in comparison to the altered sample and was very close to the value found in the untreated sample.

After the saturation and drying cycles, the P-wave velocity decreased, mainly in **TW**, with **A** and **ATW** being quite resistant to the action of water. The resistance of swelling inhibitors to the action of water showed that the product acts by ion exchange (Wangler and Scherer 2009). It was observed that the application of swelling inhibitors helped TEOS to be more resistant to removal by water. Similar results were previously found by Scherer and Jiménez González (2008), using a different swelling inhibitor (1,3-diaminopropane dihydrochloride) and consolidant (TEOS).

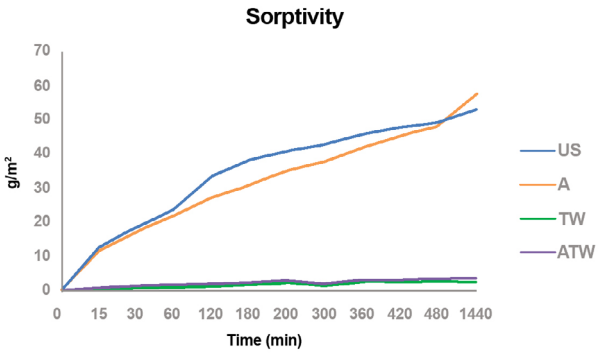

Figure 9. Capillarity test in untreated sample, treated with A, TW and ATW.

