Drying of porous building materials possibly contaminated with soluble salts: summary and findings of the DRYMASS research project

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Abstract

Moisture causes severe and recurring anomalies in the built heritage, but removing it from the solid and thick masonry walls of old constructions is not easy, especially when soluble salts are present. These salts crystallize during drying, may harm the materials and their aesthetics. Moreover, the salts themselves and the alterations they cause affect the underlying drying process through mechanisms that require clarification.

The DRYMASS project aimed at improving the current understanding of drying and of how soluble salts can influence it. It also had the objective of verifying if drying can be accelerated by means of surface layers such as coatings, which would be of high technical interest for conservation.

The work of the project involved evaporative drying tests on porous building materials contaminated with different salts. It included also a novel use of optical profilometry for monitoring salt decay processes, and NMR measurements to determine the crystallizing Na_2SO_4 phases.

Main conclusions were that salts hinder drying because they reduce sorptivity and also, when compact efflorescence or a salt crust occurs, because these types of deposit obstruct vapour transport. It was also concluded that lime coatings can accelerate drying of several types of porous building material initially saturated with pure water. However, this effect may not manifest when salts are present because efflorescence morphology incorporates a component of chaotic uncertainty.

Keywords: soluble salts, drying, porous material, optical profilometry, lime coating

1   Introduction

Moisture causes severe and recurring anomalies to the architectural heritage. This involves the loss of historic materials, aesthetical problems, poor comfort and health conditions, as well as expensive repairs. Eliminating moisture, which is present in the pores of materials such as stone, brick and mortars, may be difficult because old masonry walls are typically solid and thick.

Moreover, historical materials often contain soluble salts. During drying, these salts crystallize as efflorescence or subflorescence, which is one of the most destructive alteration mechanisms of porous building materials.

The salts themselves and the alterations they cause to the materials influence the drying process. Understanding the mechanisms through which this influence is exerted is of paramount importance for the conservation of the architectural heritage because it is essential to enable prediction of decay.

The research project *DRYMASS – Drying of porous materials possibly contaminated with soluble salts* (http://www-ext.lnec.pt/drymass/) was launched in this context and took place from February 2010 to January 2014. Its main scientific objective was to provide a better understanding of drying and of how soluble salts can affect it. This included clarifying, for example, the effects that soluble salts, in solution or as solid crystals, have on liquid and vapour transport across the pores.

Another important objective of the project was finding out whether it is possible to accelerate the drying rate of a porous material by means of a surface layer (for example, a coating). Such possibility was suggested by the fact that the drying rate of a porous material can be higher than the evaporation rate of free water surface, depending on the pore structure of the material [1–4]. Therefore, manipulating the physical properties of the material, for instance by using a surface layer, could allow accelerating its drying rate. This technology would have high technical interest for the architectural heritage, in which moisture and dampness are recurrent. However, in this heritage, salts are also frequent. Therefore, the response of the surface layer needs to be evaluated not only with pure water but with salt solutions too.

The present article summarizes most of the experimental work undertaken to respond to the above mentioned questions, and the main conclusions that it eventually led to. More detailed information, for example on the methods and results, can be found in the articles published in the course of the research [4–11].

2   Methods and results

2.1   How do soluble salts influence liquid and vapour transport during drying?

We started by examining experimentally the drying kinetics of three natural stones impregnated with solutions of NaCl or NaNO$_3$. The natural stones were the Bentheimer sandstone (B), the Ançã limestone (CA) and a current Portuguese limestone of lower porosity which we have called "grey limestone" (CC). These materials are thoroughly characterized in [5].

The tests were carried out with four NaCl solutions and three NaNO$_3$ solutions with a different concentration. The experiments consisted in assessing sequentially, on the same specimens, the following properties and aspects: a) capillary absorption with water and with the salt solutions; b) vapour pressure above the solution-filled materials; c) drying kinetics, as expressed by the evaporation curve; d) morphology of the efflorescence formed during drying; and, e) water vapour conductivity of the efflorescence-covered specimens.

In tests a, c and e, RILEM procedures [12] were followed. In test b, vapour pressure was measured using a capacitive water activity analyser (Hygrolab 3, by Rotönic). In test d the study of efflorescence morphology was carried out visually or, in some cases, by optical microscopy.

