Journal of Cultural Heritage 19 (2016) 463–466

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Original article

Investigation of ammonium oxalate diffusion in carbonatic substrates by neutron tomography

Claudia Conti [a,*], Chiara Colombo [a], Giulia Festa [b], Jan Hovind [c], Enrico Perelli Cippo [d], Elena Possenti [a], Marco Realini [a]

[a] Consiglio Nazionale delle Ricerche, Istituto per la Conservazione e la Valorizzazione dei Beni Culturali (ICVBC), Via Cozzi 53, 20125 Milano, Italy
[b] Università degli Studi di Roma Tor Vergata, Dipartimento di Fisica, Via della Ricerca Scientifica, 1, 00133 Roma, Italy
[c] Paul Scherrer Institut, Spallation Neutron Source Division, Neutron Imaging and Activation Group, 5232 Villigen PSI, Switzerland
[d] Consiglio Nazionale delle Ricerche, Istituto di Fisica del Plasma (IFP), Via Cozzi 53, 20125 Milano, Italy

ARTICLE INFO

Article history:
Received 15 September 2015
Accepted 4 December 2015
Available online 11 January 2016

Keywords:
Neutron tomography
Stone materials
Product diffusion
Ammonium oxalate

ABSTRACT

The diffusion of the organic-polymeric or inorganic-mineral products inside a decayed porous material is a key factor for the evaluation of the efficacy of a conservation treatment. Here, we present a study aimed at the evaluation of neutron imaging as a non-destructive tool for the investigation of stones treated with ammonium oxalate, an inorganic-mineral product. Neutron tomography gained an overview of products diffusion and deep insight into the interaction between product and crystalline matrix.

1. Introduction

For several years, the conservation scientists have been working to find the most suitable methods to evaluate, in a direct way, the diffusion of a treatment in a porous material. Several analytical techniques have been proposed as staining tests, micro-ATR (attenuated total reflection) spectroscopy, scanning electron microscopy coupled with energy dispersive X-ray spectrometry, X-ray photoelectron spectroscopy, micro-Raman mapping and drilling resistance [1–6].

Even though interesting results have been achieved, these techniques are destructive and they are unable to provide an overview of the treatment diffusion inside the sample in its entirety.

In order to make up for this lack of information and to find a non-destructive method, an alternative solution is here proposed: neutron imaging, an emerging method for cultural heritage investigation, which provides complementary information to the corresponding X-Ray techniques. Due to their charge neutrality, neutrons can penetrate thick samples showing hidden details past outer corrosion and/or buried layers into bulky objects. Neutrons interact significantly with light elements, and in particular they are mostly scattered by hydrogen, giving detectable image contrast. Such circumstance candidates the neutron imaging as a possible tool to determine the water absorption and distribution inside the material, identify the content and the penetration depth of hydrogen-rich conservation products (as in the case of organic treatment) inside porous stone samples or other materials such as bricks or wood [7–11].

To the best of our knowledge, no findings exist in the literature concerning neutron imaging applied to the detection of the diffusion of fully inorganic treatments, although there is a strong increase of their employ in the conservation works, while it has been used for the investigation of ethyl silicate distribution [7].

Therefore, the aim of this study is to extend neutron imaging to the study of inorganic-mineral conservation treatments, obtaining the overview of ammonium oxalate $[(NH_4)_2(C_2O_4)]$ diffusion inside a building stone; the occurrence of hydrogen in the composition of the newly formed minerals supports the hypothesis of a different neutron absorption of the treated portions compared with the untreated ones, made out of a stone almost completely wanting in hydrogen.

The experiments have been carried out at the Paul Scherrer Institut (PSI) spallation neutron source (Switzerland).

2. Materials

Neutron tomographies were carried out on Noto stone specimens (5 × 5 × 1 cm) treated with ammonium oxalate $(NH_4)_2C_2O_4$, an inorganic-mineral product.

* Corresponding author. Tel.: +39 2 66 17 33 37; fax: +39 2 66 17 32 96.
E-mail address: c.conti@icvbc.cnr.it (C. Conti).

http://dx.doi.org/10.1016/j.culher.2015.12.005
1296-2074/

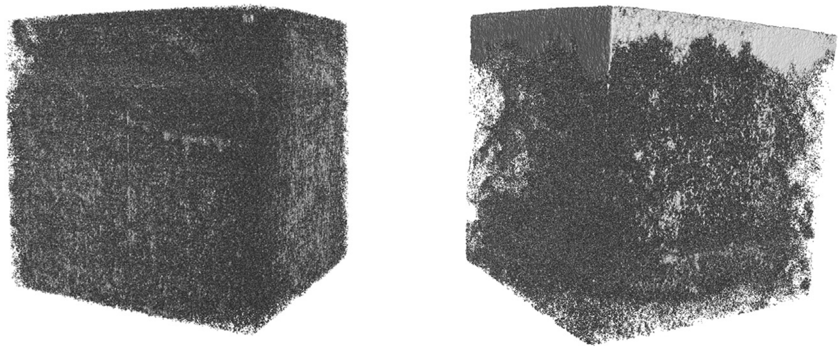

Fig. 1. Neutron tomographies acquired on S1 specimen before (left) and after (right) the ammonium oxalate treatment by capillarity. In this 3D rendering, hydrogen-rich voxels are shown as opaque gray-coloured. Note the occurrence of such voxels in the upper part of the specimen, showing the presence of the hydrogen-rich whewellite phase.