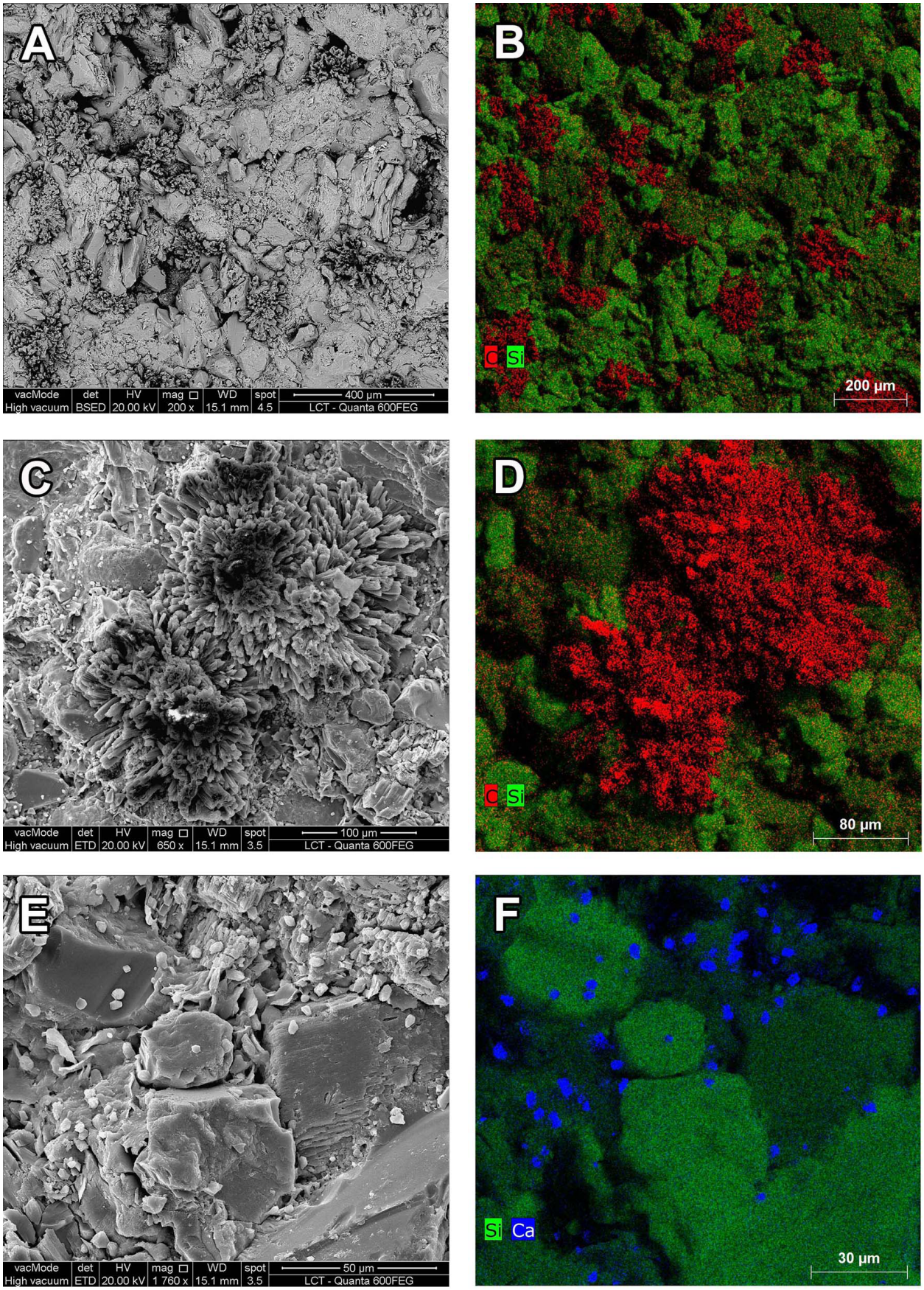

Figure 10. SEM images of samples of the Itararé Sandstone treated with swelling inhibitors. (A) Sample treated with A (detail for the flower-shaped structures shown in Fig. 10C). (B) Mapping of Si and C in the same region of Figure 10A, with artificial coloring, showing the carbon flowers. (C) Flower-shaped structures in detail. (D) Mapping of Si and C of the flower-shaped structures. (E) Spheroidal structures made of calcium. (F) Mapping of spheroidal structures.

The weight of the samples (Tab. 3) was measured during the various stages of this research (Fig. 15) and we observed that heating at 60°C is able to remove part of the water, presenting an average weight reduction of -0.9% (9 samples). Heating at 300°C still caused a weight loss of -1.4% (9 samples), likely due to the loss of intracrystalline