The test specimens were small stone cubes with 24-mm edge, except for the Bentheimer of which taller specimens (120 mm height) had to be used to measure capillary absorption because this was very fast. A minimum of three test specimens of each type of stone was always used at each experimental condition.

The vapour conductivity was measured through the dry cup method in a climatic chamber at 23⁰C and 50% RH. RH of around 0% was achieved inside the cups by the use of anhydrous calcium chloride. Measuring the vapour conductivity of porous materials with efflorescence (e) was a particularly innovative aspect of this work. To the best of our knowledge, such direct method of quantifying the obstruction posed by the efflorescence had never been tried before.

The results of drying test c revealed two main facts: (i) the higher the salt concentration the slower the drying, which agrees with what is usually observed in practice and in lab; (ii) some isolated specimens arbitrarily deviated from the general behaviour, depicting even slower drying kinetics (Figure 1). The arbitrary deviations in drying kinetics correspond to (also apparently random) variations in the morphology of the efflorescence formed during drying (test d), as also seen in Figure 1.

As to the capillary absorption (test a), it was observed that sorptivity decreased with the concentration of the absorbed salt solution and also varied with the type of salt [5]. Sorptivity (m s$^{-1/2}$) is an experimental quantity that expresses the tendency of a material to absorb and transmit liquids by capillarity [13]. It is the slope of the first linear segment of the absorption curve obtained when the cumulative volume of liquid absorbed per unit area, i.e., inflow velocity i (m), is plotted against the square root of time t (s). This is expressed by Equation (1), in which ΔM is the cumulative mass of absorbed liquid (kg), A the area of the absorption surface (m^2) and ρ the density of the liquid (kg m^{-3}).

$$S = i\, t^{-1/2}, \text{ with } i = \Delta M\, A^{-1}\, \rho^{-1} \tag{1}$$

The observed changes in sorptivity were proportional to $(\sigma/\eta)^{1/2}$, which means that they were due to the effect of the salts on surface tension (σ) and viscosity (η) of the salt solution. Indeed, when the sorptivity of a given material is measured using different liquids, it should scale as $(\sigma/\eta)^{1/2}$. This is shown in Equation 2, in which σ (mN/m) and η (cP) are the surface tension and viscosity of the liquid, respectively, and *S* is the intrinsic sorptivity of the material [13].

$$S = (\sigma/\eta)^{1/2}\, S \tag{2}$$

This indicates that salts can hinder liquid capillary transport, which could explain, at least partially, the observed differences in drying kinetics. However, this influence agrees with what is predicted theoretically from thermodynamic principles [13] and, therefore, cannot account for the seemingly arbitrary variations observed in some cases.
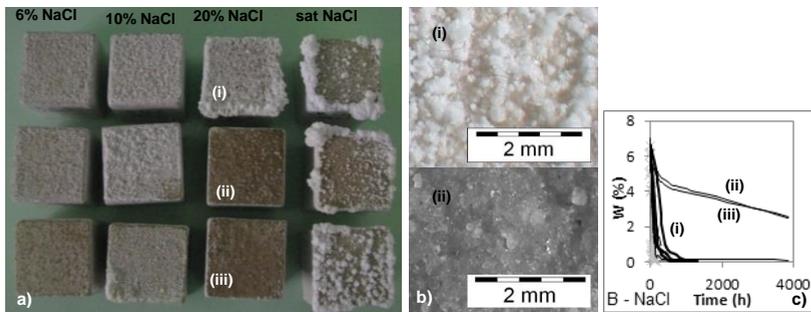

Figure 1: Decay patterns and drying kinetics of Bentheimer sandstone with NaCl solutions of different concentration: (a) vitreous salt crusts were observed on two out of three specimens tested with 20% NaCl solution; (b) details of the two types of efflorescence obtained with the 20% NaCl solution; (c) drying curves showing that the vitreous NaCl crusts on specimens (ii) and (iii) correspond to a much slower drying kinetics.

The vapour pressure measurements (test b) were carried out above the surface of CA and CC specimens saturated with NaCl solutions of different concentrations. They took place 24h after drying had begun, i.e., at the start of the process as this lasted in total close to one month or more. The results showed that, regardless of the initial concentration of the solution, the RH above the specimens was similar to the RHeq of the saturated salt solution [5]. This means that the solutions saturated very early at the evaporation front and, so, that the initial differences in vapour pressure are not relevant to explain the differences in drying behaviour.

