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Neutron radiography as a tool for assessing penetration depth and distribution of a phosphate consolidant for limestone

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HIGHLIGHTS

- Consolidants are applied to re-establish cohesion among grains in weathered stones.
- Neutron radiography (NR) was used to study distribution of a phosphate consolidant.
- Three application methods were compared (brushing, poulticing, partial immersion).
- Homogeneity of the consolidant distribution can be reliably evaluated by NR.
- Penetration depth can be reliably evaluated by combination of NR with FT-IR and XRD.

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ABSTRACT

Neutron radiography was used to determine the penetration depth and the homogeneity of distribution of an innovative inorganic consolidant, based on formation of hydroxyapatite. The consolidant was applied to a porous limestone by three alternative methods (brushing, poultice, partial immersion). Neutron radiography was complemented by XRD, FT-IR and SEM/EDS, which provide information also on mineralogical composition and morphology of the new phases. Neutron radiography proved to be a powerful tool to determine the presence of hydrogen-rich hydroxyapatite and to evaluate the homogeneity of its distribution in the substrate. Nonetheless, combination with other techniques is necessary to reliably assess its penetration depth.

1. Introduction

Stone consolidants are products aimed at penetrating into weathered stone and restoring its cohesion and mechanical properties [1–4]. Penetration depth and ability to distribute homogeneously in the substrate are among the most important parameters determining the efficacy and the compatibility of a stone consolidant. In fact, a suitable penetration depth is necessary to reach the unweathered substrate and to bind it to the consolidated portion. Similar properties in the consolidated and non-consolidated parts are desired, to prevent formation of hard crusts, weak areas or abrupt changes with depth, which could result in damage, detachments and/or scaling [1–7].

For these reasons, numerous characterization techniques have been proposed for evaluating the penetration of consolidants into porous substrates. The obtained data can point out the presence of a consolidant in terms of (i) alterations in microstructure (e.g., pore occlusion detected by mercury intrusion porosimetry, MIP); (ii) alterations in physical properties (e.g., contact angle, water

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uptake, drying rate, water vapor permeability); (iii) mechanical properties (e.g., micro-drilling resistance (MDR), resistance to abrasion, ultrasound wave velocity) or (iv) presence and distribution of new phases crystallized after treatment (e.g., detected by scanning electron microscopy (SEM) or optical microscopy, X-rays diffraction (XRD), Fourier Transform infrared spectroscopy (FT-IR), Raman spectroscopy, visible spectrometry) [5,8–14]. However, at present the combination of these techniques does not allow to fully define the penetration profile, i.e. the depth and the gradient of penetration of the consolidant and the areas where the product does exert its consolidating action. In fact, many of these techniques have the severe limitation of being punctual [13], so that numerous analyses need to be repeated to track the presence of a consolidant along a profile. Therefore, having a complete representation of the consolidant distribution across the whole volume of a sample becomes virtually impossible. In addition, the more heterogeneous the material to be examined, the more important this limitation is, as the number of analyses needed to have a somehow reliable representation also increases.

Thanks to their ability to provide information about significant volumes of material and thanks to their non-destructiveness, radiation imaging techniques (e.g., X-ray and neutron radiography and tomography) are gaining increasing attention in the field of materials science for cultural heritage conservation [5,6,9,13,15–25].

X-ray radiography and tomography have been proposed to evaluate porosity [16], weathering [17,18], water uptake [17,18], uptake and distribution of consolidants and water repellents [5,6,8–10,13,19,20] inside different stones and ceramic substrates. To obtain a reliable evaluation of the uptake and distribution of consolidants by X-ray techniques, a sufficient contrast is needed, which normally requires the use of contrast agents [10]. However, the distribution of these markers in the porous substrate might differ from that of the consolidant itself, especially when stone has small pores and high specific surface, so that stone might act as a sort of a chromatography column [10].

While X-rays interact with the electron cloud of atoms, neutrons are able to penetrate more deeply and interact with the nuclei of atoms, hence their interaction forces depend on the isotope of the element [21]. Thanks to the different attenuation coefficient of the various elements, neutron radiography can visualize materials structures hardly distinguishable by X-rays [6]. In particular, neutrons have high sensitivity to light elements and isotopes (while they are insensitive to heavier elements), hence they have a strong attenuation by hydrogen, mainly by scattering [5,6,21–23]. Because of the higher attenuation by hydrogen compared to X-rays, neutron-based techniques are a powerful tool for visualizing water and, more in general, hydrogen-rich fluids in porous media, including stones [21]. In addition, the visualization of hardened consolidants inside stone is possible even after drying and/or polymerization, as a strong contrast between treated and untreated regions can be achieved without the need for doping [5], because both calcite and quartz contain elements with weak-absorbing nuclei [24]. For this reason, neutron imaging has been proposed for studying the distribution of consolidants in different stones (e.g., limestone and sandstone), before and after polymerization/curing [5,6,22,25]. So far, applications have been mainly focused on organic consolidants (e.g., organosilicon, acrylic, epoxy consolidants) and ethyl silicate, but, recently, neutron imaging has been successfully proposed for investigating the distribution of an inorganic oxalate-based consolidant in limestone [13].

