Stains in Pavement Applications of a Portuguese Limestone

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ABSTRACT

The use of natural stone on pavements follows a number of requirements that are important for the success of its application.

Among these requirements, in addition to the application method, the knowledge of the different materials involved is critical to the performance of a natural stone work.

The recent application of an ornamental Portuguese limestone widely used in the market resulted in the appearance of reddish brown spots on the stone surface applied in a building floor.

This effect, aesthetically undesirable, brought troubles both to the supplier and the customer. As an attempt to detect the origin of the spots experiments were performed in the laboratory isolating each of the constituents of the system: base mortar, epoxy mortar and stone.

The evolution of the process was monitored and the alteration products that appeared the stone surface were characterized.

1 INTRODUCTION

The use of natural stone follows a series of specifications and methodologies that are important to the success of their application in various situations in a building. For the application success it is essential the knowledge of the materials involved in the support base and the technological and petrological properties of the stones.

The occurrence of stains on ornamental stone slabs applied in pavements and facades are, in general, one of the first pathologies to be detected. They are the result of the release of moisture from the materials of the support, from the stone itself or from the stone absorption of air humidity, rain and salt mist.

Several studies have reported up these situations not only because the unpleasant effects that it causes, but also to try to explain and eliminate the problem before it has an economic impact.

Among these studies, Camposinhos et al. (2009) reported the appearance of spots on the facades of stones of granitic composition and Simão et al. (2010) in carbonated stones. Galembeck et al. (2009) reported the colour variation of silicate stones after exposure to polluted atmospheres. The alteration of carbonated and silicate stones slabs when exposed to salt spray has been studied by Alves et al. (2011), Angeli et al. (2007), Benavente (2007), Cardell et al. (2003), Silva et al. (2013), Silva and Simão (2009) and Leal et al. (2011) in rocks with various treatments and surface finishing. Salt spray implications on slab dimensioning for cladding was also studied by Pires (2013).

The case study reported in this paper is related to the appearance of spots on a floor covered with a Portuguese ornamental limestone in a hotel in Portalegre (Portugal).

These stains had an orange to red-brown colour and appeared soon during the first year after the application of the stone slabs on the floor. The source of the stains is not known and they can be caused by the cement base or by the stone. Even after washing and completely removing the stains they reappeared.

This type of situation can be observed in different locations in applications in outdoor pavements as well as in interior cladding (Figure 1).

A laboratory method was developed to try to determine the source of the spots appearance. It consisted in mounting stone slabs directly in: base mortar; base mortar but with a layer of epoxy mortar in between. The same two arrangements were made but without gluing the different materials together using also base mortar and epoxy mortar slabs. The four arrangements were placed inside different containers and water was added until 5 mm of materials surface. Three extra containers with: a stone slab, a base mortar slab and an epoxy mortar slab were also used to expose the isolated materials to the same testing conditions.

Figure 1 — Example of stains in limestones applied in pavements (up) and cladding (down).

The alterations were registered and macroscopic and microscopic observations were made under the binocular microscope and the scanning electron microscope.

It was found that the origin of the stains could be in the base mortar, because they were found both in the slab stones in direct contact with that material, either when glued together or without gluing. That effect was reduced whenever there was a layer of epoxy mortar in between.

Special care should be taken in knowing the technical specifications of the fixing materials, which are going to be in direct contact with the stone products. Making the right choice, as well as the correct preparation and application will avoid unpleasant situations for suppliers, appliers and customers.

2 GEOGRAPHICAL AND GEOLOGICAL SETTING AND STONE MACROSCOPIC DESCRIPTION

The quarry where the studied limestone is explored is located in the Place of Maxieira, which belongs to Fátima Parish, Ourém Municipality, Santarém District (Portugal). It has 210m long and 90m wide (Figure 2).

Projecting the coordinates of Maxieira quarry on the 27-A Sheet - Vila Nova de Ourém of the Geological Map of Portugal on the scale 1/50 000 (Figure 3), it is concluded it is located in the formation J^2_{SA} - micritic limestones from Serra de Aire, currently known by Serra de Aire formation (Azerêdo, 2007).

Figure 2 - Aerial view of Maxieira quarry, where the limestone of this case study is explored.