The results of the vapour conductivity test (test e) are given in Figure 2 in terms of equivalent air layer thickness Sd. As seen, the Sd of the efflorescence-covered specimens is, in most cases, similar to that of the blank specimens. This means that no significant blocking of vapour transport by the efflorescence took place in these cases.

By crossing these results with those of test d, it was verified that the deviant drying kinetics correspond to dense salt deposits, namely the mentioned vitreous NaCl crusts formed on Bentheimer specimens ii and iii (Figure 1) and compact NaCl efflorescence formed on the Ançã specimens [5]. The rest corresponds to porous efflorescence. Therefore, it was concluded that only dense salt layers effectively hinder the transport of vapour.
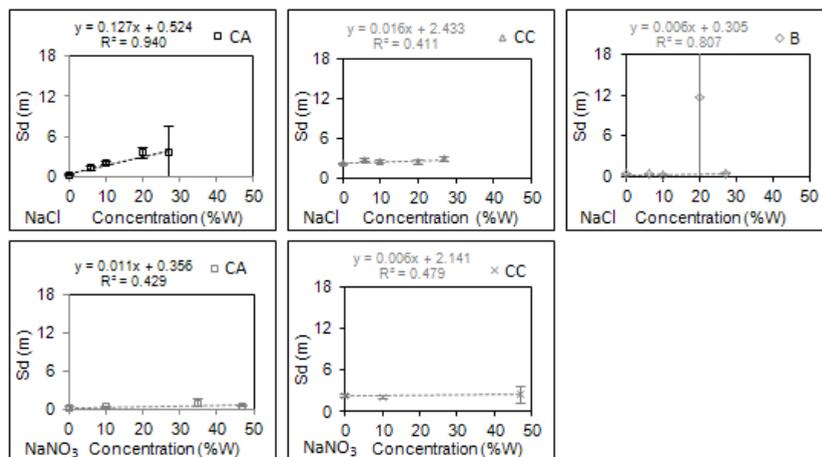

Figure 2:   Equivalent air layer thickness (Sd) of the efflorescence-covered specimens as a function of the initial concentration of the salt solution [5]

In fact, when the efflorescence present on the surface was porous and, therefore, had no relevant blocking effect in relation to vapour transport, the drying kinetics is similar for solutions with similar σ/η ratio (Figure 3, on

the left). This indicates that, in these cases, the differences in drying kinetics are due to the changes salts induce on sorptivity.

Differently, when compact salt crusts which hinder vapour transport are present, there is an additional decrease in drying kinetics, as seen for the CA limestone with NaCl (Figure 3, on the right). This indicates that compact salt crusts can further slowdown the drying kinetics.
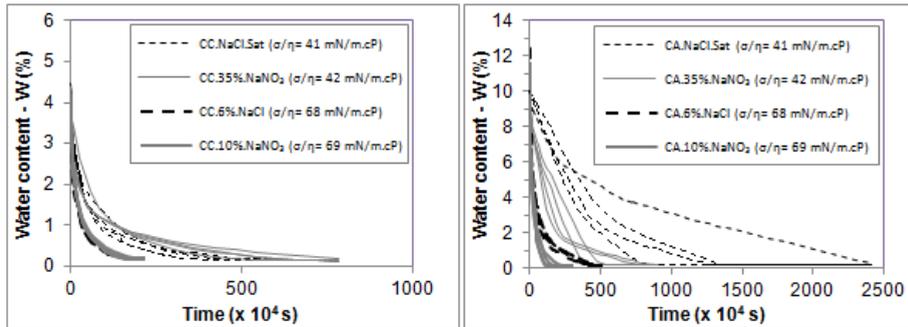

Figure 3: Drying kinetics, for solutions with similar σ/η ratio, of specimens depicting either: (i) only porous efflorescence (on the left, CC stone); (ii) porous efflorescence and compact salt crusts, respectively (on the right, CA stone) [5]

2.2   Unpredictability in salt decay

The results presented in the previous section show that thermodynamic considerations are not enough to explain the drying kinetics of porous materials in the presence of soluble salts. As seen, the drying kinetics of several specimens suffered occasional deviations which derive from apparently random variations in efflorescence morphology. This shows that there is also a component of unpredictability in the process [5].

