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THE ALTERATION KINETICS CURVE AND TIME-LAPSE IMAGING

Useful features in salt crystallization tests

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Useful features in salt crystallization tests

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THE ALTERATION KINETICS CURVE AND TIME-LAPSE IMAGING:
USEFUL FEATURES IN SALT CRYSTALLIZATION TESTS

Abstract

The decay of porous building materials due to salt crystallization is very frequent and often significant in the built heritage and, thus, a proper understanding of the underlying processes has major importance for conservation. In this light, a new method for characterization of salt decay processes was developed within the DRYMASS research project, which is based on continuously measuring by optical profilometry the micrometric changes that occur on the material surface during drying. This method produces three different types of output: the so-called "alteration curve", as well as the current gravimetric evaporation curve and time-lapse photographs of the decay. But the three features had, until now, to be recorded using different specimens. This is an important limitation because the high uncertainty of salt decay processes may give rise to different decay patterns in similar specimens.

Here, we present a development of the original study, which was afterwards carried out within the same project to allow evaluating the three features in a single specimen, by using an integrated set-up. This new study was carried out with two salts often found in salt decayed constructions, Na_2SO_4 and NaCl, and a material frequently used in the architectural heritage, Ançã limestone. Some of the experiments were performed after application of a water repellent treatment on the stone.

Keywords: Soluble salts, Crystallization, Drying, Crystallization tests, Alteration curve, Drying curve, Optical profilometry, Time-lapse photography

CINÉTICA DE ALTERAÇÃO E FOTOGRAFIA "TIME-LAPSE":
CARACTERÍSTICAS ÚTEIS EM TESTES DE CRISTALIZAÇÃO DE SAIS

Resumo

A degradação dos materiais de construção porosos devido à cristalização de sais solúveis é muito relevante no património construído e, portanto, uma adequada compreensão dos processos subjacentes é extremamente importante para a conservação. Nesta perspectiva, foi recentemente desenvolvido, no âmbito do projecto de investigação DRYMASS, um novo método de caracterização que se baseia na medição contínua por perfilometria óptica das alterações micrométricas que ocorrem na superfície do material durante a secagem. Este método produz três tipos de resultado: a chamada "curva de alteração", a curva gravimétrica de evaporação e fotografias time-lapse da degradação. Mas as três características tinham, até agora, de ser medidas em diferentes amostras. Esta é uma limitação importante, porque a elevada incerteza dos processos de degradação por cristalização de sais pode dar origem a diferentes padrões de degradação em amostras semelhantes.

Aqui, apresentamos um desenvolvimento do trabalho, subsequentemente realizado no âmbito do mesmo projecto para permitir efectuar a avaliação das três características com um único provete, através do uso de um dispositivo experimental integrado. Neste novo estudo, utilizaram-se dois sais frequentes em construções degradadas por cristalização de sais, o Na_2SO_4 e o NaCl, e um material muito utilizado no património arquitectónico, o calcário de Ançã. Alguns dos testes foram realizados após a aplicação de um tratamento hidro-repelente na pedra.

Palavras-chave: Sais solúveis, Cristalização, Secagem, Ensaios de Cristalização, Curva de alteração, Curva de secagem, Perfilómetria ótica, Fotografia “time-lapse”

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1 | Introduction

Salt crystallization is one of the major degradation causes of the porous materials that constitute our built heritage. These salts may be originally present in the material or may come from external sources. The presence of water in the material pores and its subsequent evaporation results in the crystallization of the salts, which can lead to two main types of physical alteration: efflorescence (when the feed rate of solution is high and, therefore, the salts crystallize on the outer surface of the material) or subflorescence (when the feed rate of solution is insufficient to compensate the evaporative demand and, therefore, the wet front recedes into the material).

Is in this context, it becomes crucial to understand how drying can be influenced by the salts and by the alterations they cause, as well as to assess how different materials and treatments respond to such changes. But there is one major difficulty which is that salt crystallization tests, which are those used to evaluate the behaviour of materials and treatments in relation to salt crystallization, are often unrepresentative of reality. This happens because in these tests the specimens are typically subjected to extreme conditions, such as high temperatures or successive wet/dry cycles, in order to obtain measurable changes within a reasonable period of time. However, these conditions may also significantly distort the results. The distortion can be particularly relevant for salts like sodium sulphate that can give rise to massive contact- or temperature-induced crystallization processes which hardly occur in the architectural heritage.