Noto stone is a calcarenite (mainly consisting of calcite [$CaCO_3$]) employed for a long time as construction material for historical buildings in the eastern Sicily. Its porosity ranges from 33% to 35% and it is extremely heterogeneous in terms of distribution and shape of the pores. Ammonium oxalate has been widely used for several years in order to preserve the surfaces of carbonatic porous materials. This compound reacts with calcium carbonate ($CaCO_3$) of the substrate to induce the formation of the two most common calcium oxalate phases, the monohydrate whewellite ($CaC_2O_4 \cdot H_2O$) and the dihydrate weddellite [$CaC_2O_4 \cdot (2+x)H_2O$].

Here, we report on the tomographies carried out on two specimens, chosen as representative of two common methods of treatment: the specimen called S1 was analysed before and after the capillarity treatment (24 hours), while the specimen called S2 was analysed after a poultice treatment (composed by cellulose paste soaked with the solution) for 2 hours on a single surface. In both cases, ammonium oxalate solution 5% w/w in water was used.

3. Analysis methods

Neutron tomography is an analysis technique based on the reconstruction of slices (i.e. 2D maps of the insight of a sample) by the application of a suitable algorithm to neutron projections (i.e. radiographies of the sample obtained with neutrons as an illuminating probe). Details on the technique may be found elsewhere [12]; in this paper, we just mention some basic concepts:

- neutrons interact with matter via absorption or scattering; in both cases, they are removed from the original beam. When a neutron beam passes through a sample, it is thus attenuated by an extent due to the nature of the elements in the sample itself. If the transmitted beam is then collected by a suitable neutron (2D) detector, the resulting image (projection) shows more or less dark or light areas due to the neutron attenuation through matter;
- a large number of projections (typically some hundreds) at different angles may be collected and a retroprojection algorithm (usually the filtered-back projection algorithm [13]) is applied to the whole series;
- the result of the application of the algorithm is a 3D map of the insight of the sample in which the colour (gray value) of every voxel (i.e. the minimum visible volume of the image) is a measure of the local attenuation coefficient in this voxel;
- such a map is usually presented as slices of the internal volume; however, thank to suitable visualisation packages, the slices can be stacked over into a full 3D representation. Both 2D slices and 3D representations are shown into this paper as an aid for the interpretation of data.

The experiments were carried out at the Neutron Transmission Radiography (NEUTRA) beam line of the SINQ spallation neutron source at PSI (Paul Scherrer Institut, Villigen, Switzerland). Tomographical measurements were acquired with a neutron flux of 1.3×10^7 cm^2/s, L/D collimation ratio of 350, field of view of 121 mm × 102 mm and pixel size 94 μm. The source to detector and source to object distances were 10.3 m and 10.25 m, respectively. The detector used was a 50 μm Li/ZnS neutron-sensitive scintillator, coupled to an Andor Neo sCMOS camera via a suitable optical system. For every tomographic measurement, a total of 360 projections were acquired, with 13 s exposition time each.

The reconstruction of tomographies from the projections was made with the Octopus package [14]. Images were processed through the ImageJ package and VGstudio software: ImageJ [15] is an image processing program used to measure distances in the image, to reduce to a binary image with Otsu's method and to perform functions, such as contrast manipulation, background subtraction and signal to noise ratio improvement for the enhancement of image quality.

The VGStudio MAX software [16] is an image visualization tool used for the visualization and analysis of CT data. The software was used to obtain three-dimensional renderings from the tomographies of the samples, distinguishing treated areas (lighter zone) and untreated areas (darker zone) thanks to differences in terms of neutron absorption coefficients of the consolidant and the matrix (see further for details).

4. Results and discussion

To investigate the diffusion of ammonium oxalate into the Noto stone, neutron tomographies of S1 specimen have been performed before and after the ammonium oxalate treatment by capillarity. Neutron attenuation of the treated specimen is dramatically different compared with the untreated one, as shown in Fig. 1. The interaction between neutron and hydrogen of whewellite, the most stable hydrated mineralogical phase of calcium oxalate [17], allows to exactly locate the treatment, both in the surface and inside the crystalline matrix: the lighter, opaque areas, observed in the tomography carried out after the treatment, correspond to the calcium oxalate distribution, while the darker zones are ascribed to the stone not involved in the reaction of ammonium oxalate with calcite. The tomography after the treatment shows that the edges of the stone reacted more diffusely than the internal volume, as a consequence of the capillarity effect. Also from the elaboration of the slices, it is possible to gain a deep insight into the treatment distribution. In Fig. 2, a selection of the most meaningful horizontal slices (parallel to the treated surface) are shown, comparing the same slice (namely the same depth into the specimen volume) before and after the treatment. Calcium oxalate is distributed in