

# A preliminary study on dynamic measurement of salt crystallization and deliquescence on a porous material surface using optical microscope

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## Abstract

This paper reports on our preliminary attempt to perform dynamic laboratory measurements of salt crystallization and subsequent deliquescence on a surface of a porous material specimen (autoclaved aerated concrete as a model material) by using a high-resolution digital optical microscope that allows generating three-dimensional images. A specimen that is initially filled with a NaCl solution is dried in a room at ~26°C and ~40% RH for 14 days and is then wetted in a desiccator at ~95% RH during the next 14 days. A temporal change of the spatial distribution of the volume occupied by salt crystals on the specimen surface is determined based on the contrast between two microscopic images successively taken with a certain interval of time. The mass of the specimen is also measured simultaneously to determine the rate of water evaporation/absorption. The results show that salt crystallization during drying is not spatially uniform throughout the specimen surface, which likely depends on the spatial distribution of the pore structure in the specimen, and salt crystal deliquesces faster near the edges of the specimen than in the centre, which indicates a stronger dependency of salt deliquescence on the geometry of the specimen than on the inner pore structure of the specimen.

Keywords: light microscopy, efflorescence, sodium chloride, absorption/desorption

## 1. Introduction

Cycles of crystallization and deliquescence of salt can be often observed on a surface of building and heritage materials such as stones, bricks, mortar, etc. In general, salt crystals grow in cold seasons and disappear in warm seasons, often as a result of hygrothermal responses of the materials to changes of ambient air temperature and humidity, rain, solar radiation and so on. To physically understand such phenomena and propose a sufficient countermeasure, it could be useful to quantitatively determine the rates of water evaporation and the subsequent salt crystallization and those of water absorption and the subsequent salt deliquescence on the surface of the material.

Water and salt transport in porous building materials has been steadily and rather well studied over the last years. This phenomenon can be characterized by two main material properties: the sorption isotherm and the liquid water conductivity, both of which are dependent on the salt concentration, water content and temperature. Apart from water and salt transport, crystallization of salt in pores of a porous material or at/near the surface of the wall still needs fundamental studies for quantification. Regardless of difficulty of measurement, recent non-destructive measurement techniques enabled to visualize the volume of salt in pores of the material.<sup>1-3</sup> Another approach to quantify the amount of salt in a porous material is to measure the pore size distribution of the material, i.e. to show that although the total pore

volume is basically reduced due to the presence of salt crystals, the specific pore volume for some pore sizes can increase.<sup>4</sup> This means that salt crystals can provide a new pore structure that exhibits different water and salt transport properties in the material.<sup>5,6</sup>

Compared to crystallization in pores, less attention has been paid to crystallization at surfaces of porous materials in the past<sup>7-15</sup>, because in-pore crystallization is more harmful for damage of porous materials. However, recently, the work of Veran-Tissoires<sup>13-15</sup> using 1 mm glass beads gave an important motivation to understand the phenomena at the material surface, indicating that salt structures forming efflorescence are porous and transfer salt solution by capillarity, influencing the water evaporation rate at porous material surfaces, which is called the screening effect. Rad and Shokri<sup>10</sup> also studied salt precipitation on sand grains with an average particle size of 0.48 mm and the relation of evaporation with salt precipitation. Rad et al<sup>11</sup> further conducted three-dimensional imaging of using x-ray microtomography, to understand more in detail the relation of the pore sizes and the initial salt concentration with the dynamics and patterns of salt precipitation during drying. Our current study focuses on salt on a material surface that crystallizes during drying and furthermore deliquesces during subsequent re-wetting. It reports on our preliminary attempt to perform dynamic laboratory measurements of salt crystallization and subsequent deliquescence on a surface of a porous material specimen (autoclaved aerated concrete as a model material) by using a high-resolution digital optical microscope that allows generating surface three-dimensional images. A temporal change of the height of salt crystals on the specimen surface is determined based on contrast between two microscopic images successively taken with a certain interval of time.