To overcome this difficulty, a novel test method was developed within the DRYMASS project (ref. PTDC/ECM/100553/2008) [1]. This method is based on measuring the alterations that take place during drying at the micrometre scale, which makes it unnecessary to expose the material to extreme conditions. The measurements are carried out with an optical profilometer and are complemented with gravimetric measurements and time-lapse photography. From the gravimetric data we obtain the standard evaporation curve [2] and from the topographic data a so-called “alteration curve” [1]

In the initial experiments carried out during the project, the alteration and drying kinetics curves were measured on different specimens, and the time lapse photography carried out on a third specimen [1]. However, the use of different specimens can pose problems to the interpretation of the results because identical specimens subjected to similar conditions may depict significant differences in the decay patterns and drying kinetics due to the uncertainty inherent to salt decay processes [3, 4, 5].

Therefore, after the interest and viability of the method had been confirmed [1], a second phase of the work was undertaken with the objective of upgrading it to permit the simultaneous recording of the three features on a single specimen. The present report describes this second phase of the work, which was carried out with an integrated version of the experimental set-up. This includes the optical perfilometer, a digital balance and a camera for time-lapse photography.

The report is organized as follows. The materials are characterized and the experimental methods described in section 2. The results are presented in section 3 and discussed in section 4. This discussion focuses first the alteration curves (subsection 4.1) and then compares them to the drying curves (subsection 4.2). The main conclusions of the study are summarized in section 5.

2 | Materials and Methods

2.1 General

The experimental program consisted of evaporative drying tests carried out on Ançã limestone specimens, either untreated or treated with a water repellent, and contaminated with either NaCl or Na_2SO_4. An integrated set-up composed of an optical perfilometer, an electronic balance and a camera for time-lapse photography was used to monitor the alterations undergone by the material during the first 100 hours of drying.

2.2 Substrates

Ançã limestone (CA) is a fine-grained, beige colored stone. It was selected because it is often present in the built heritage, especially in Portugal, and also because in previous work of the project it gave rise to a very interesting delamination pattern typical of those often observed in the field [1].

The physical characteristics of this limestone, capillary porosity, pore size and sorptivity, are given in Table 1. Sorptivity (S) is a quantity that expresses the capability of a material to absorb and transmit liquids by capillarity [6]. It is calculated from the absorption curve obtained when the cumulative volume of liquid absorbed per unit area, i.e., the inflow velocity *i* [L], is plotted against the square root of time *t* [T]. Sorptivity is the slope of the first linear segment of this absorption curve, as expressed by Eqs. 1 and 2, in which ΔM is the cumulative mass of absorbed liquid [M], *A* the area of the absorption surface [L^2] and ρ the density of the liquid [M L^{-3}].

$$i = \frac{\Delta M}{\mathrm{A}\rho} \quad \text{(Eq 1)}$$

$$S = \frac{\mathrm{i}}{t^{\frac{1}{2}}} \quad \text{(Eq 2)}$$

Table 1- Physical characteristics of the Ançã limestone

Capillary porosity [a]	22.8 %(V)
Mercury Intrusion Porosimetry - MIP (μm) [b]	0.32 (average pore radius) 0.35 (modal pore radius)
Sorptivity (x 10^6 m/$s^{1/2}$) [c]	166 (pure water) 114 (saturated Na_2SO_4 solution) 119 (saturated NaCl solution)

[a] by RILEM procedure II.1 [2]; [b] by ASTM procedure [7]; [c] by RILEM procedure II.6 [2].

2.3 Water repellent

With the objective of testing the experimental set-up under different conditions, a water repellent was applied on the top surface of some specimens. The product utilized was SILRES® BS280, a solution of silane/siloxane, with dilution in white spirit by a 1:11 weight ratio.

The treatment was applied on the stone surface with a paint brush. The procedure was carried out four times, always waiting for the complete absorption of the solution before each new application.

2.4 Method

2.4.1 Integrated equipment

The morphological alterations undergone by the material due to salt crystallization were characterized after contamination with the salt solution, while the specimens dried, through the integrated set up shown in Figure 1. This set-up allowed to simultaneously apply the three characterization methods described below in subsections 2.4.2 to 2.4.4 to a unique specimen.

The specimen is placed on the small digital scale, which allows measuring its weight loss during drying. The scale stands on the platform of the profilometer, programed to measure 2D topographic profiles of the surface at predefined time intervals (every three hours, in the present case). Meanwhile, the digital camera, equipped with an intervalometer, performs time-lapse photography (one picture every 10 minutes, in this case). The pictures comprise the specimen and also the screen of the digital scale (because a scale without data output had to be used in this prototype-phase of the work).

