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Investigations of stone consolidants by neutron imaging

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ABSTRACT

The chemical preservation and structural reintegration of natural stones applied in historical buildings is carried out by the use of different stone strengtheners. As these agents contain hydrogen, they offer good properties for neutron imaging. The main interest in the restoration process is the development of a suitable stone consolidant. In cooperation with the St. Stephans Cathedral and the geologists at Vienna University of Technology, we are investigating the penetration depth and distribution of different stone consolidants. These studies are being carried out with different stone samples, mostly porous natural building stones, limestones and sandstones. The two strengtheners used in this study are ethyl silicate ester (Wacker OH100) and dissolved polymethylmetacrylate (PMMA, Paraloid B72). Neutron radiography and neutron tomography can be used successfully to visualize the distribution of consolidants both in two and three dimensions.

1. Introduction

A stone consolidant[1] should have sufficient stability and penetration so that the mechanical properties of the stone will be improved. The stone surface must not be sealed to ensure that the weathered stones are permeable to any existing humidity in the fabric as well as protected against further deterioration [1]. One of the properties that a consolidant must have is the ability to penetrate. Visualization of the penetration depth and distribution inside the stone is very helpful for conservators. Neutron imaging has been found to be very useful due to its high sensitivity and detection of hydrogen [2–4]. Neutron transmission analysis is suitable for sandstones because they are made of quartz (SiO_2) or calcite ($CaCO_3$), both of which are weak-absorbing nuclei. In the case of weathered stones long after strengthening as the solvent evaporates, neutron attenuation decreases. Neutron attenuation is therefore dominated by the hydrogen content.

2. The consolidants

In this study, two consolidants have been used—silica ester (Wacker OH100) [5] and acrylic resin (Paraloid B72) [6]. These two strengthener types are very common in conservation. Silica ester is mostly used for the conservation of sandstone, whereas restorers use acrylic resin primarily for the conservation of marble or granite in Austria. In other European countries the use of Paraloid B72 for conservation of sandstones is also common. Silica ester is inorganic while Paraloid B72 is an organic consolidant. There is a reluctance to use organic consolidants because acrylic resins are preferred by bacteria and other micro-organisms. There is a danger of growing and feeding micro-organisms. But if the change in physical properties is considered, the change of diffusion, strength, etc., Paraloid B72 maybe preferred in a low concentration as it fixes the particles together like glue, while silica ester fills the pores, reduces water absorption and delays the dry out behaviour.

3. Sample characterization and treatment

Characterization of the samples used is summarized in Table 1 and their properties are presented in Table 2. Thin sections of samples are presented in Figs. 1a–c.

4. Experimental procedure and results

Neutron radiography (NR) and neutron tomography (NT) were performed. All samples have been strengthened in the laboratory by the capillarity method. The stone was placed in a glass bath containing the strengthener. After strengthening, the stone was removed from the bath and systematic NR and NT experiments were performed at the neutron imaging facility at

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[1] Consolidant: Serving to unite or consolidate; having the quality of consolidating or making firm. These are chemicals used to consolidate weathered stones. An explanation may be read in The New Encyclopaedia Britannica in the article "Sculpture restoration" under the heading "Art conservation and restoration—Stone sculpture" on page 90, ISBN 0852297874, 9780852297872.

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Table 1
Characterization of the samples.

Sample	Description	Treatment
Sample 1 (S1)	Cuboid with dimensions 120 mm × 51 mm × 51 mm. Calcareous arenite from Aflenz, Austria. Fresh sample from the quarry	Strengthened with silica ester on one side and Paraloid B72 5% on the other side
Sample 2 (S2)	Cylindric with diameter 47 mm, height 200 mm Calcareous arenite, with large pores homogeneously distributed. From St. Margarethen, Austria	Strengthened with silica ester on one side and Paraloid B72 5% on the other side
Sample 3 (S3)	Cylindric, diameter 47 mm and height 180 mm. Quartz arenite from the Flyschzone near Vienna; a strongly weathered sample from a building stone of the Cartusian Monastry in Mauerbach, Austria. Very homogeneous and fine pored	Strengthened with Paraloid B72 1%

Table 2
General physical properties of these stones.