## **2. Methodology**

Dynamic laboratory measurements of salt crystallization and subsequent deliquescence on a surface of a porous material specimen (Autoclaved Aerated Concrete (AAC) as a model material) are carried out with use of a high-resolution digital optical microscope that allows generating three-dimensional images. The spatial resolution at the top surface of the specimen is horizontally  $10\mu\text{m} \times 10\mu\text{m}$ ; vertically the stage moves with a resolution of  $0.1\mu\text{m}$ , to calculate the height of the object (the specimen surface or precipitated salt) based on focus. The dry bulk density of the specimen is  $507\text{ kg/m}^3$ . The moisture transport properties of the same type of AAC as this specimen is given in e.g.<sup>16</sup> The mass of the specimen as well as the temperature and humidity of the ambient air is also measured simultaneously. A temporal change of the height  $h$  of salt crystals on the specimen surface is determined based on contrast between two microscopic images successively taken with a certain interval of time.

The following steps are taken:

- (1) A cubic specimen of  $27\text{ cm}^3$  is dried completely to determine the porosity and dry density of the specimen. Then, the surfaces of the specimen except the top and bottom surfaces are made vapor tight.
- (2) The specimen is immersed in pure water and then a drying test is conducted to know how fast the specimen is dried in the laboratory. The temporal change of the mass of the specimen is measured.
- (3) The specimen is again completely dried and then immersed in saturated NaCl aqueous solution with a salt concentration of  $0.1\text{ kg/kg}$ . Note that in this paper, the salt concentration is

defined by the mass of salt divided by the mass of the solution. Afterwards, the bottom of the specimen is made vapor tight; only the top of the specimen is open to vapor transfer.

- (4) The specimen is stored at a constant temperature ( $\sim 26^{\circ}\text{C}$ ) and humidity ( $\sim 40\%$  RH). The height  $h$  of salt crystals on the specimen surface is recorded with a certain interval of time using the microscope that can allow to generate three-dimensional images. The weight of the specimen is also measured to determine the evaporation rate. The drying process is continued for approximately 14 days.
- (5) The specimen is stored at almost the same temperature but at a humidity of  $\sim 95\%$  RH. Salt crystals on the surface and the specimen's weight are recorded, by the latter of which the rate of water vapor absorption is determined. The wetting process is continued for approximately 14 days.

In the following sections, results are discussed based on the properties of the specimen and salt at the given temperature and humidity conditions.

### 3. Results and discussion

*Figure 1* shows photographs of the center (2.4 cm x 2.4 cm) of the top surface of the specimen taken at  $t=0.71$ , 1.79, 2.79 and 6.79 days during the drying stage. To omit the effect of the edges of the top surface on three-dimensional image analysis, only a square of 2.4 cm x 2.4 cm is taken though the top surface area of the specimen is 3 cm x 3 cm. Based on the difference of two three-dimensional images successively taken with a certain interval of time, the increment  $\Delta h$  of the height  $h$  of salt on the specimen surface

at the drying stage is calculated.  $\Delta h$  and  $h$  at  $t=1.79$ , 2.79 and 6.79 days are illustrated in *Figure 2*. Note that  $h$  is equal to 0 at  $t=1.79$  days and for example,  $h$  at  $t=2.79$  days is the sum of  $h$  at  $t=1.79$  days and  $\Delta h$  at  $t=2.79$  days.

The results show that during drying, there is a large spatial distribution in the crystallization rate in a shorter time scale ( $\sim$ one day) as also measured by Rad et al<sup>11</sup>; but at the end of drying, salt is rather uniformly distributed on the surface. Although salt crystals first grow at some specific areas, it seems that crystal growth stops after some time. However, next salt crystal growth occurs at other areas, where successive water evaporation occurs due to a lower liquid water conductivity. This could be explained by the intrinsic spatial distribution of the pore structure of the specimen<sup>11</sup>, which determines the in-pore liquid water transport and the evaporation at the surface.