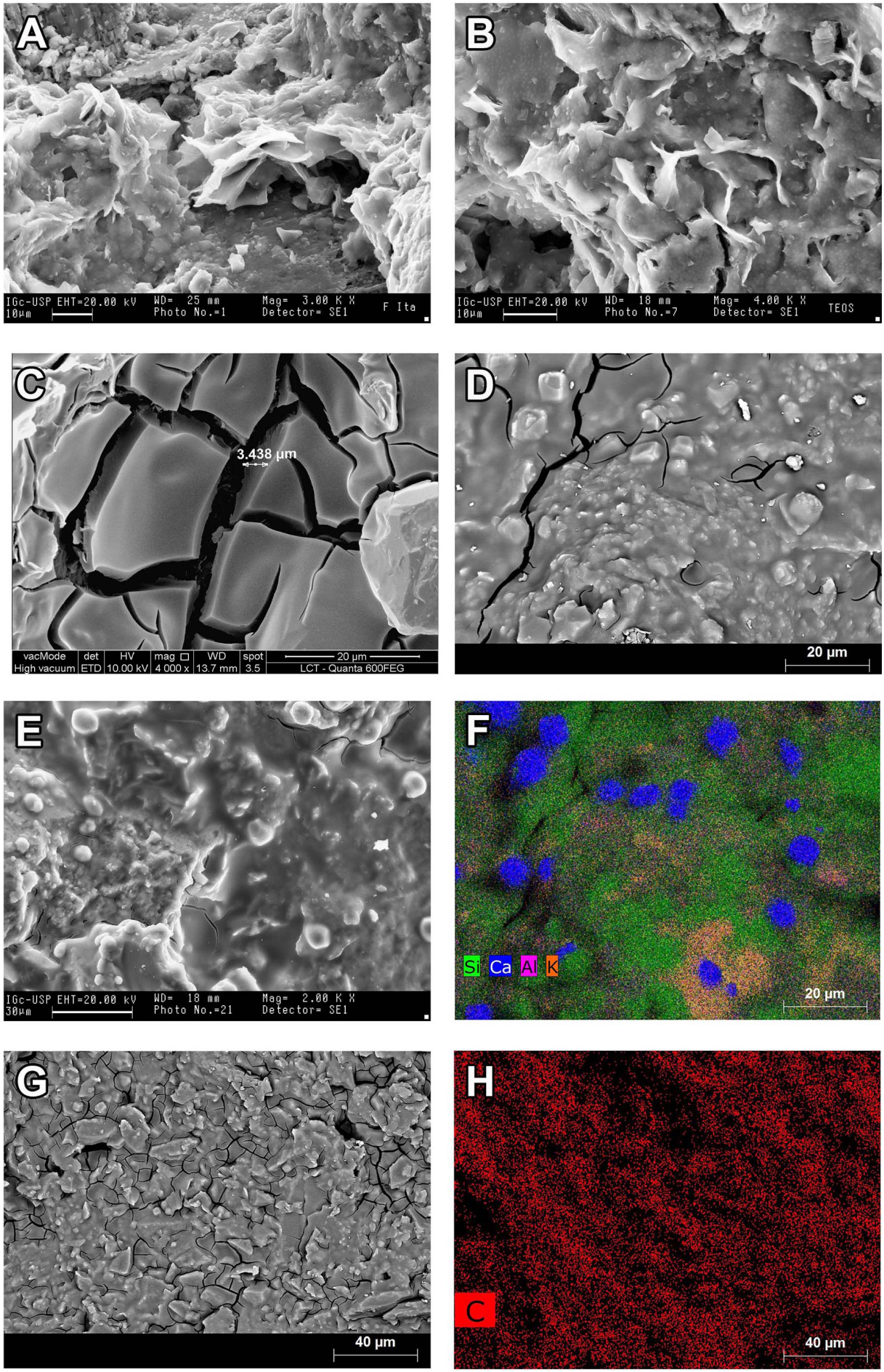

Figure 11. SEM images samples of the of Itararé Sandstone treated with swelling inhibitors and consolidant. (A) Porosity of Itararé Sandstone. (B) Montmorillonite covered by TW. (C) and (D) Fractures formed by TW. (E) Sample treated with ATW, showing minor fractures and spheroidal calcium structures. (F) Mapping showing that the spheroidal structures are made of calcium. (G) Image of the sample treated with ATW. (H) Mapping of this area showing a large presence of carbon.

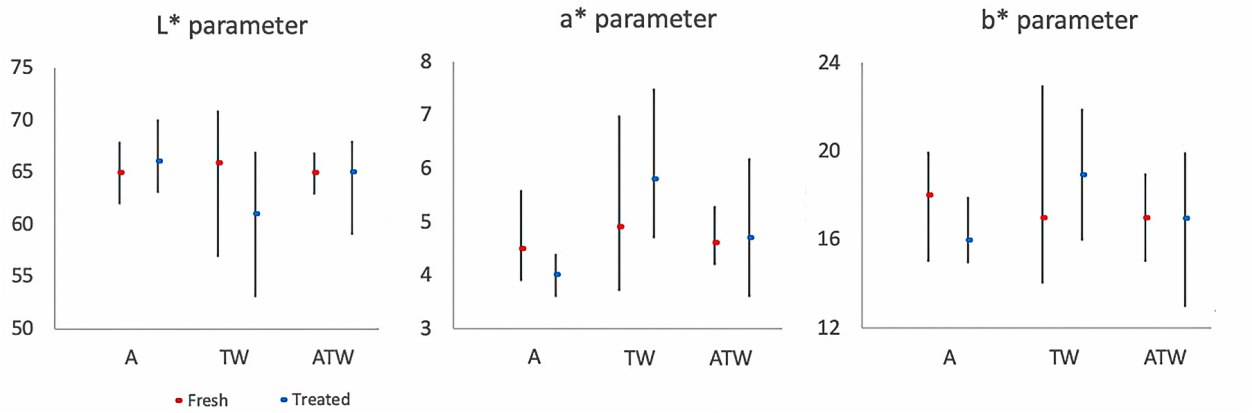

Figure 12. Average of L*, a* and b* parameters for untreated samples and treated with A, TW and ATW.