This kind of uncertainty was observed also in a second experimental study of the project carried out with NaCl and Na_2SO_4 [7]. Figure 4 shows some of the results. As seen, the drying kinetics are not only slower, but also more irregular showing higher dispersion for the salt solutions than for pure water. Also, it sometimes diverges among specimens of the same material subjected to similar experimental conditions. These chaotic features [14] are in agreement with the decay patterns and suggest that soluble salts amplify the effects of the natural heterogeneity of porous materials.

A third study of the DRYMASS project [10, 11] showed that this type of phenomenon occurs not only in relation to efflorescence, but also in relation to decay patterns that involve material degradation. Fissures and

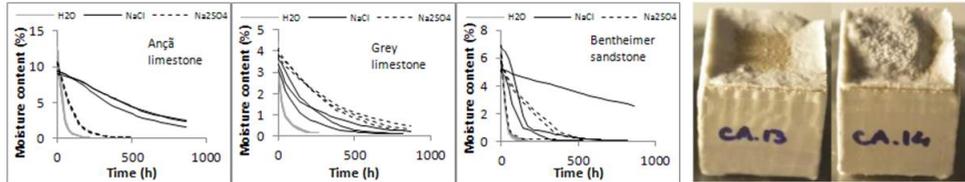disaggregation, for example, can create preferential pathways for vapour transport.

Figure 4: On the left: drying kinetics of the three tested stones. On the right: variation in the decay patterns of two specimens of Ançã limestone tested simultaneously and under similar conditions with saturated NaCl solution [7]

This study was carried out with six individual salts, NaCl, NaNO$_3$, Na$_2$SO$_4$, Na$_2$CO$_3$, KCl and KNO$_3$, on two current materials, lime mortar (A) and red ceramic brick (T). It involved measuring the sorptivity and the drying kinetics of the salt laden materials, the last over a span of more than 7 months. The testing protocols are those described in the previous section.

Figure 5 shows that also in this study the degradation patterns varied occasionally for similar materials subjected to the same experimental conditions. And, again, the drying kinetics varied accordingly: in this case, the more altered the material the faster the drying.
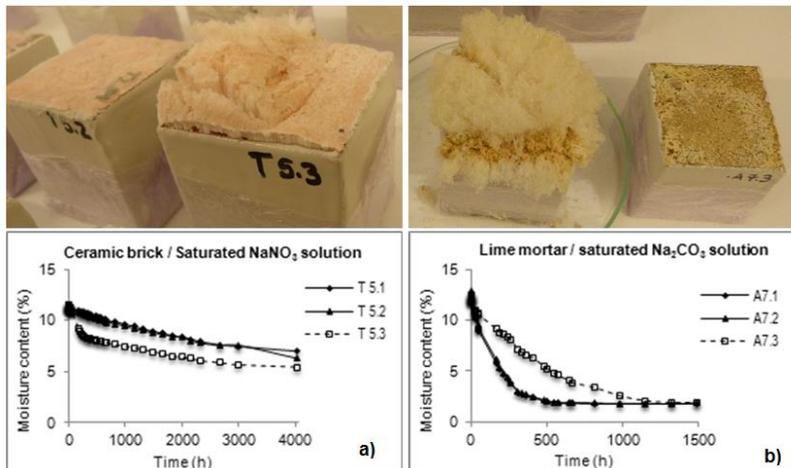

Figure 5: Variations in the decay patterns and drying kinetics of brick and mortar with NaNO$_3$ and Na$_2$CO$_3$: (a) one brick specimen depicted fluffy efflorescence while the other two developed compact salt crusts and had slower drying

kinetics; (b) two lime mortar specimens showed abundant efflorescence that caused material disintegration and was accompanied by faster drying kinetics, while the other did not [8].

2.3   Measuring the alterations

But it is not only arbitrariness that makes it hard to predict and deal with decay salt processes. Another important problem is that salt crystallization tests, which are used to assess treatments and materials, are often unrepresentative of reality. This happens because, to obtain measurable changes within a reasonable period of time, the specimens are typically subjected to extreme conditions, such as high temperatures or successive wet/dry cycles. The consequent distortion of results can be particularly significant for salts such as Na_2SO_4, which in these extreme conditions can give rise to massive contact-induced [15] or temperature-induced [16] crystallization processes that hardly occur in the architectural heritage.