This formation that contains all the Bathonian, is characterized by the occurrence of dominantly micritic lithofacies practically throughout the all unit (Azerêdo, 2007). It occurs intercalated by other formations consisting of oolitic, bioclastic and calciclastic limestones, in general (Manuppella, et al. 2000). The thickness of the series is about 350-400m (Manuppella, et al. 2000) and it cannot be entirely seen at a single location (Azerêdo, 2007).

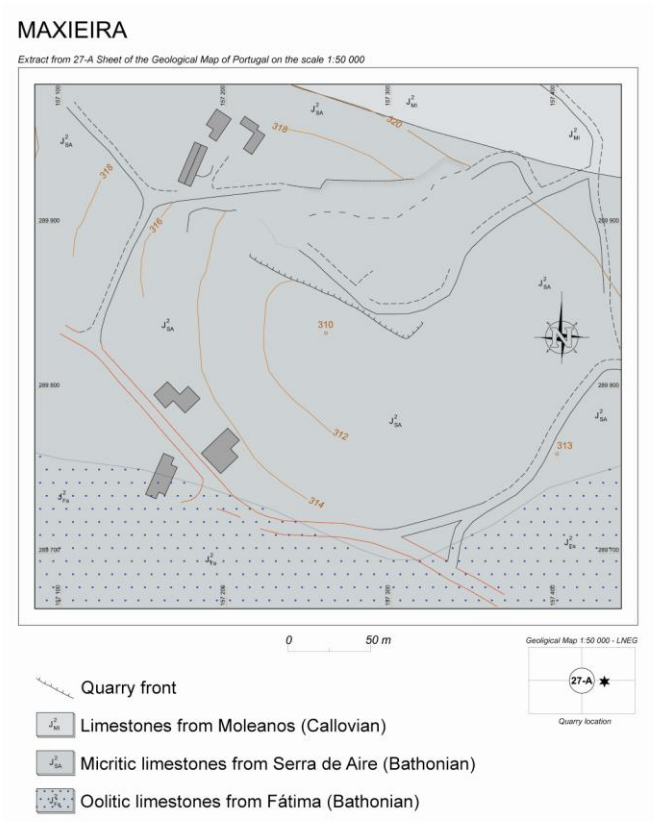

Figure 3 - Projection of the Maxieira quarry coordinates on the Geological Map of Portugal on the scale 1/50 000, Sheet 27-A - Vila Nova de Ourém.

Macroscopically (Figure 4), the studied stone it is a cream-coloured, compact, micritic limestone, in which various fossil remains can be seen.

Figure 4 - Macroscopic aspect of the limestone explored in the Maxieira quarry.

3 METODOLOGY

The methodology developed in the laboratory consisted in placing different samples in plastic containers followed by filling them with water up to 1 cm from the surface. The experimental procedure consisted on:

- A container with a stone slab bonded to base mortar with cement diluted in water (Figure 5a).
- A container with a 3 layer arrangement: base mortar at the bottom, epoxy mortar in the middle and stone slab at the top, all bonded together (Figure 5b).
- Three containers only with a: stone slab (Figure 6a); base mortar slab (Figure 6b); - epoxy mortar slab (Figure 6c).
- Two containers with slabs of the different materials just on top of each other (without gluing them): base mortar+stone (Figure 7a); base mortar+epoxy mortar+stone (Figure 7b).