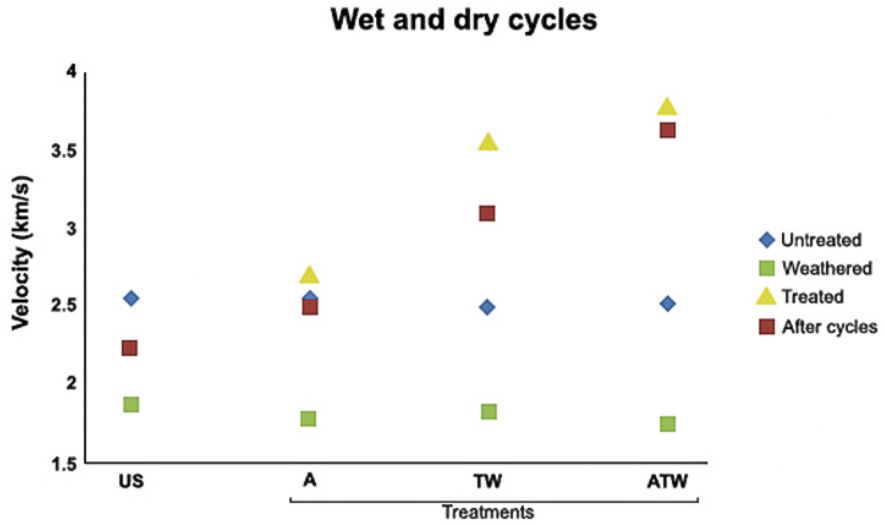

Figure 13. P-wave velocity before and after treatments with A, TW and ATW.

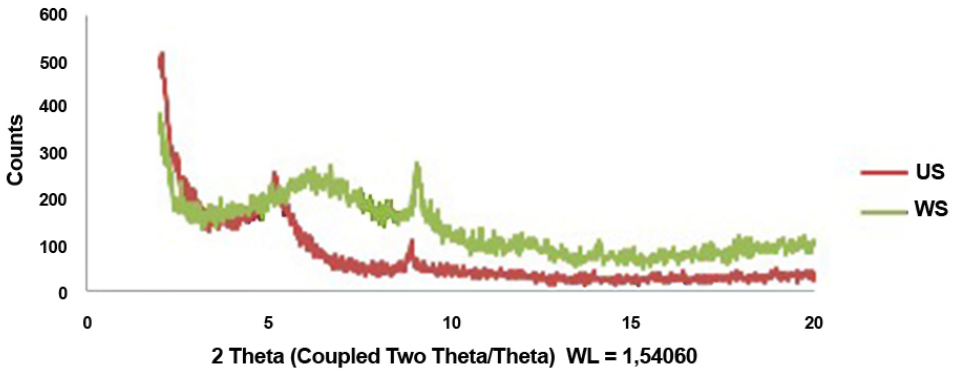

Figure 14. XRD of the untreated sandstone clay fraction (US) and heating-altered sandstone (WS).

water found mainly between the clay layers. When swelling inhibitors were applied, there was an increase in average weight of 0.8% compared to the values found in samples heated at 300°C (6 samples). When the consolidant was applied (**TW** and **ATW**), an average weight increase of 2.8% was observed since 1.8 g of TEOS remained in the sample after drying the product. After the wetting and drying cycles, there was a weight loss of -0.2, -0.5% and -0.4% for samples treated with **A**, **TW** and **ATW**, respectively, showing that swelling inhibitors are quite resistant to water removal. The statistical error is 0,001 g.

CONCLUSION

The treatment of the Itararé Sandstone was partially successful and some issues require further study.

Table 3. Weight (g) and standard deviation of the samples: untreated, dried at 60°C, heated at 300°C, treated, and after saturation and drying cycles.

Sample	Untreated	σ	60°C	σ	300°C	σ	Treated	σ	After cycles	σ
A	67.8	3.1	66.8	3.3	66.6	3.3	67.0	3.3	66.8	3.3
TW	67.5	0.8	66.9	0.9	66.5	0.8	68.9	1.0	68.3	1.0
ATW	67.7	4.7	67.3	4.8	67.1	4.9	69.1	4.6	68.7	4.9

σ: standard deviation.