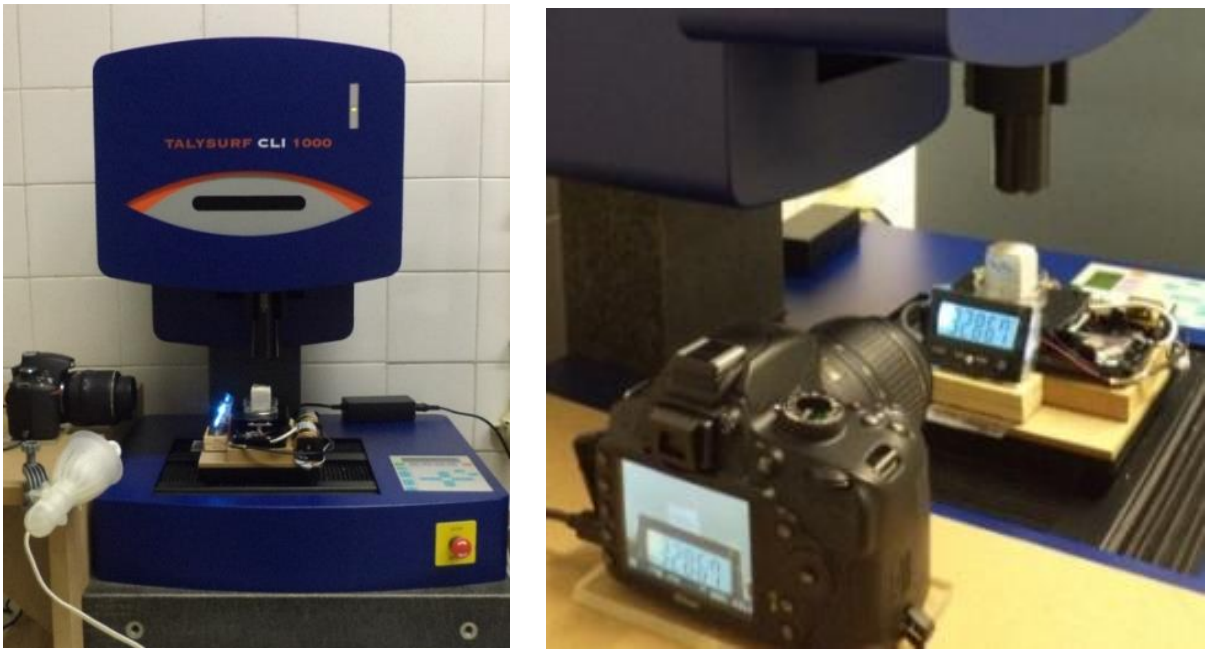

Figure 1 - Integrated set-up: general view (on the left); detail of the digital camera framing the specimen and the screen of the digital scale (on the right)

2.4.2 Evaporation test

The evaporation test followed the procedure of RILEM Test No. II.5 “Evaporation curve” [2]. The specimens were small stone cubes, with 24-mm edge, laterally sealed with epoxy resin. They were placed in partial immersion in saturated sodium sulfate or sodium chloride solutions for three days, until capillary saturation. Afterwards, they were removed from immersion and their bottom surface was immediately sealed with polyethylene film. Drying took place in a conditioned room with controlled environmental conditions of 20ºC, 50% RH and low air velocity.

Mass variation was monitored by continuous weighing of the specimen placed on the digital scale (resolution of 0,001g), as can be seen in Figure 1. The results of this test are expressed by the drying kinetics curve which expresses the solution content of the material as a function of time. The drying rate corresponds, at any instant, to the slope of this curve.

2.4.3 Time-lapse image recording of the alteration patterns

Time-lapse photography was used to record the alterations undergone by the stone due to salt crystallization during drying. A digital camera Nikon D3200 (18-55 mm), equipped with an intervalometer, was used for the purpose.

The specimens were photographed with lateral grazing light, in order to highlight the three-dimensional morphological features of the surface.

2.4.4 Alteration kinetics curve

An optical profilometer Talysurf CLI 1000 by Taylor Hobson was used to quantify the morphological alterations of the limestone surface due to salt crystallization. The instrument is equipped with a non-contact confocal white light gauge which provides high-resolution measurements. In this work, two-dimensional topographic profiles were obtained every three hours by scanning a central section of the specimen, as shown in the images on the left of Figures 3 to 6.

The result of each test is a set of profiles, from which the “alteration kinetics curve” or simply “alteration curve” is afterwards calculated [1]. In this curve, the ordinates correspond to the average height obtained in one topographic profile, and the abscissa to the instant in which that profile was measured (Figure 2). The curve expresses, thus, the average lifting of the surface as function of time.

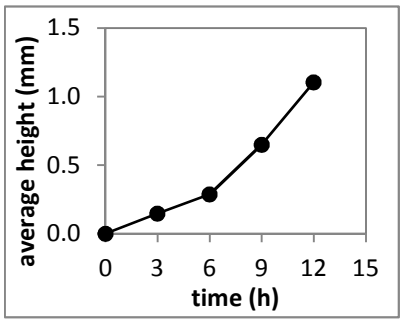

Figure 2 - Example of an alteration curve

3 | Results

The experimental results are presented, in the following sections, in two ways. First, we show the topographic profiles obtained with the profilometer during the drying experiment. Then, we show the alteration curves and the drying kinetics curves, as well as selected time-lapse images illustrating the decay process.