To overcome this major difficulty, a novel method based on optical profilometry was developed within the DRYMASS project [6]. Topographic profiles are measured during drying, from which an alteration kinetics curve is afterwards calculated (Figure 6). Each point in the alteration curve corresponds to a different profile, so, this curve expresses the (average) lifting of the surface during the process. As we are able to measure the small changes undergone by the material at the micrometre scale, it becomes unnecessary to subject it to extreme experimental conditions.

This new method was used in a set of crystallization tests with saturated Na_2SO_4 solution. The specimens, laterally sealed with epoxy, were first lead to capillary saturation by partial immersion in the salt solution. Then, their bottom face was sealed with polyethylene sheet, which was followed by a single drying event at 20ºC and 50% RH.

The results showed that, under these less radical conditions, Na_2SO_4 can develop decay patterns similar to those observed in buildings. Ançã limestone, for example, developed a typical delamination pattern (Figure 6). As shown, the alteration process was successfully monitored by optical profilometry and, afterwards, characterized by the alteration curve [6].
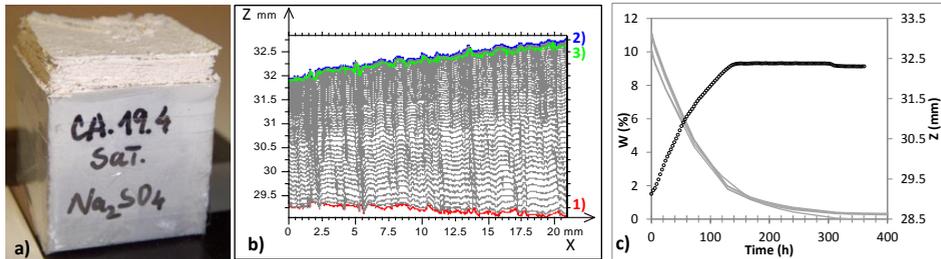
Figure 6: Delamination of Ançã limestone: **a)** image of a test specimen at the end of drying; **b)** topographic profiles obtained every 3 h during drying: 1) first profile; 2) uppermost profile after 305 h of drying; 3) last profile after 320 h of drying; **c)** alteration kinetics curves in black, and drying kinetics curves in grey [6]

2.4 NMR identification of sodium sulfate phases crystallizing on Ançã limestone

NMR experiments showed that the Na_2SO_4 phase causing the damage seen in Figures 6 and 7 was mirabilite [9]. Indeed, the two Na_2SO_4 hydrated phases, mirabilite and the metastable heptahydrate, can form under a wide range of conditions, including the present (20ºC / 50% RH).

The NMR tests were repeated under different experimental conditions of temperature and RH (20ºC-50%RH, 20ºC-0%RH and 7.5ºC-0%RH). The two last conditions included also pre-heating the specimens at 40ºC to ensure that no mirabilite crystals were present in the pores when drying started. That would exclude heptahydrate crystallization because heptahydrate is metastable and, therefore, the two phases cannot coexist.

The conclusions were that both mirabilite and heptahydrate can be responsible for this type of decay, as seen in Figure 7. The heptahydrate tends to crystallize first when there is no previous presence of mirabilite crystals in the porous material [9].
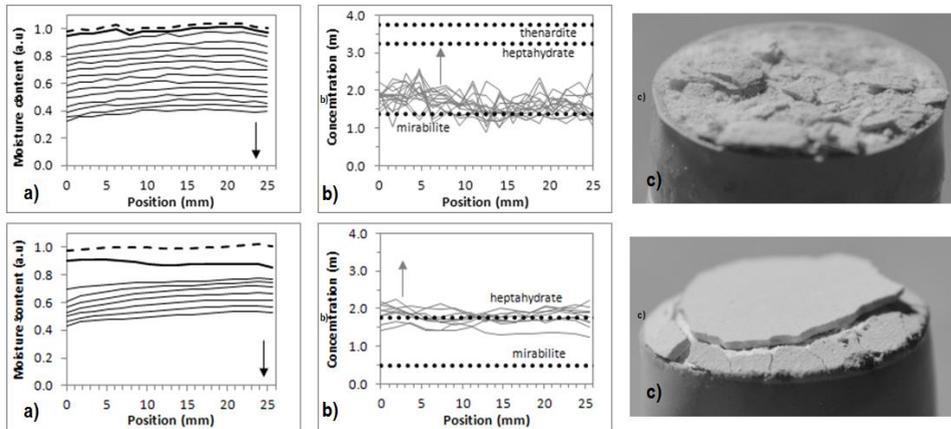
Figure 7: NMR-monitored drying experiments on Ançã limestone specimens at 20ºC / 50% RH (left) and 7.5ºC / 0% RH with pre-heating (right): a) moisture profiles, b) ion concentration profiles, c) test specimens after the experiment [9]