Properties	S1—calcareous arenite from Aflenz (Styria, Austria)	S2—calcareous arenite from St. Margarethen (Burgenland, Austria)	S3—quartz arenite from the Flyschzone near Vienna (Austria)
Compressive strength—dry (N/mm^2)	9–16.5	49.0 (42.6–56.1)	70
Apparent density (g/cm^3)	1.75–1.95	2.08 (1.97–2.26)	2.59 (2.2–2.64) in correlation with the state of weathering
Water adsorption (M%)	12–16	7.9 (3.6–10.2)	4 (3–7)

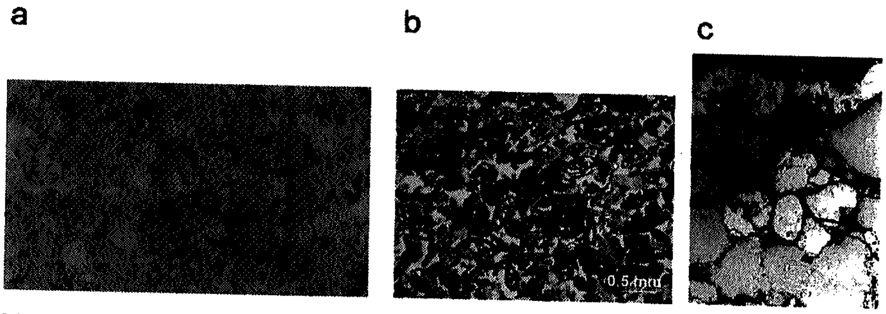

Fig. 1. (a) S1—thin section of the highly porous calcareous arenite from Aflenz (blue stained resin) consisting of debris from calcareous red algae and foraminifers. (Length of the picture is about 10 mm.) (b) S2—thin section of the highly porous calcareous arenite from St. Margarethen (blue stained resin) consisting of debris from calcareous red algae, echinoderms and foraminifers. (c) Thin section of weathered quartz arenite from Lower Austria (Mauerbach) with a layer of crystallised gypsum on the surface (top of the picture); scale about 3 × 5 mm^2 (crossed nicols).

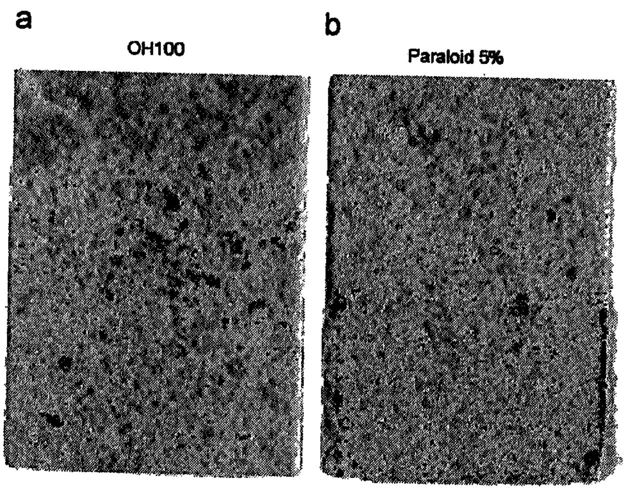

Fig. 2. NT of S1 with different consolidants. (a) A homogeneous distribution of OH100. The dark regions represent the strengthener. In (b) there is a surface effect. This NT was performed 1 month after strengthening when the consolidants had stabilized. The neutron attenuation was higher in the initial NT measurements and lower afterwards, which is due to the evaporation of the solvent over time. A 400 μm ^{6}Li based scintillator and a CCD camera were used. The exposure time was 40 s per image and the number of projections was 180.