Looking at e.g. *Figure 2b*, a very larger increase of  $h$  is observed at some large open pores on the specimen surface seen in e.g. *Figure 1a*. This can be attributed to the difficulty of determining the height of the surface of the material in the pores.

Photographs of the center of the top surface of the specimen taken at  $t=0.47$ , 0.86, 1.24 and 1.86 days during the wetting stage are given in *Figure 3*. The decrement  $\Delta h$  of the height  $h$  of salt on the specimen surface at the wetting stage and  $h$  at  $t=0.86$ , 1.24 and 1.86 days are illustrated in *Figure 4*. Note that  $h$  is equal to 0 at  $t=1.86$  days.

Although the spatial distribution of salt crystals that are deliquescing is more uniform compared to that of crystallization and independent of the in-pore structure of the specimen, it seems clear that deliquescence occurs faster near the edges of the specimen than the center of the surface due to a geometry effect on the heat and moisture transfer. Note that

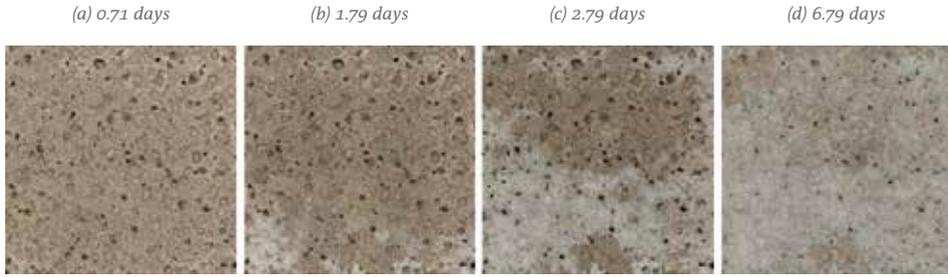


Figure 1: Photographs of the center (2.4 cm x 2.4 cm) of the top surface of the specimen taken at the drying stage