3.1 Topographic profiles

The sets of topographic profiles obtained during drying are presented in Figs. 3 to 6, together with an image of the macroscopic appearance of the specimens at the end of each test (100 hours). These profiles were always measured in a central section of the specimen (indicated in the image with a red line). On each set of profiles, the distance on the Y direction expresses the lifting of the surface during the salt crystallization process (note that the absolute height is the height of the specimen plus that of the platform on which the specimen stands – see Figure 2). Because of the trial character of the experiment, the direction of the scan and the measured length varied from specimen to specimen. The red profile on the bottom was the first to be measured (time=0 hours) while the one on the top was the last (time =100 hours).

The images show the frontal or top surface of the specimens, depending on the type of degradation developed in each case, which varied as follows:

- With NaCl, the untreated stone (Figure 3) developed efflorescence, while the treated stone (Figure 4) delaminated due to formation of subflorescence beneath the hydrophobic surface layer; the delaminated surface layer is around 0.7 mm thick.
- With Na_2SO_4, both the untreated (Figure 5) and the treated stone (Figure 6) gave rise to a multi-layer delamination pattern composed of thin stone layers intercalated with subflorescence; the first delaminated layer is the thicker and has around 0.1 mm thickness.

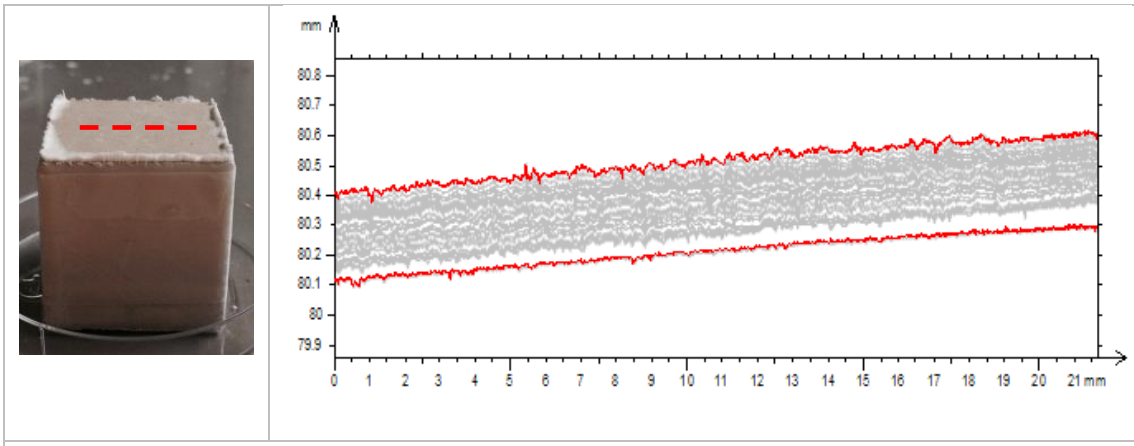

Figure 3 - Image of the untreated specimen saturated with NaCl at the end of drying (on the left) and corresponding set of topographic profiles obtained during drying (on the right)

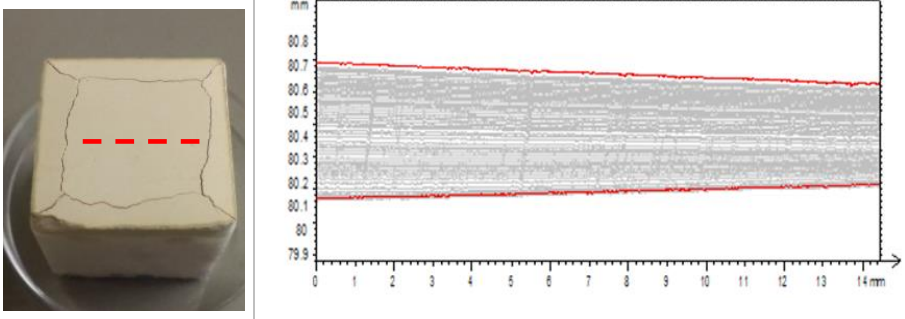

Figure 4 - Image of the treated specimen saturated with NaCl at the end of drying (on the left) and correspondingset of topographic profiles obtained during drying (on the right)

