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Crystallization of hydrated and anhydrous salts in porous limestone resolved by synchrotron X-ray microtomography



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ABSTRACT

The crystallization processes of two anhydrous salts (NaCl and Na_2SO_4) and one hydrated (sodium sulfate) salt in the pore space of a natural building stone, Savonnières limestone, are studied. We imaged the salt solution distribution before and after crystallization and the solid crystal distribution in between repeated crystallization cycles using synchrotron X-ray microtomography. This technique proves to be very useful to study salt crystallization processes at the pore scale. The use of simultaneous phase-and-amplitude retrieval during X-ray tomographic reconstruction allows a clear segmentation of sodium sulfate solution and hydrated sodium sulfate crystals without the need for a dopant. Salt crystals can precipitate under unconfined as well as confined conditions in the multiple pore systems of Savonnières limestone, depending on their interconnection. Salt solution and salt crystals are located in mechanically weak zones of the limestone, which can be linked to damage patterns observed in this stone after repeated salt weathering cycles. The distribution and the process of pore filling by salt crystals that are revealed here advance the understanding of salt damage in porous media and may open ways to perform remediation.

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1. Introduction

The crystallization of salts in porous building materials is one of the main causes of physical deterioration of civil engineering constructions and cultural heritage. Due to the high crystallization-induced pressures that can develop in the confined pore space, cracks may form. The risk for salt damage in building materials depends on the degree of pore filling by the crystals and the magnitude of the crystallization pressure [1]. The crystallization-induced stresses are determined by the combination of a sufficient amount of salt crystals with a sufficient high crystallization pressure. Today, there is general consensus in the literature that the crystallization pressure is a supersaturation driven phenomenon [2–8]. When a crystal fills a pore, a liquid film (in the order of a few nanometers [4]) remains between the crystal and the pore wall. This liquid film originates from repulsive forces between the crystal and the constraining pore wall and is necessary to allow that a crystal can grow upon its loaded surfaces. The growth upon a loaded crystal face can only exert pressure if this face is in contact with a supersaturated solution [5]. A schematic representation is given in Fig. 1. The supersaturation and thus the crystallization pressure depend on the temperature and the salt solution concentration. For small pore sizes, i.e. below 0.1 µm, also the crystal curvature and the surface tension contribute to the crystallization pressure [6]. When an equilibrium situation is reached, i.e. when the crystal has its equilibrium form, the crystallization pressure uniquely depends on the surface tension and the curvature [6]. For example, for a cigar-like crystal growing in a cylindrical pore, the crystallization pressure is inversely proportional to the pore radius. This means that larger crystallization pressures occur in smaller pores. Consequently, under equilibrium conditions, the risk for salt damage increases when crystallization occurs in decreasing pore sizes. For this specific case and under the assumption of crystals in their equilibrium state, Coussy [7] derived that crystallization should start in the larger pores and consequently propagate in the smaller ones.

The depletion of the supersaturation depends on the nucleation and the growth of the salt crystals. This determines how fast the phase transitions occur and how they are spread in the porous

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Fig. 1. Representation of a crystal in a cylindrical pore. A liquid film is maintained between the crystal surface and the pore wall. The crystallization pressure expresses the difference between the pressure acting on the loaded crystal face p_{tr} and the pressure acting on the unloaded crystal face p_{l} .

structure. Depending on the kinetics of crystal nucleation and growth, the equilibrium state will be reached after a certain time. During the period that the kinetics are dominant, the crystallization pressure can be much larger than the values at equilibrium, due to the fact that high supersaturations can prevail. Nucleation can potentially occur in all pore ranges. Consequently, the conclusion of Coussy [7] that crystallization occurs from large to smaller pores cannot be generalized for non-equilibrium conditions during crystal nucleation and growth and there is not necessarily a unique relationship between the pore sizes and salt damage risks. Therefore, understanding salt damage risks in porous building materials asks for detailed experimental observations of salt crystallization at the scale of the pores. The key is to determine the tridimensional distribution of salt crystals and the pore filling in a direct manner. In this paper, we make a first step in this direction. We show that a thorough understanding of the porous structure, the location of mechanically weaker zones in which stress localization can occur, and the understanding of liquid transport and the location of crystal precipitation are necessary to assess salt damage risks in the porous natural building stone studied in this paper.

Salt crystallization in porous building materials occurs over repeated cycles of crystal growth and dissolution. These cycles are due to the cyclic nature of the environmental conditions to which the materials are exposed. To reproduce these natural cycles in the laboratory, non-destructive techniques are needed to investigate the material between cycles. The study of hydrated crystals requires by definition that water needs to be kept in the sample. Thus, measurements cannot be performed by techniques such as scanning electron microscopy or mercury intrusion porosimetry. X-ray micro-computed tomography (µCT) is known to be a well suited technique to visualize and characterize the pore space of porous materials and its variations non-destructively. As the attenuation of X-rays by solutions or hydrated phases is low, other researchers enhanced the image contrast by using specific solutions such as calcium iodide solution [9,10]. 3-bromopropyltrimethoxysilane doped water repellent or consolidant [11] or highattenuating particles, e.g. zirconium dioxide particles [12]. Recent advances such as phase-and-amplitude retrieval [13] provide however new possibilities to image low-X-ray absorbing components such as water and hydrated salts. In this paper, we explore the possibilities offered by synchroton X-ray µCT to study the formation of anhydrous (NaCl and Na₂SO₄) and hydrated (sodium sulfate) crystals in a porous limestone, Savonnières limestone. This is done without adding a dopant, thus without possibly altering the crystallization kinetics or crystal morphology.

In the next section, we describe the studied materials, i.e. Savonnières limestone, sodium sulfate and sodium chloride salt, the experimental setup and procedure and the applied image processing and analysis techniques. In the third section, the results are described and discussed with respect to salt solution and crystal distribution and presented in comparison with damage patterns observed in Savonnières limestone. The conclusions and possible follow-up research are formulated in the last section.

2. Materials and methods

2.1. Materials

2.1.1. Savonnières limestone

Savonnières limestone is a French layered oolitic limestone (Late Jurassic, Tithonian). The stone belongs to the Oolithe Vacuolaire, a stratigraphical unit (Tithonian) that also includes the Brauvillier stone, Chévillon stone, Combles stone and other local variations. Their microfacies are very diverse and are mainly characterized by hollow ooids, shell fragments, pellets and the presence of dolomite [14,15]. Savonnières limestone has been frequently used as a natural building stone in Belgium and the Netherlands [16] and recently for restoration purposes [17]. It is an almost pure calcitic stone (99.8% CaCO₃ [18]). A thin section representing the porous structure is given in the inset of Fig. 2. The stone consists of spherical grains, ooids, which were formed during the deposition stage. They are developed around a nucleus and have a radial and concentric structure. Some ooids are intact, but most of them are only partly preserved. The inner structure has been dissolved during diagenesis, creating a cavity. These cavities can include only the center of the ooid or they can cover the entire ooid, leaving only the perimeter intact. They form the



Fig. 2. Pore volume distribution of Savonnières limestone, with the top inset showing a thin section of the stone. The figure represents (1a and 1b) the intergranular micropores of the ooids, (2) the intergranular micropores in between the sparitic calcite crystals, (3) the intergranular macropores and (4) the intragranular macropores. The pore systems 1a and 1b cannot be resolved in the X-ray micro-computed tomography datasets as the voxel size is limited to $3.7 \,\mu$ m.

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