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Micro-destructive mapping of the salt crystallization front in limestone

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ABSTRACT

Salt crystallization is widely recognized as one of the most damaging factors affecting stone monuments and buildings. Conservation of structures suffering from weathering due to salt crystallization can be immensely expensive and time-consuming. The assessment of salt-laden buildings alone is often challenging and costly in its own right. In this paper, the Drilling Resistance Measurement System (DRMS) and the scratch tool are evaluated for their ability to map salt crystallization in natural building stone. The laboratory results indicate that the two aforementioned micro-destructive techniques are indeed capable of detecting the location of the salt crystallization front in limestone impregnated with sodium sulfate. This is facilitated due to the increased resistances recorded during drilling and scratching in areas where pore clogging due to salt crystallization exists. The DRMS was further successfully employed in-situ on masonry exhibiting the effects of salt decay. The successful application of both micro-destructive techniques in the laboratory, and of the DRMS alone in-situ, suggests that these may potentially be used to detect subflorescence before it becomes damaging.

1. Introduction

It is widely accepted that soluble salts may cause extensive permanent damage to porous building materials, such as stone and brick. In most cases, it is inevitable that structures built with such materials will become contaminated with salts. This applies particularly to structures of cultural and architectural significance built without damp-proof courses and other moisture barriers.

Salts may accumulate in natural stone over time in several ways. Some of the primary sources of salt contamination include capillary uptake of ground and surface water, or absorption of salt-laden precipitation or moisture from the surrounding atmosphere. Salts may also appear as a result of the interaction of aerosol pollutants with certain minerals, as in the case of gypsum (Espinoza-Marzal and Scherer, 2010; Halsey et al., 1995), or may originate from mortar in contact with stone, or even from the stone itself (e.g. Lopez-Arce et al., 2009; McKinley et al., 2001). Other important sources of salts include biological activity (e.g. Gómez-Heras et al., 2004) and polychrome, cleaning and conservation treatments (e.g. Přikryl et al., 2004, 2011). In the presence of moisture, salts are mobilized in solution and may therefore enter the porous network of a stone. Upon drying and subsequent loss of water through evaporation, or indeed due to changes to pore salt solution solubility during cooling, salts may crystallize.

Salt crystallization may occur either within the pores of a material, as damaging subflorescence, or on its surface, as more innocuous efflorescence. The precise location at which salts crystallize is highly dependent on the rate of drying, the building material and the salt itself (e.g. Espinoza-Marzal and Scherer, 2010; Ioannou and Hoff, 2008; Benavente et al, 2004). Subflorescence (or cryptoflorescence) usually leads to pore clogging (Espinoza-Marzal and Scherer, 2010). However, until a relatively large proportion of pores essentially become filled with salt, it is suggested that subflorescence is unlikely to cause permanent damage to a building material (Scherer, 1999). Permanent damage may develop at later stages, when salt crystals, or indeed aggregates of crystals, large enough to fill pores, begin to exert pressure on the pore walls. If this pressure exceeds the tensile strength of the material, cracking can occur (Scherer, 2004). Therefore, initial changes to the pore structure of a material, such as pore clogging, may be an important primary indication that could be used to detect salt crystallization damage before it actually takes place. Pore clogging should be detectable if the methods employed to monitor it measure at the correct scale.

There are several examples of experimental work in the literature employing non-destructive methods to map both solution transport and salt crystallization within porous materials at or near the size scale of interest. For example, Goethals et al. (2009) and Derluyn et al. (2008) have used X-ray radiography for moisture transport imaging in porous materials and for model validation. Ioannou et al. (2005) utilized synchrotron X-ray diffraction to map the location of sodium sulfate crystallization in limestone in one dimension, and stated that the methodology could be adjusted slightly to provide two- or even three-dimensional distribution data. X-ray computed tomography (X-ray CT) and micro-tomography (μCT) are other methods which produce three-dimensional information and have been employed by several researchers in experiments designed to monitor salt weathering (Derluyn

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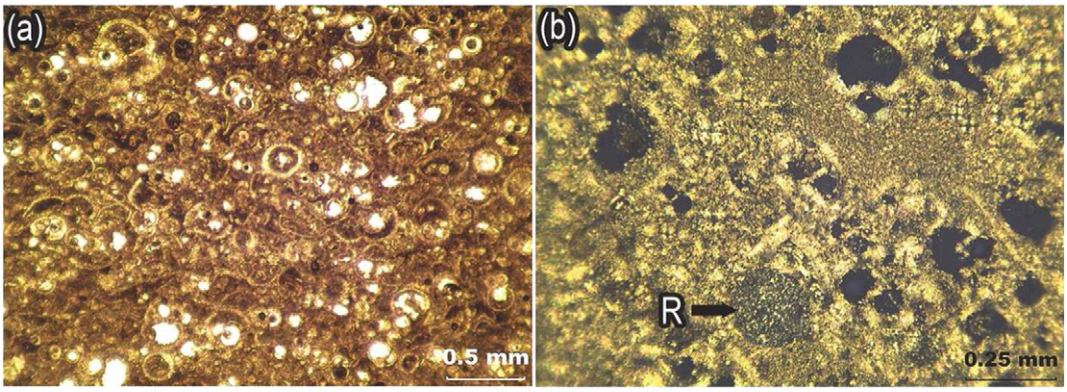

Fig. 1. Thin section of Lympia stone showing (a) abundant foraminifera fossils (plane polarized light) and (b) a rare radiolarian (R) (crossed polars).

et al., 2014; Cnudde and Jacobs, 2004), for the visualization of various conservation treatments within the porous network of natural stone (Cnudde et al., 2009) and for the determination of changes caused by consolidation to the hydric properties of sandstones (Ruiz de Argandoña et al., 2009). Nuclear magnetic resonance (NMR) imaging has also been employed by several researchers. Rijniers et al. (2005), for example, used NMR to monitor changes in salt solution properties at the pore scale during cooling experiments.