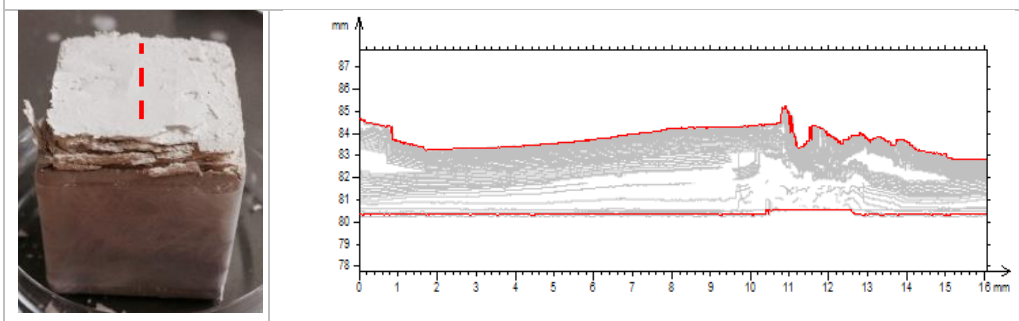

Figure 5 - Image of the untreated specimen saturated with Na_2SO_4 at the end of drying (on the left) not treated and corresponding set of optical topographic profiles obtained during drying (on the right)

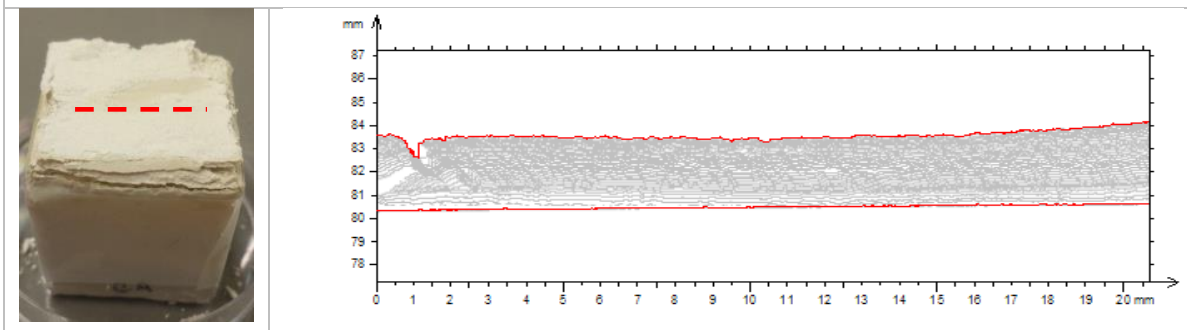

Figure 6 - Image of the treated specimen saturated with Na_2SO_4 at the end of drying (on the left) and correspondingset of topographic profiles obtained during drying (on the right)

3.2 Alteration kinetics, drying kinetics and time-lapse images

The alteration kinetics curves and drying kinetics curves calculated from the data collected, respectively, with the optical profilometer and electronic scale are presented in Figures 7 and 8. In these figures, time-lapse images depicting the state of the specimen at the beginning, middle and end of the experiment are also presented to provide a clear understanding of the decay process.

Note that the maximum duration established for the test (100 hours), and the slower drying caused by the presence of salt, especially NaCl, did not allow in most cases recording the full drying process (only in the case of the untreated stone contaminated with Na_2SO_4 a full drying curve was obtained, which is seen in Figure 8, on the left).