2.5 Influence of a traditional lime coating on drying

To find out whether it is possible to accelerate the drying rate of porous building materials by means of surface layers, we started by evaluating experimentally the influence of a traditional lime coating on the drying of five materials [7]. The materials were the previously mentioned Ançã limestone (CA), grey limestone (CC) and Bentheimer sandstone (B), as well as the well-known Maastricht limestone (M).

Lime coatings were considered a good first choice for this work because they are hydrophilic and vapour permeable, and also because of the relevance they have in conservation. The traditional lime coating used in our study had a 1.4 water/lime ratio and was applied manually, by brush or with a spatula, depending on the substrate material [7].

The drying tests were carried out, as previously, according to the RILEM procedure [12]. The outputs of the test were quantified: (i) through the drying index (DI), an empirical quantity which translates the drying curve into a single quantitative parameter and is based on the measurement of the area below that curve [17]; (ii) through the Stage I drying rate which is the drying rate of the material while its moisture content is high enough to sustain a saturated condition at the surface and is given by the slope of the initial straight branch of the evaporation curve.

The results obtained with pure water were extremely interesting. They showed that the lime coating not only does not hinder drying, but it is also, able to accelerate it (Figure 8).
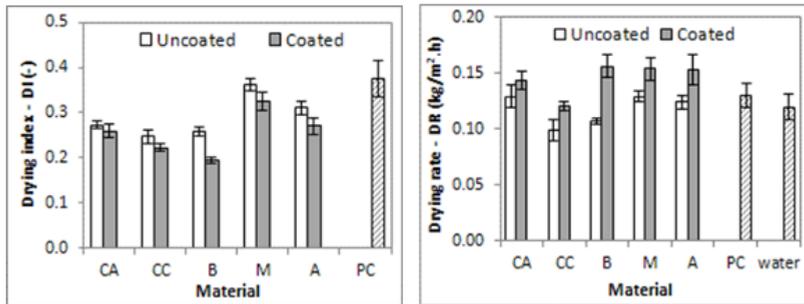
Figure 8:   Results of the drying test with pure water on lime coated materials given in terms of: drying index (on the left) and Stage I drying rate (on the right) [7]

The increase in drying rate was very significant under Stage I conditions (Figure 8, on the right), i.e., when the moisture content of the substrate is high, as it often happens at the base of walls suffering from rising damp. It has, therefore, nothing to do with the vapour permeability of the coating, because during Stage I the drying front is at the surface of the material.

The main explanation for the observed increase in the Stage I drying rate is that, due to the complexity of its pore structure, the coating is able to generate a larger effective surface of evaporation.

2.6   Behaviour of the traditional lime coating with soluble salts

To verify the behaviour of the traditional lime coating when salts are present, we carried out a set of crystallization tests on coated and uncoated specimens with solutions of NaCl or Na_2SO_4 [8].