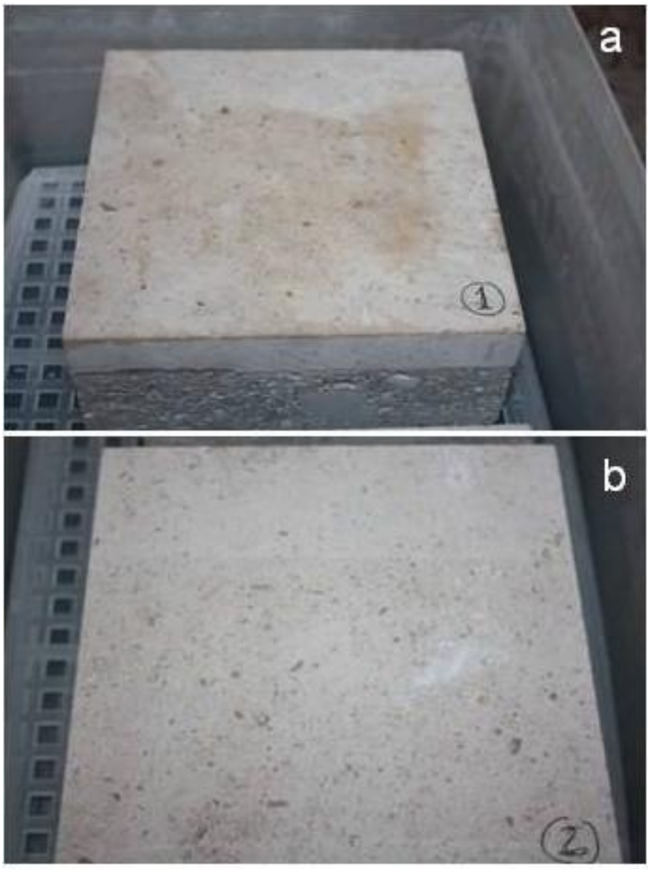

Figure 5 - Container with a stone slab bonded to base mortar with cement diluted in water (a) and container with a 3 layer arrangement: base mortar at the bottom, epoxy mortar in the middle and stone slab at the top, all bonded together (b).

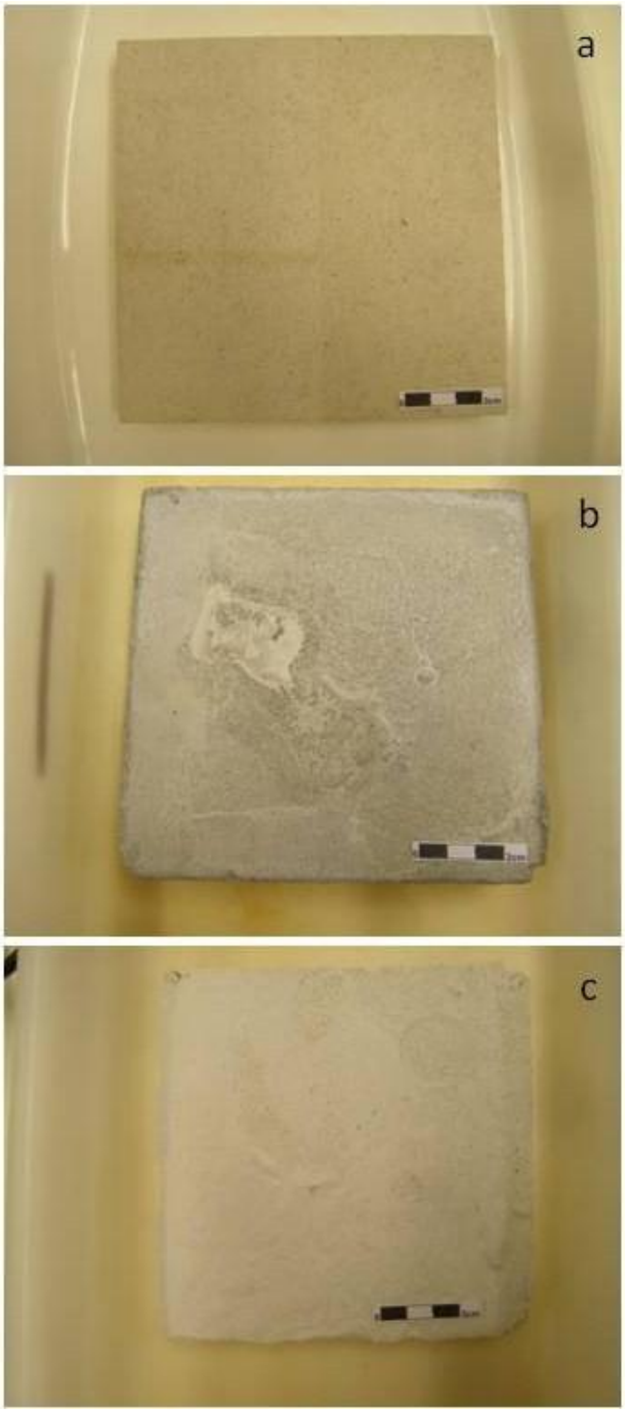

Figure 6 - Containers with slabs of the individual materials: stone (a), base mortar (b), epoxy mortar (c).

An initial macroscopic photographic record of the samples surface was made with an Olympus SP500UZ camera. The samples were monitored daily and the alterations were recorded and photographed. After observation with a binocular microscope Olympus SZ51 and after the photographic record, efflorescence materials formed on the surface of the samples were collected for subsequent analysis by X-ray diffraction and scanning electron microscope.