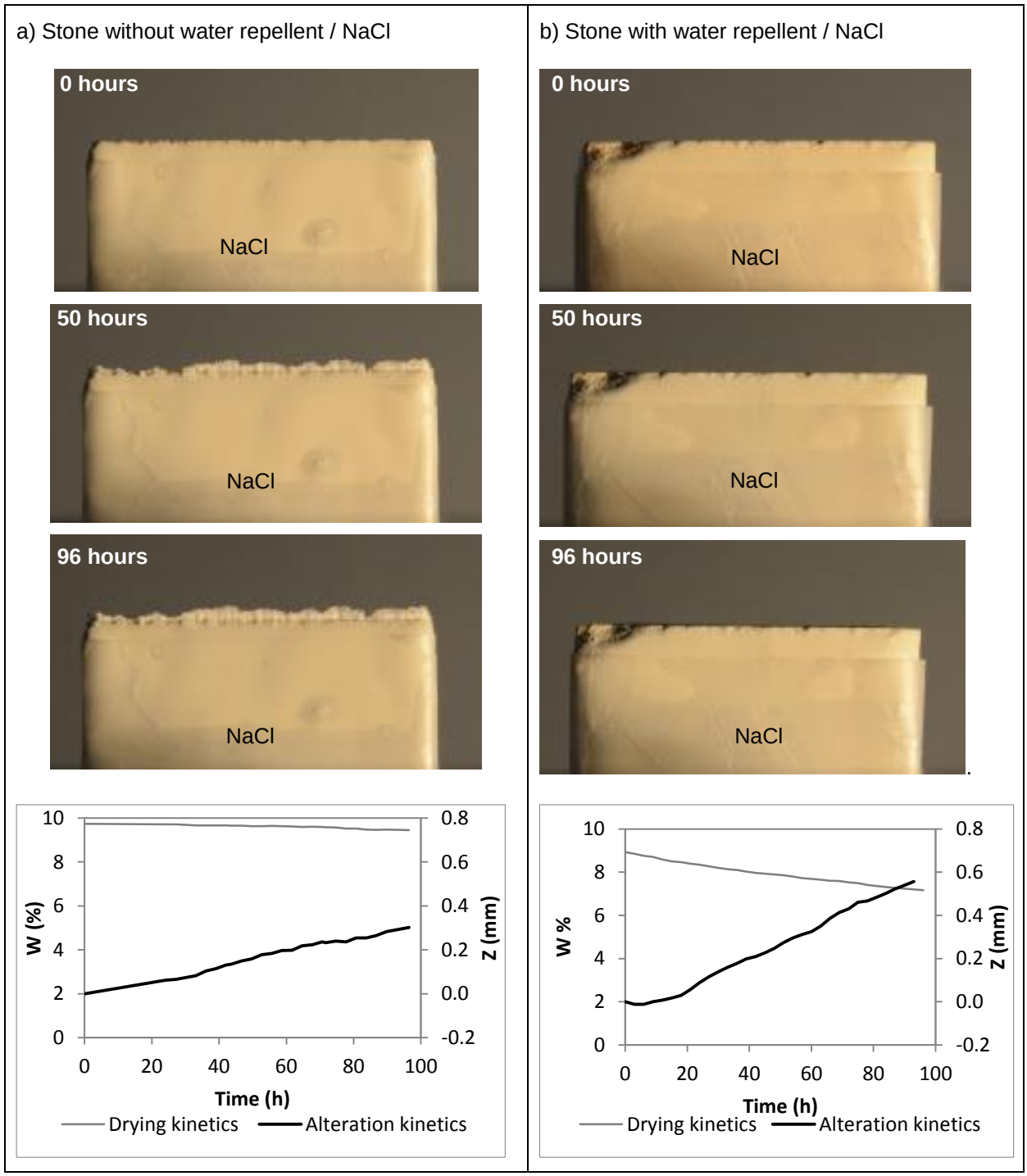

Figure 7 - Alteration kinetics, drying kinetics and time-lapse images of the untreated and treated specimens saturated with NaCl