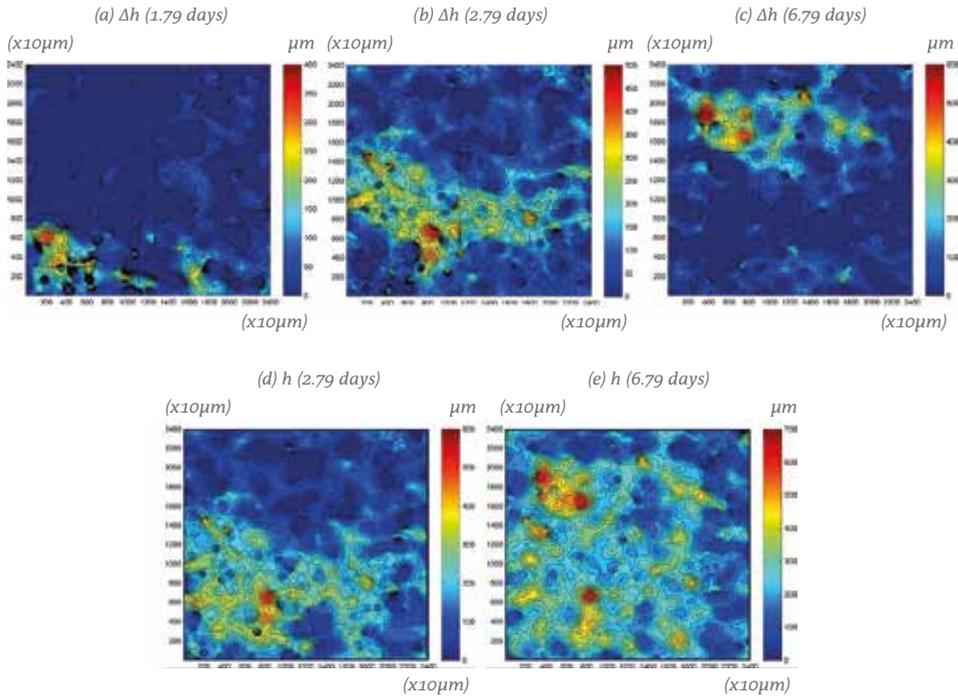


Figure 2: The spatial distribution of (a, b, c) the height change  $\Delta h$  of salt crystallizing on the top surface (2.4 cm x 2.4 cm) of the specimen for three consecutive drying periods and (d, e) the height  $h$  at the end of the last two periods (2.79 and 6.79 days). (a)  $\Delta h$  for 26 hours between 0.71 and 1.79 days; (b)  $\Delta h$  for 24 hours between 1.79 and 2.79 days; and (c)  $\Delta h$  for 96 hours between 2.79 and 6.79 days.

when the specimen absorbs moisture, the temperature of the surface gets higher due to heat of condensation. Because the change rate of the temperature is larger near the edges of the specimen, the solubility near the edges may have become more increased due to the temperature increase. However this effect is considered to be extremely small because

of the low temperature dependency of the solubility of NaCl.

A clear difference in time is observed between crystallization and deliquescence processes. This can be explained as follows. The specimen was completely wetted with the salt solution at the beginning of drying and salt solution transfer in the specimen took some time.

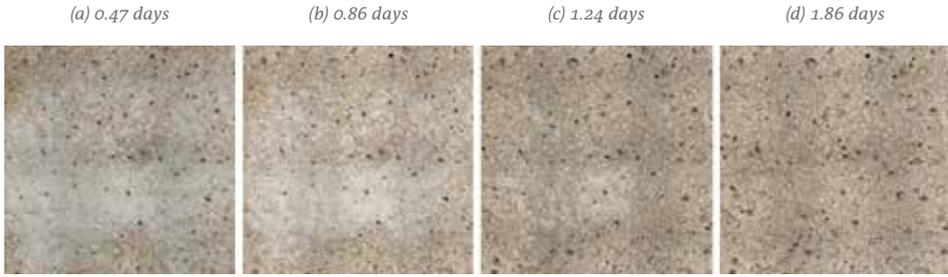


Figure 3: Photographs of the center (2.4 cm x 2.4 cm) of the top surface of the specimen taken at the wetting stage

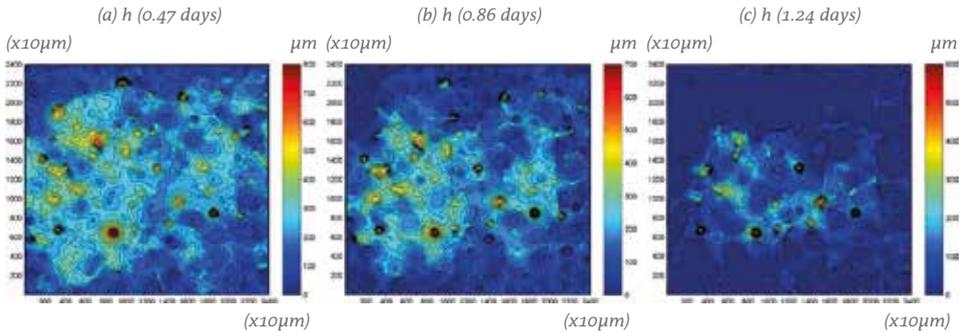


Figure 4: The spatial distribution of the height  $h$  of salt deliquescence on the top surface (2.4 cm x 2.4 cm) of the specimen at  $t = 0.47, 0.86$  and  $1.24$  days of wetting periods.  $h$  is defined to be 0 at 1.86 days.