As seen in Figure 9, the coating can still, in few cases, enhance drying when soluble salts are present. However, in comparison to pure water, the drying kinetics are slower. The drying behaviour is also more irregular and has higher dispersion, which suggests that salt decay processes have a high sensitivity to the initial conditions. This means that small changes in the microstructure of the materials may result in large differences in terms of decay patterns and, consequently, of drying kinetics. That explains why, as previously, the drying kinetics occasionally diverged between specimens of the same material subjected to similar experimental conditions.
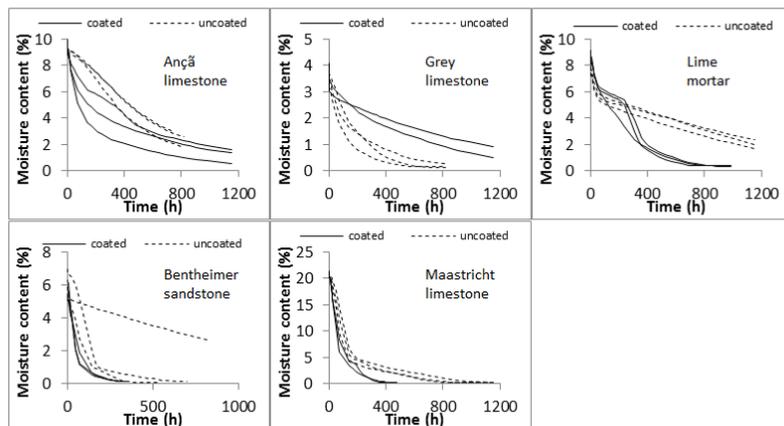
Figure 9: Drying kinetics of coated and uncoated materials contaminated with NaCl [8]

3 Conclusions and perspectives

In relation to the first objective of the DRYMASS project, of advancing the understanding of how soluble salts affect the drying of porous materials, two main conclusions were reached:

- Factors that influence drying

  The drying kinetics of the tested materials were generally slower with salt solutions than pure water. This was expected because it is what is normally observed in practice and in the lab.

  Our work indicates that this slower drying has two main causes that may overlap. The first is a reduction in sorptivity due to the effect that salts have on surface tension and viscosity. The second is the obstruction to vapour transport by the crystallized salt.

  Only compact salt crusts can obstruct the pores, and these occurred only occasionally in our experiments. In most cases, porous efflorescence occurred, which poses no obstruction to water vapour transport.

  In addition to these two main factors of influence, others may occur, which often have the opposite effect. For example, fissures and disaggregation can create preferential pathways for vapour transport and, therefore, accelerate drying.

- Unpredictability in salt decay

  When soluble salts are present, the drying kinetics are more irregular and show higher dispersion than for pure water.

Furthermore, it may diverge significantly among specimens of the same material subjected to similar conditions.

We believe this happens because salt decay processes have a chaotic component and, therefore, salts amplify the dispersion effects that material heterogeneity has on the drying kinetics. Due to this chaotic character of salt decay, the morphology of efflorescence, and of other decay patterns with an influence on drying, incorporates a component of unpredictability [14]. This explains the apparently random variations in drying kinetics that were observed.

In relation to the second objective of the project, i.e. of finding out whether it is possible to enhance the drying rate of porous building materials using a surface layer, there were two main conclusions:

- Lime coatings such as traditional lime washes not only do not hinder drying, but can even accelerate it. This happens when the moisture content in the substrate is high enough so that the drying front is at the surface, and is likely to occur because the coating generates a larger effective surface of evaporation.

- In the presence of soluble salts, lime coatings can, sometimes, still enhance drying, but not systematically , and this due to the chaotic nature of the salt crystallization process.

In addition, the DRYMASS project allowed developing a novel method to monitor and quantify salt decay patterns by optical profilometry:

- This new method allows defining more realistic salt crystallization tests because we are able to measure the small changes undergone at the micrometre scale. Therefore, it becomes unnecessary to subject the material to (unrealistically) extreme experimental conditions.

- It was confirmed that sodium sulfate can be very destructive in field-representative conditions, i.e., in the absence of high temperature or fast successive wet/dry cycles. A delamination pattern similar to that found in real constructions was observed on the well-known Ançã limestone, which was thoroughly characterized with the help of the new optical method.

Finally, the work allowed concluding that NMR is appropriate to determine which crystal phases are crystallizing during drying. It showed that both mirabilite and heptahydrate can cause delamination of Ançã limestone under different environmental conditions. The heptahydrate tends to crystallize first when there is no previous presence of mirabilite crystals in the porous material.

Among future research perspectives suggested by the project, we highlight those related to the uncertainty in salt decay processes. In parallel to establishing an effective theoretical framework, there is a pressing need for data about what happens in reality. This will allow defining ranges of situations (types of salt, salt contents, etc.) to be considered in experiments and modelling.

Acknowledgments

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