In this study, we investigate the use of neutron radiography to evaluate the penetration depth and the distribution in a porous limestone of new crystalline phases, formed after stone treatment with a di-ammonium hydrogen phosphate (DAP) solution. The DAP-based treatment is attracting growing interest for protection and consolidation of carbonate stones, due to the great chemical-physical affinity with the substrate [26–38]. Briefly, calcium phosphate (CaP) phases, containing hydrogen, are formed by impregnating the stone with an aqueous solution of di-ammonium hydrogen phosphate (DAP – $(NH_4)_2HPO_4$); the DAP solution reacts with the calcium ions deriving either from the substrate [26,27,33–40] or from an external source [29,41,42], forming CaP phases. Together with hydroxyapatite (HAP – $Ca_{10}(PO_4)_6(OH)_2$), other CaP phases might form, depending on the treating conditions and on the substrate composition and contamination [26,40–45]. The penetration depth of the treatment has been investigated by different methods so far: (i) by mapping the distribution of P by SEM/EDS and the formation of CaP phases by XRPD, FT-IR and Raman; (ii) by determining the presence of new phases and PO_4^{3-} ions in the liquid solution inside stone pores by ion chromatography; (iii) by measuring the variation with depth of parameters indicative of the consolidant presence (e.g., porosity, resistance to abrasion) [35–38]. However, by these techniques only partial representations of CaP phases distribution across the whole volume of the samples could be achieved, hence in this study a more complete evaluation was undertaken by neutron radiography.

A further aspect investigated in this study is the influence of the method used to apply the phosphate solution on the penetration depth and the distribution of the consolidating solution, because previous studies have pointed out that the amount of CaP phases that form and their distribution inside the substrate significantly depend on the application procedure [35,38]. Here, we compared three application methods (namely, brushing, poulticing and partial immersion), which were found to lead to different distribution of the liquid consolidant during impregnation and drying and, hence, to formation of different amounts of CaP phases [35]. All tests were carried out at the end of the consolidation process, after crystallization of the new phases.

To evaluate the potentialities and the limitations of neutron radiography to study the distribution and the penetration depth of the DAP-treatment (and virtually inorganic stone consolidants in general), neutron radiography was complemented with, FT-IR, XRPD and SEM/EDS.

2. Materials and methods

2.1. Stone

Tests were carried out on Globigerina limestone (GL), an organogenic stone with high porosity (~40%), containing mainly calcite (~93%) and small amounts of quartz and/or clays. This stone is severely affected by weathering in the field, mainly in the form of alveolarization and pulverization due to salt decay, so that finding a suitable material for its consolidation is an urgent task [8,46]. For the experimental tests, cubes with 5 cm side were cut from one same quarry slab, to mitigate the effects of stone heterogeneity. Following a previously developed procedure [47], prior to consolidation samples were artificially pre-weathered by heating in an oven at 400 °C for 1 h. In this way, samples undergo uniform weathering throughout their entire volume, mainly in the form of nano-cracks formed between calcite grains [48,49]. Although not exactly corresponding to the weathering phenomena mainly affecting this lithotype in the field (i.e., alveolarization and pulverization), so-produced decayed samples exhibit decreases in mechanical properties and increase in water absorption that resemble those of naturally weathered stone [47–49].

After consolidant application, the cubes were wet sawn to obtain prisms suitable for neutron radiography, having 2.5 × 2.5 cm^2 frontal size and 1 cm thickness, as illustrated in Fig. 1. One of the prisms was used for neutron radiography, FT-IR and XRPD and another one for SEM/EDS.

2.2. Treating procedures

All samples were treated by a 3 M solution of DAP (Sigma-Aldrich, assay ≥ 98%, reagent grade) in deionized water, but treatments were applied following 3 different procedures: brushing, poulticing and partial immersion. For all treating procedures, the DAP solution was applied onto one face parallel to the bedding planes and it was let penetrate into the samples perpendicular to the planes. This condition was selected because all the cubic samples had been obtained from a single slab sawn parallel to the bedding planes, so in this way it was possible to ensure that exactly the same direction was tested in all cases.