This means that the drying rate was dependent on the salt solution permeability of the specimen. As a result, crystallization continued for at least 7 days of the drying process. *Figure 5* shows the temporal change of the average moisture content  $w$  in the specimen that contained salt water, calculated from the dry mass of the specimen and the mass of water in the specimen, and the content of precipitated salt estimated based on  $w$  and the initial salt content; *Figure 6* does the same during wetting. In *Figure 5*, the data for the specimen that contained pure water are also plotted. Although a rapid change of the evaporation rate for pure water is observed at approximately 2 days, this would be mainly due to the typical transition from a capillary-driven to a vapor-driven drying and partly due to a large change of the humidity

condition ( $>10\%$  RH) which was not well controlled during the experiment. The evaporation rate from the specimen with the salt solution is much lower than that from the specimen with pure water.

If  $wc > 0$ , the water content is not sufficient to dissolve all the salt crystals both in the specimen and at the surface of the specimen. In *Figure 6*,  $wc > 0$  after 2 days indicates that salt crystals still surely remain during absorption, which can lower the vapor absorption rate.

In our current work, we only conducted measurements under limited conditions, but future work should address more different conditions to enable to develop a model that can predict cycles of crystallization and deliquescence of salt on and near the specimen surface as a function of the type of a porous material and salt, the initial salt concentration, the ambi-

ent temperature and relative humidity, and so on.

#### 4. Conclusions

In this paper, we reported our preliminary dynamic measurements of salt crystallization and subsequent deliquescence on a surface of a porous material specimen (autoclaved aerated concrete as a model material) with use of a high-re-

solution digital optical microscope that allows generating three-dimensional images. The obtained results are analysed to quantify the spatial distributions of the rates of salt crystallization and subsequent deliquescence on the surface and their spatially averaged values. The results also showed that salt crystallization during drying is not spatially uniform on the specimen surface and depends on the spatial distribution of the pore structure in the specimen as demonstrated by Rad et al<sup>11</sup>, and salt crystals deliquesce faster near the edges of the specimen than in the centre, which indicates a stronger dependency of salt deliquescence on the geometry of the specimen than the inner pore structure of the specimen. The obtained data and future measurements with different conditions are to be used for model development and validation.

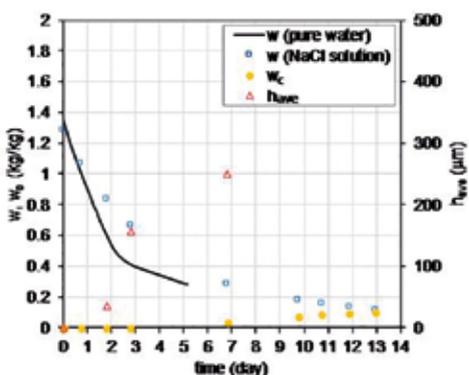


Figure 5: The average moisture content  $w$ , the estimated precipitated salt content  $w_c$  and the average height  $h_{ave}$  of salt on the specimen surface for the drying process of 13 days. The solid line shows the measurement result of  $w$  for pure water evaporation from the same specimen for 5 days.  $h_{ave}$  is defined to be 0 at 0 day.

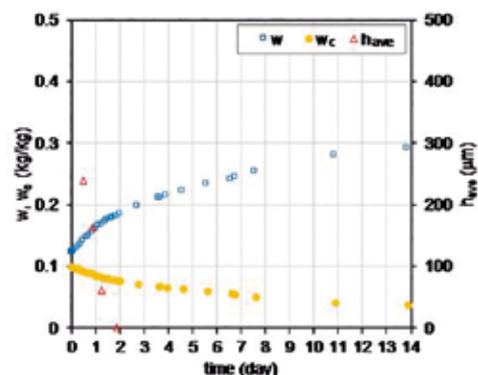


Figure 6: The average moisture content  $w$ , the estimated precipitated salt content  $w_c$  and the average height  $h_{ave}$  of salt on the specimen surface for the wetting process of 8 days.  $h_{ave}$  is defined to be 0 at 1.86 days.

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