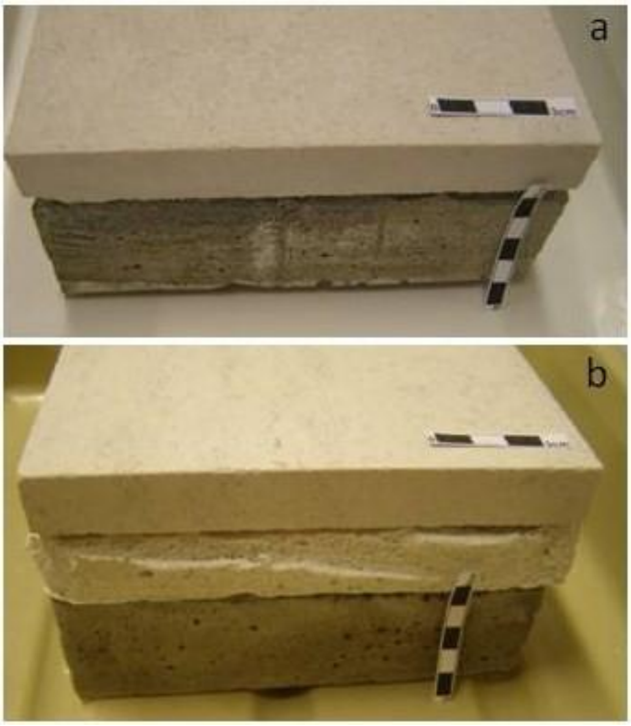

Figure 7 - Containers with slabs of the different materials just on top of each other (without gluing them): plain mortar+stone (a); plain mortar+epoxy mortar+stone (b).

4 OBSERVATIONS AND RESULTS

On the stone slabs bonded to the base mortar reddish brown stains appeared after 3 days of the beginning of the test.

These stains gradually grew getting stronger and more intense reddish brown colour, and after two months showed the very negative aspect that can be seen in Figure 8a.

Efflorescences corresponding to alteration minerals were formed and were photographed (Figure 8b) and collected for analysis.

The stone slab was washed and it was difficult to remove completely the stains. The test was repeated and the stains reappeared and the stone slabs acquire the same aspect after two more months of testing.

In the stone slabs which were in direct contact with epoxy mortar but with base mortar at the bottom, the effect was similar to the described above but in this case the stains were more light-coloured, brownish orange, and its appearance was slower and less intense showing the inaesthetic aspect shown in Figure 8c .

Efflorescence also formed in this limestone slab (Figure 8d) which was collected for analysis.