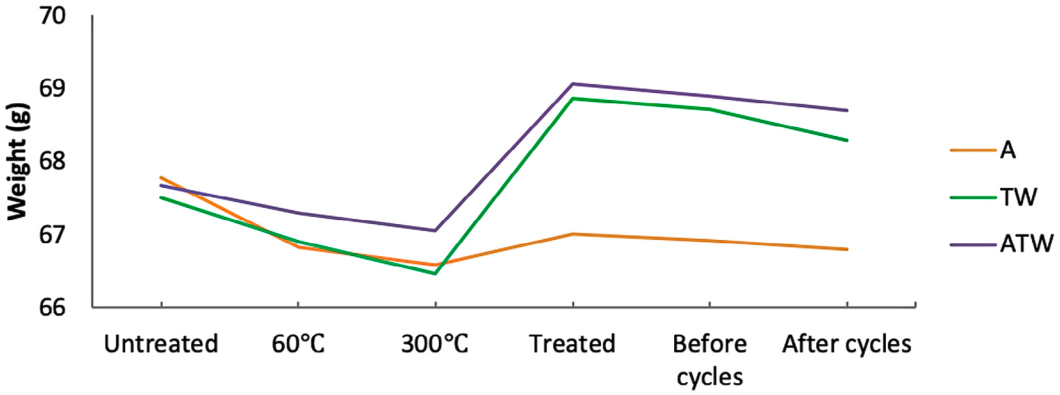

Figure 15. Monitoring of the weight of the samples in the various stages.

The application of swelling inhibitors (**A**) in the Itararé Sandstone was able to inhibit the swelling of the clay minerals, which is the greatest cause of damage in this stone, demonstrated by X-ray diffraction and cation exchange capacity analyses with the disappearance of the montmorillonite peak and the decrease in the cation exchange capacity, respectively. Treatment with swelling inhibitors was quite resistant to water interference, with good maintenance of porosity, capillarity and color. The best method of application was the cellulose pulp with the diaminoalkane pretreatments with a sequence of 2 and 3 carbons (**A23**), penetrating up to nearly 3 cm. Flower-shaped structures of carbon formed on the surface, but not deep in the stone, probably due to the lack of space for their development. Further tests will be carried out to investigate these structures in the future.

The application of the ethyl silicate consolidant (**TW**) was not effective because it caused a marked reduction in porosity and significantly modified the capillarity, which are parameters of high importance for the evaluation of restoration works. This behavior is due to over-consolidation, as indicated by SEM images, and to the consolidant's hydrophobic characteristic, which is present in the first months after its application, according to information provided by the manufacturer. Indeed, in the samples used in this study kept in the laboratory and not exposed to weathering, the hydrophobic behavior is maintained after many months of its application. Therefore, dilutions should be tested to verify if the over-consolidation that caused reduction in porosity and alteration of capillarity can be minimized. This treatment also darkened the stone. As the brush and spray techniques did not allow the product to penetrate deeply, it is advisable to continue looking for a way to apply the ethyl silicate consolidant (**TW**) by poultices, as the cellulose pulp did not adhere to the vertical surface and the bentonite pulp left residues that could not be removed by rinsing after the consolidant dried.

The application of swelling inhibitors before the consolidant (**ATW**) improved some aspects compared to the application of the consolidant (**TW**) alone: lower decrease in porosity, small changes to the chromatic parameters, fewer fractures in the ethyl silicate (**TW**) gel, and better resistance to the action of water. As in the case of ethyl silicate (**TW**), another type of material must be investigated to apply poultice.

This is the first time that a study of consolidating and swelling inhibitors has been carried out in the Itararé Sandstone. After this study, it can be said that to assist in the conservation of the Municipal Theater of São Paulo, which has its front facade dressed with Itararé Sandstone, one option is to avoid the expansion of clay minerals with the application of the swelling inhibitors diaminoalkanes with 2 and 3 carbons (**A23**), which penetrated more deeply. Nevertheless, for the consolidation of this stone, further studies should be carried out.

ACKNOWLEDGMENT

We would like to thank FAPESP - São Paulo Research Foundation (processes 2012/24067-4 and 2015/10858-8) for the fellowship to the first author and for research funding. Part of the work of this research was done at Princeton University at prof. George W. Scherer's laboratories and we are very grateful to him. We are also grateful to Mirian C. Shinzato (Universidade Federal de São Paulo) for the CEC analysis.

ARTICLE INFORMATION
Manuscript ID: 20210061. Received on: 08 AUG 2021. Approved on: 09 MAR 2022.

How to cite this article: Grossi D., Del Lama E. A. 2022. Inhibition of swelling clays and consolidation of Itararé Sandstone using diaminoalkanes (DAA) and ethyl silicate (TEOS). *Brazilian Journal of Geology*, 52(3):e20210061. https://doi.org/10.1590/2317-4889202220210061.

D.G. developed all stages of the research, wrote the first draft of the manuscript and created all figures; E.D.L. guided the study in all stages, revised the text and the figures, improving the manuscript through corrections and suggestions. Provided funding acquisition.

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