The aforementioned non-destructive methods are able to provide a plethora of one-, two- or even three-dimensional information, at high resolution, about the pore system, during or after salt crystallization. However, to the best of the authors' knowledge, none of them have been successfully implemented in-situ, at a scale capable of mapping the location of salts. Furthermore, most of these methods are not easily accessible and require extensive training of the users. Finally, their application usually bears significant cost and requires sampling (e.g. removal of cores or other samples). This indicates a need to develop a readily accessible method to assess the location and extent of salt crystallization, both in-situ and in the laboratory. Such a method should also minimize destructive sampling.

In this paper, two micro-destructive techniques designed to measure variations in the resistance to cutting through a material are applied as salt front mapping tools in natural stone. The term micro-destructive implies that both methods do not require large samples and destroy only very small portions of the test material. The techniques employed are the portable Drilling Resistance Measurement System (DRMS), or micro-drilling technique, and the scratch tool. Both methods have already been proven useful for assessing the mechanical properties of building materials either in the lab or, in the case of the DRMS, in-situ (e.g. Theodoridou et al., 2015; De Clercq et al., 2014; Richard et al., 2012; Fernandes and Lourenço, 2007; Dagrain and Germay, 2006; Tiano, 2001). Furthermore, they provide comparable results due to their similar mode of operation; this is based on cutting a material either by linear scratching or rotational drilling and subsequently recording its respective resistance (Theodoridou et al., 2015; Dagrain et al., 2010a).

2. Materials and methods

2.1. Materials

A limestone from Cyprus, popularly named Lympia stone due to its provenance, was chosen for this study. This stone has been used traditionally and contemporarily for building and decorative purposes in many locations across the island. Nevertheless, it is quite susceptible to salt weathering, as shown in standardized tests carried out in accordance with EN 12370 (Modestou et al., 2015).

Lympia stone (Fig. 1) is a massive chalk dating back to the Eocene (Bear, 1963). It is a packstone, primarily composed of globigerina foraminifera with a few rare silica radiolaria (Wilson and Ingham, 1959); therefore its mineral composition is very homogeneous. Porosity visible in thin section is mainly intragranular (within foraminifer tests) indicating that the pore size is at least partially controlled by the foraminifera test size. Lympia stone is well known locally for its bright white color and lack of macrofossils or sedimentary structures (Kähler and Stow, 1998).

Mineralogical analysis using powder X-ray diffraction (PXRD) indicated that the Lympia stone used in this study is nearly exclusively calcitic with traces of quartz. For the purposes of the current research, the physico-mechanical characteristics of freshly quarried Lympia stone were determined using standardized tests and mercury intrusion porosimetry (MIP). The results are summarized in Table 1 (Modestou et al., 2015).

2.2. Description of micro-destructive experimental techniques

The two micro-destructive techniques applied in this study to map the position of the crystallization front (i.e. the DRMS and the scratch tool) were designed to measure variations in the resistance of materials to cutting. Originally developed for use in petroleum engineering, the latter device has also recently been used (e.g. Theodoridou et al., 2015; Richard et al., 2012; Dagrain and Germay, 2006) to investigate material properties for various purposes, including conservation (e.g., Campbell et al., 2011; Dagrain et al., 2010b). Its mode of operation relies on the incremental formation of a groove on the surface of the test sample using a diamond cutter. The force necessary to scratch the material at any given point along the groove is continuously recorded. In principle, the resistance of the material to cutting is related to properties such as the intrinsic specific energy, which is in turn directly proportional to the classical uniaxial compressive strength (Dagrain et al.,

Table 1
Physico-mechanical properties of Lympia stone.

Mercury porosimetry (three sample average)		Standardized test results	
Apparent density (g/cm^3)	1.55	Apparent density[a] (g/cm^3)	1.54
Skeletal or solid density (g/cm^3)	2.70	Real density[a] (g/cm^3)	2.72
Open porosity (%)	42.6	Open porosity[a] (%)	42.8
Average pore opening size (μm)	0.227	Total porosity[a] (%)	43.0
		Capillary absorption coefficient[b] (g/m^{2}s$^{1/2}$)	140.5
		Compressive strength[c] (MPa)	30
		Flexural strength[d] (MPa)	5.8
		Resistance to salt crystallization[e] (wt.% loss)	10.7

Testing in accordance with European standards: [a]EN (1936), [b]EN (1925), [c]EN (1926), [d]EN, 12372, and [e]EN, 12370.