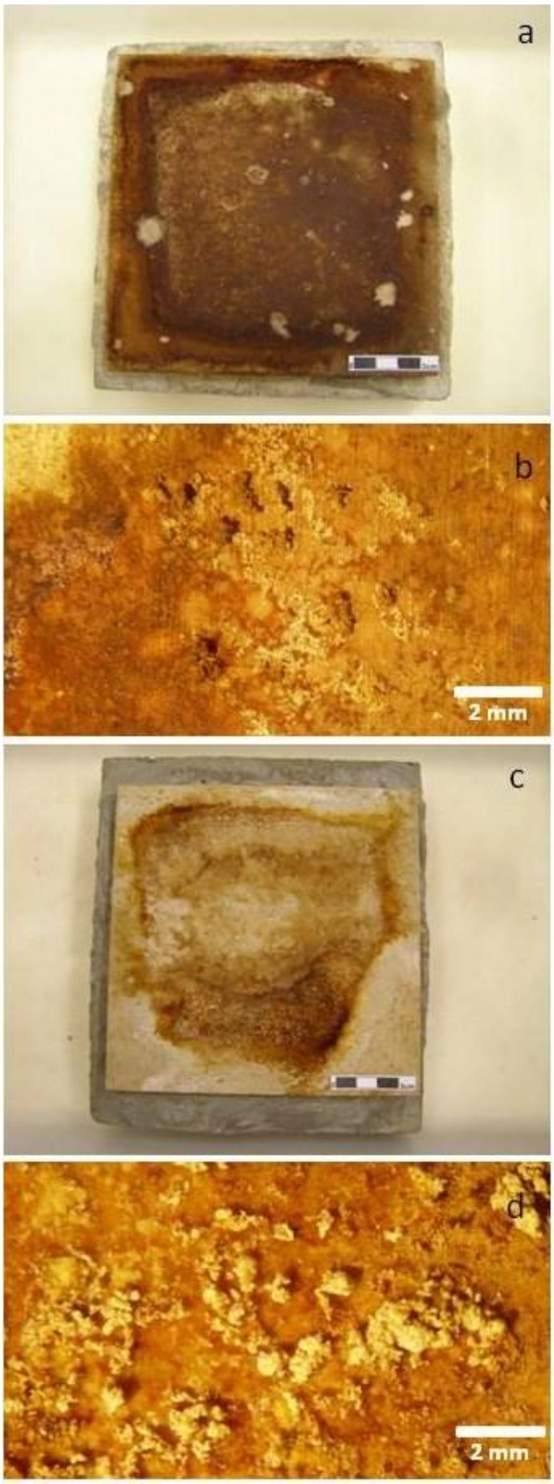

Figure 8 - Reddish brown stains in stone slabs bonded with base mortar (a) and efflorescences (b). Reddish brown stains in stone slabs glued with epoxy mortar but with base mortar at the bottom (c) and efflorescences (d).

This stone slab was also washed and in this case all stains and efflorescence were removed. The test was also repeated for another two months and only a few light-coloured stains appeared.

In the containers with the slabs of the isolated materials: stone, base mortar and epoxy mortar, there were no changes after soaking for 4 months.

In the slabs of the three materials only in contact with each other but not glued together (Figures 9a and 9b) the appearance of light-coloured stains similar to those of the bonded samples was recorded.

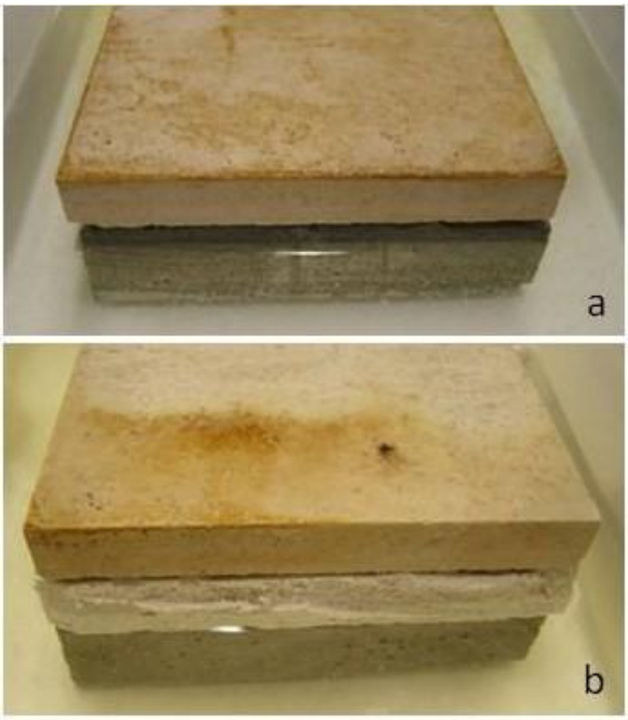

Figure 9 - Reddish brown light-coloured stains in stone slabs in contact with the base mortar (a) and in contact with the epoxy mortar above the base mortar (b).

The contact between the stone slab and the fixing materials was done only at some points but it was still enough for the material that constitutes the spots migrate by capillarity to the surface and edge of the samples.

Thus, it was found that the sources of the stains would be in the base mortar.

The cement used to make the base mortar was analysed and it is a common type II produced in Portugal, with pure portlandite mineral ($Ca(OH)_2$) with quartz (silica), calcium carbonate and microcline (K silicate) corresponding to the sand mixture used to make the base cement and some sulphates and iron oxides.

The SEM analysis confirms also that the main composition of the stone is calcite (99 %) with some residues of Fe, Cu and Zn, perfectly standard for this kind of stone.

It was also found that the effects were stronger and negative in systems where the stone directly contacts the base mortar.