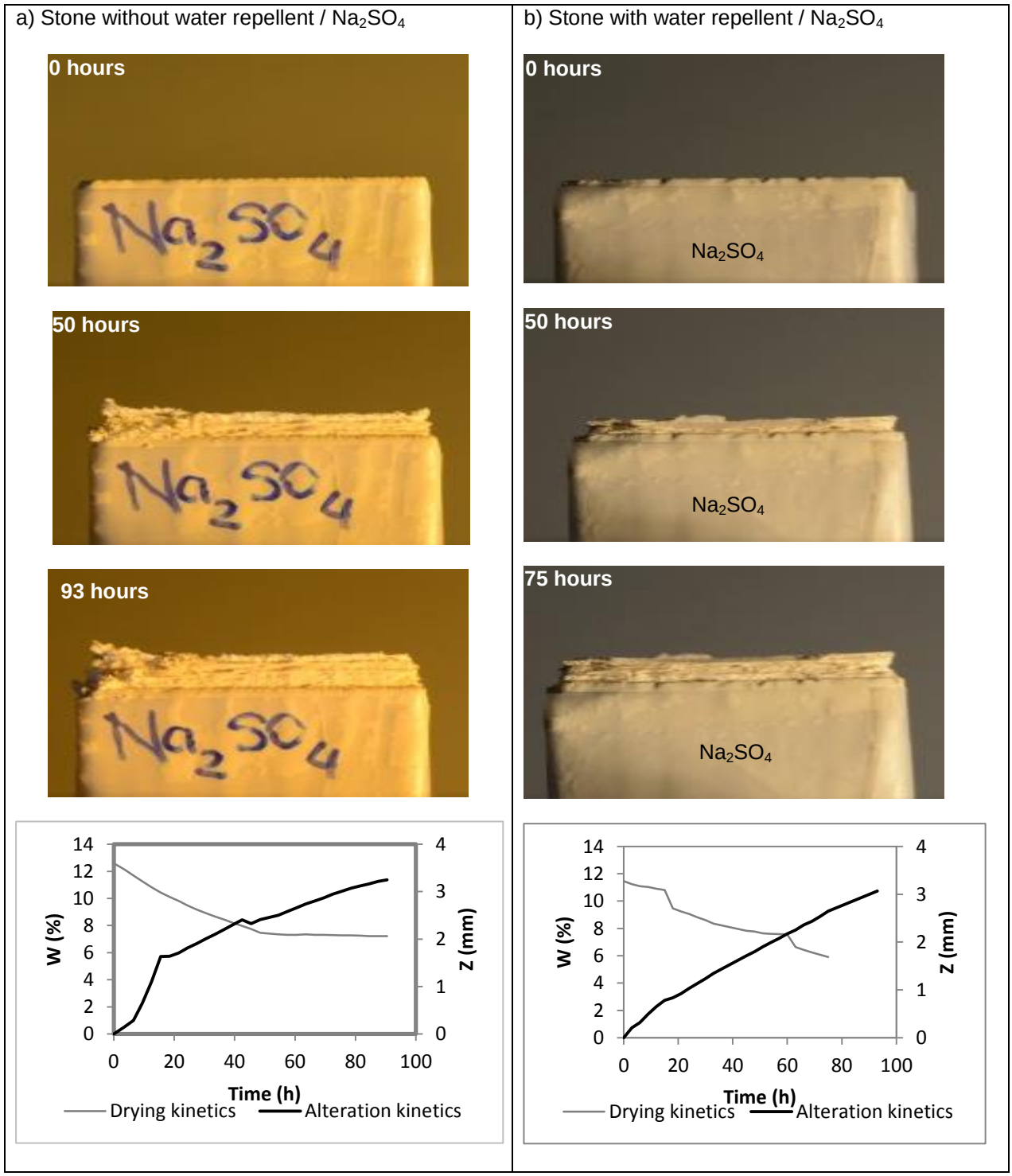

Figure 8 - Alteration kinetics, drying kinetics and time-lapse images of the untreated and treated specimens saturated with Na_2SO_4. In the last case, the reported weight values are only until the 75 hours, due to a shutdown of the electronic scale caused by battery exhaustion.

4 | Discussion

In the present chapter, we discuss the results of the experimental work. First (section 4.1), we analyze if the alteration curves offer a clear representation of the degradation shown by the time lapse imaging and vice-versa. Afterwards (section 4.2), we examine whether the combination of the two techniques that provide the alteration kinetics and drying kinetics curves, respectively, is helpful to characterize the alteration and drying processes.

4.1 Alteration curve

In this section, we discuss if the alteration curve obtained from the data collected with the optical perfilometer and the images obtained by time lapse imaging are consistent with the observed degradation. The following considerations can be drawn from each experiment:

1) NaCl on stone without water repellent treatment

The main degradation pattern is the growth of efflorescence, which is more expressive along the perimeter of the specimen surface and occurs as a thin salt crust in the center (Figure 3). The time lapse images (Figure 7, on the left) show only what happens along the edge because of the frontal position of the digital camera and, therefore, give an exaggerated idea of the decay. In contrast, the alteration kinetics curves (also in Figure 7, below) show only what happens in the center, i.e., the slight lifting of the surface due to the formation of the central salt crust. The crust achieves 0.3 mm.

Two lessons can be drawn from this inconsistency between the optical profilometry and time lapse results: (i) images should be collected using two cameras or from an oblique perspective, in order to see both the side and the top surface of the specimen; (ii) if the optical measurements had caught the full section of the surface, and not only its central part, the border effect would be perceptible in the topographic profiles; the incorporation of this localized effect would not improve the representativeness of the alteration curve, but would allow quantitatively analyzing its significance (and the profiles may be cut before calculating the alteration curve).

2) NaCl on stone with water repellent treatment

Due to the application of the water repellent treatment, the surface stone layer does not allow liquid migration. Therefore, the salt crystallizes beneath this hydrophobic layer, detaching it from the specimen, as seen in Figure 4. The lifting of the surface due to this delamination effect is of around 0,6mm in the central part. This is accompanied by the formation of a peripheral fissure along on the top surface, because the delaminated stone layer is laterally attached to the epoxy coat.

The alteration curve shows just the small lifting of the top surface in the center, because this was the only part scanned by the profilometer. The fissures are also not detected in the time lapse images

because of the lateral positioning of the digital camera. Again, an oblique shooting perspective would have been more appropriate also in this case.

3) Na_2SO_4 on stone without water repellent treatment

A multi-layer delamination pattern occurred, which consists in the detachment of thin stone layers intercalated with efflorescence (Figure 5). This type of degradation had already been observed previously under similar experimental conditions [1].