Atomic Institute (ATI) in Vienna [7]. Later on neutron imaging was performed at a higher flux at ANTARES, FRM 2 in Munich, Germany [8,9].

4.1. Comparison of ethyl silicate and Paraloid B72 5% measured at ATI

This experiment was performed with S1. The sample was strengthened with ethyl silicate on one side and Paraloid B72 5% on the other side. From the results obtained, it was understood that the distribution of the two strengtheners is different. In the case of Paraloid B72 5% a high unwanted concentration of the strengthener on the surface was visible (Fig. 2). This had to be investigated further. So experiments were planned at ANTARES, where neutron imaging was performed with cold neutrons at a high flux. Hence a higher sensitivity and better resolution was expected.

4.2. Comparison of ethyl silicate and paraloid b72 5% measured at ANTARES

S2 was strengthened with the two different strengtheners and then the NT measurements were made. These measurements were made with a commercially available scintillator (NE 426) coupled to a CCD camera. In this case the exposure time per image was 9 s and the L/D ratio used was 800. The total number of projections was 400.

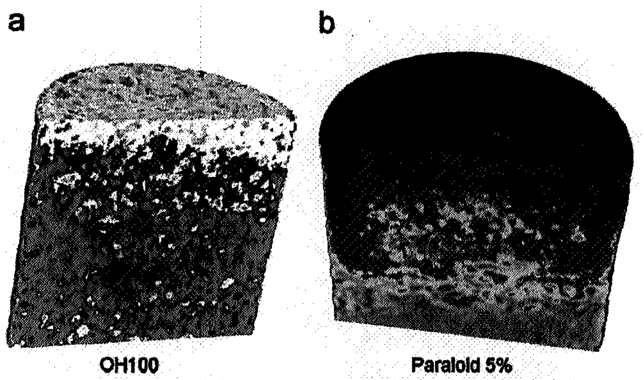

Fig. 3. (a) NT-bottom part of the stone strengthened with OH100. The NT measurement shows that OH100 is homogeneously distributed. (b) NT of the top part of the stone strengthened with paraloid B72 5%. It is well seen that the distribution is different from the first case. The grey region shows low density of strengthener and the dark segments represent high-density areas. These results are very interesting for geologists and conservators.

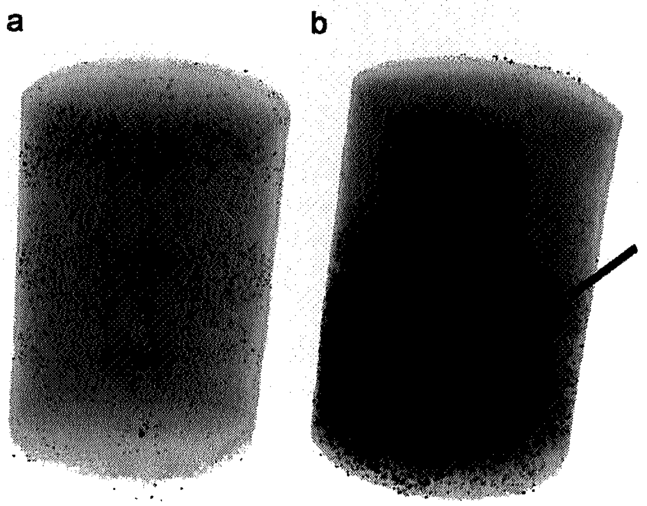

Fig. 4. NT of S3. (a) NT before treatment, the dark segments represent humidity or mica. (b) NT after treatment with Paraloid B72 1%. In (b) the arrows indicate layers where a lower concentration of the solution is visible. NT of the stone soon after strengthening is shown. A low concentration of the dark segments could be a result of sedimentary layering in more porous weathered regions. A rather homogeneous distribution has been obtained. On reducing the concentration, there is no negative surface effect visible.