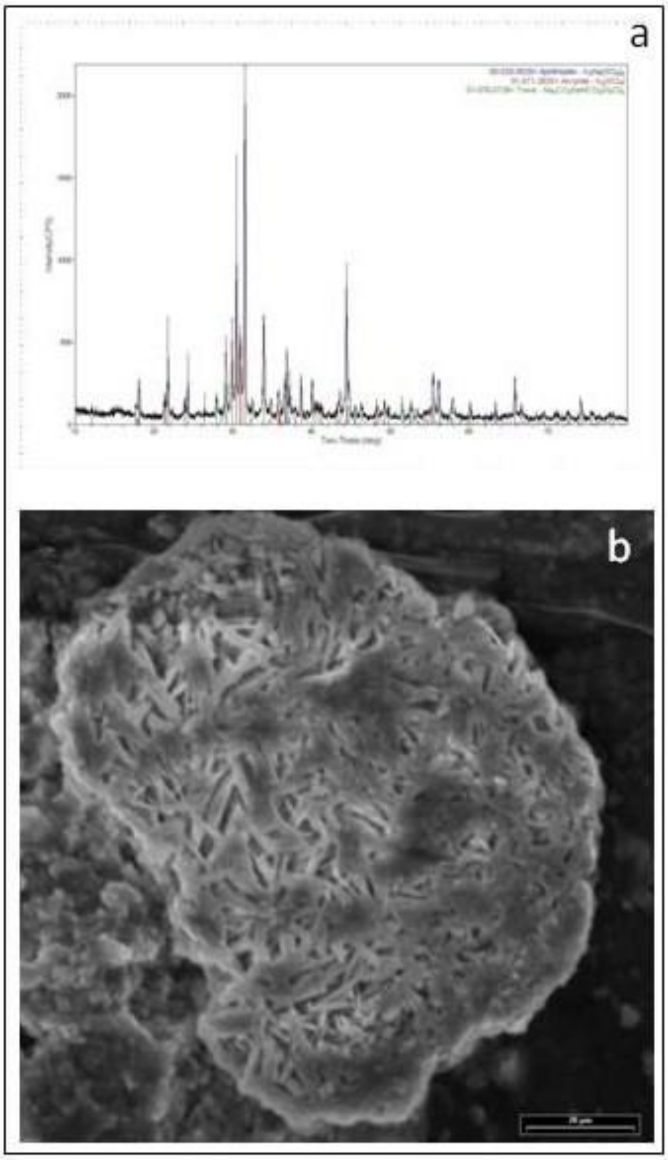

Figure 10 – a) X-ray diffractogram of the efflorescence and b) SEM microphotograph of an aggregate of these materials.

The epoxy mortar had an isolating effect, but it is still not enough to prevent migration of fluids from the base mortar into the stone which will result in blemishes on the surface.

The efflorescences on the reddish brown stains collected from the slabs stone surface bonded directly to the base mortar and to the epoxy mortar were grinded and the powder was analysed by a scanning electron microscope with EDX microprobe (JEOL JSMT330A) and X-ray diffraction (Philips X'Pert XRD) to determine its chemical and mineralogical composition.

The x-ray diffractogram shown in figure 10a identifies the crystalline phases of the efflorescence where Na and K sulphates and Na hydrate carbonates were found. This identification was confirmed by the SEM analysis and a microphotograph of an aggregate of these materials can be observed in figure 10b.

5 FINAL REMARKS

The knowledge of the materials applied on a construction as a support or as cladding is important for the success of an application.

Unfortunately many of the pathologies cannot be predicted and only when they occurred they can lead to a case study.

The reaction between the different materials used can also vary and is related not only to their nature and characteristics but also with the conditions of the application site.

The reddish brown stains detected on the limestone slab pavement were the pathology detected that lead to this study.

To better understand the origin of the stains the different involved materials were tested isolated and in different combinations: stone/base mortar, stone/epoxy mortar/base mortar, bonded and only in contact with each other.

It was concluded that the base mortar is at the origin of the stains. The substances in the constitution of the base mortar were dissolved by water and migrated by capillary to the surface of the stone.

This migration was intense and, besides the reddish brown stains, probably due also to iron oxides (to be confirmed), resulted in the formation of efflorescences of hydrated sulphate and carbonate minerals.

Whenever there was a layer of epoxy mortar between the stone and the base mortar, the effects were attenuated resulting in lighter and smaller stains that can be washed. The epoxy mortar had an isolating effect but not completely efficient.

Studies involving different types of cement, epoxy cement and stones are in development in the laboratory to detect the influence of the different phases involved in the stains formation.

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