The alteration curve and the time lapse imaging (Figure 8) are in this case both helpful to characterize and understand the phenomena. The topographic profiles show significant lifting of the top surface (3 mm) and the alteration curve allows identifying different periods which, as previously seen [1], are related to the drying kinetics.

4) Na_2SO_4 on stone with water repellent treatment

Also in this case, a multi-layer delamination pattern is observed. This is the same pattern originated in the absence of water repellent treatment (Figures 5 and 6), which is somewhat surprising. Indeed, the water repellent forms a hydrophobic surface layer and since liquid solutions are expected to be unable to traverse the hydrophobic material, crystallization should happen only beneath this layer. This was seen in the case of NaCl (Figures 3 and 4) for which efflorescence occurred on the untreated stone while in the treated stone subflorescence formed which eventually lead to detachment of a 0.7 mm thick surface layer. However, the sodium sulfate solution seems to be able to penetrate in the hydrophobic layer, a behavior which clearly requires further investigation.

4.2 Alteration kinetics versus drying kinetics

The present subsection is about whether the combination of the techniques (alteration kinetics and drying kinetics) is helpful to characterize the alteration process and the underlying drying process.

1) NaCl without water repellent (Figure 7, on the left)

In this case, drying proceeds slowly and uniformly until the end of the test. The constant drying rate is characteristic of drying Stage I, in which the drying front is at the surface of the material, with pure water. A constant drying rate may also happen during Stage I with soluble salts if the efflorescence and material decay patterns have no significant influence on drying [3], which seems to be the case here. Accordingly, the alteration curve shows a slow and uniform lifting of the surface due to the grow of efflorescence at a constant rate on the top surface of the specimen.

2) NaCl with water repellent (Figure 7, on the right)

Drying proceeds at a constant rate until the end of the experiment, as before. But the drying rate is now a little faster than when the stone had no water repellent. This difference is counterintuitive because the application of water repellents delays drying with pure water [8]. However, in the present

case the salts eventually cause material breakdown (Figure 4) which can lead to an increase in drying rate [4].

Looking at the alteration curve, we see that there is an initial period without changes, after which the surface starts lifting at a constant rate, and proceeds so until the end of the experiment. We can hypnotize that in the beginning the surface does not lift because the salt is crystallizing inside the material. It is only after enough pressure has built to break the material that the surface starts lifting due to the unrestrained growth of subflorescence. Further experiments are necessary to understand why this difference is not reflected in the drying curve (perhaps the cracking of the surface happens fast enough to allow an almost immediate release of water vapor, while the total detachment that leads to the unrestrained lifting of the surface occurs only at a later moment).

3) Na_2SO_4 without water repellent (Figure 8, on the left)

The first observation is that, as expected, drying is faster with Na_2SO_4 than with NaCl [1]. In fact, with Na_2SO_4, 100 hours were enough to achieve a complete drying curve that, as seen in Figure 8 (on the left), has the regular shape typically obtained for pure water. Differently, the alteration curve is segmented. It is possible that the first segments, until the 15 hours, correspond to Stage I, while the other, which have lower and progressively decreasing slope, to Stage II, as previously observed in a similar experiment [1]. The smooth drying process is due to the fact that the multilayer delamination pattern consists of the progressive detachment of very thin stone layers, which corresponds in practice to an unrestrained florescence growth process. As to the alteration curve, this is probably much more uneven, with abrupt transitions, because, as seen in Figure 5, the detached layers are not as regular as in the remaining (Figure 6) and previous [1] experiments.

4) Na_2SO_4 with water repellent (Figure 8, on the right)

With the application of the water repellent treatment, the degradation phenomena observed is the same, the multi-layer delamination. The drying rate is also not very different, but is atypically irregular. The causes of this behavior are hard to explain and would require replicating the experiment.

5 | Conclusions

In the present work, the salt degradation process during drying of Ançã limestone with NaCl and Na_2SO_4 was simultaneously investigated via different methods. This was possible through an integrated set-up that permits full characterization of a unique specimen in relation to the alteration kinetics (quantified by topographic measurements performed with an optical profilometer), drying kinetics (measured by means of gravimetric monitoring) and decay patterns (recorded by time-lapse photography). This innovative approach showed great potential to achieve a better understanding of salt decay phenomena, by means of a more accurate and comprehensive characterization of drying and alteration features. In particular it reduces the uncertainty associated to the use of different specimens to investigate different features.

However, some aspects still need to be improved, namely:

- Continuous acquisition of data from the weighting device should be implemented, because the need to change battery can lead to loss of values;
- All the data (from the weighting device, profilometer and camera) should be collected in a single computer file.
- The camera has to be in an oblique position or, alternatively, on a position defined case-by-case as the most appropriate to capture each type of degradation pattern.
- The profilometer should scan the whole width of the specimen.

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VISTOS

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