On the surface of the stone there is a high-density distribution of paraloid. With the help of these measurements this effect can be clearly seen. It has been shown that the distribution of the two strengtheners in the same stone is different. Fig. 3b shows that the pores at the surface are completely filled, which is very bad as humidity cannot leave the stone through the dense surface. A stone needs to "breathe". In other words, the stone should remain permeable to water vapour and liquid, in order to avoid any build up of moisture (and consequent shear stresses) at the interface between the treated zone and the untreated stone below. After these results it was suggested that the concentration of Paraloid B72 should be reduced. Further experiments were performed with Paraloid B72 in 1% concentration.

4.3. Experiments with reduced concentration of Paraloid B72 on real weathered samples

Several weathered samples were investigated. The most interesting results have been discussed for S3. These measurements were performed at ATI. The concentration of the consolidant was now reduced from 5% to 1% (Fig. 4).

4.4. Time series experiments with different strengtheners

Time series NR images were made during the strengthening process at ATI. An image was acquired every minute approximately. The line profiles obtained from these images may be used to determine the speed and depth of penetration of the strengtheners (Fig. 5). For small absorption and scattering the neutron attenuation can be approximated by the exponential attenuation law. Neutron transmissions due to single and multiple scattering are only slightly enhanced (<10%) at the tomography position. Using simple exponential attenuation, we get the transmission

$$T \cong e^{-\Sigma t} \tag{1}$$

Σ denotes the total macroscopic neutron cross-section and t the path length through the sample. Using Eq. (1) Σ can be determined from the NR image. This value was obtained for the strengthened stone and then the density of hydrogen ρ_H was found as follows:

$$\rho_H = \frac{\Sigma_H A_H}{\sigma_H N_A} \frac{\bar{\lambda}}{\lambda_{th}} \tag{2}$$

where A_H is the atomic weight and σ_H the microscopic cross-section of hydrogen at thermal wavelength $\lambda_{th} = 0.18$ nm. N_A is the Avogadro number. By transmission tomography the volume distribution of total cross-section $\Sigma(x, y, z)$ can be visualized, which allows us to distinguish volume effects from surface effects.

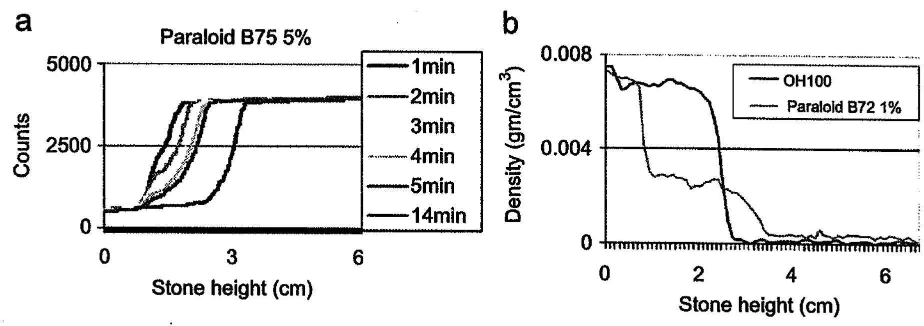

Fig. 5. (a) Line profile taken vertically along the centre of NR images of the time series. (b) Density distributions of two different strengtheners along the height of the stone. The stones were strengthened to a height of approximately 3 cm. The higher density at the bottom of the stone is due to the liquid in the bath.

5. Summary and outlook

Different penetrations and distributions of the strengtheners have been found with NR and NT. The results show clearly that the penetration of different stone consolidants depends on the physical properties of the stones, pore size, grain size and state of weathering. Paraloid B72 5% is at a very high concentration for successful consolidation. The concentration has to be reduced. Neutron imaging techniques could become a very useful tool to evaluate conservation and restoration in combination with classical methods. NT is non-destructive and complete, yielding a 3D mapping of the consolidants.

Acknowledgements

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