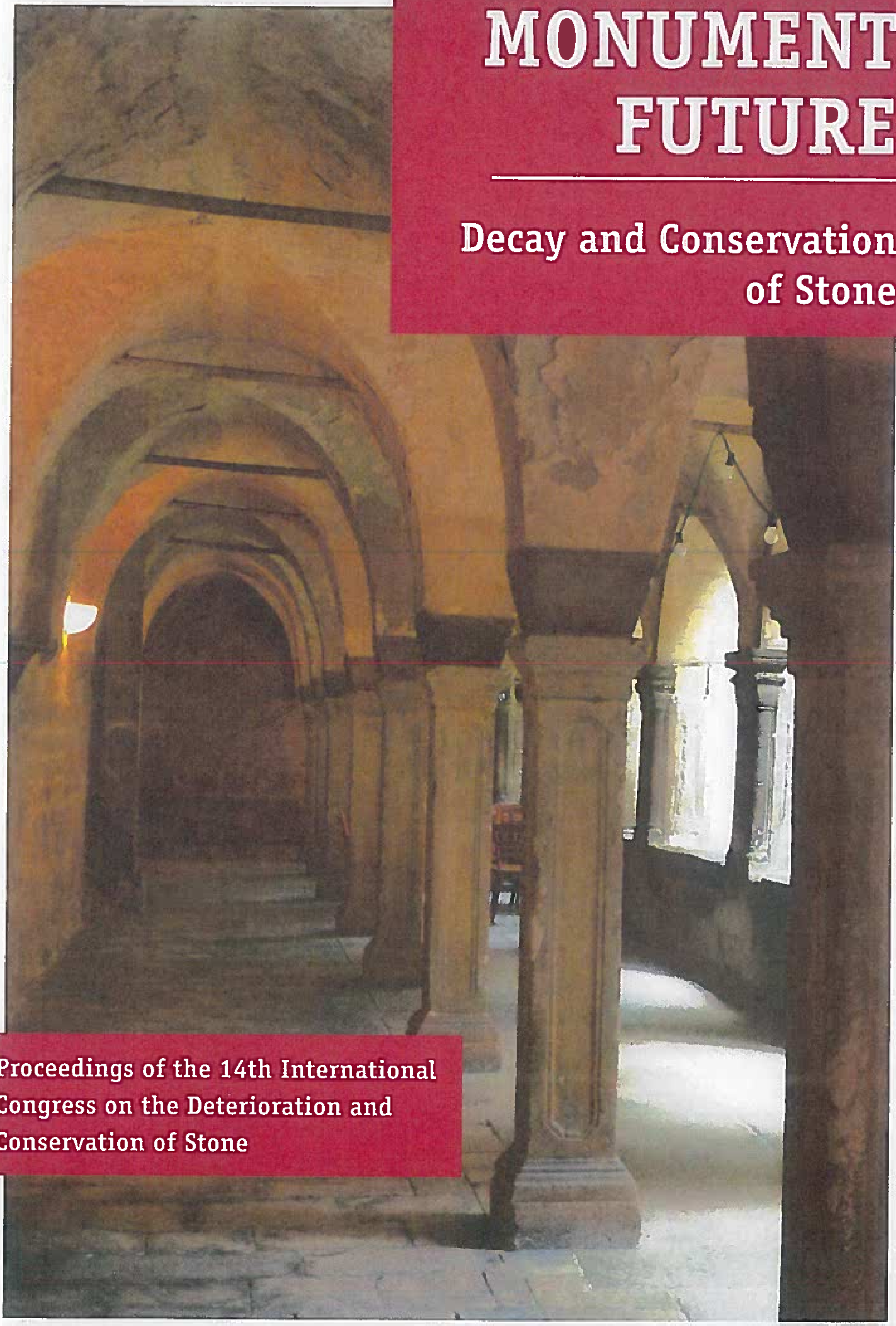
Siegfried Siegesmund/Bernhard Middendorf (Eds.)

MONUMENT FUTURE

Decay and Conservation of Stone



Proceedings of the 14th International Congress on the Deterioration and Conservation of Stone

Bildnachweise der ganzseitigen Fotos: Bernhard Middendorf – S. 2; Brigitte Siegesmund – S. 4, 8, 158, 300, 392, 480, 618, 706, 1010, 1038, 1046, 1118, 1200; Carolin Pfeuffer – S. 10; Heiner Siedel – S. 790; Mathias Hueck – S. 220; Torben Fetzner and Gerd Reis – S. 968; Wanja Wedekind – S. 32, 238

„Monument Future: Decay and Conservation of Stone" – Proceedings of the 14th International Congress on the Deterioration and Conservation of Stone, University of Goettingen and University of Kassel

Druckkosten gefördert durch die Deutsche Bundesstiftung Umwelt (AZ 34720/01)

Umschlagabbildungen: Kreuzgang im ehemaligen Kloster Schulpforta bei Naumburg von Brigitte Siegesmund

Bibliografische Information der Deutschen Nationalbibliothek
Die Deutsche Nationalbibliothek registriert diese Publikation in der Deutschen Nationalbibliografie; detaillierte bibliografische Daten im Internet unter https://d-nb.de.

1. Auflage

www.mitteldeutscherverlag.de

Gesamtherstellung: Mitteldeutscher Verlag, Halle (Saale)

ISBN 978-3-96311-172-3

Printed in the EU

IN: SIEGESMUND, S. & MIDDENDORF, B. (EDS.): MONUMENT FUTURE: DECAY AND CONSERVATION OF STONE.
– PROCEEDINGS OF THE 14TH INTERNATIONAL CONGRESS ON THE DETERIORATION AND CONSERVATION OF STONE –
VOLUME I AND VOLUME II. MITTELDEUTSCHER VERLAG 2020.

THE POTENTIAL OF NEUTRON IMAGING IN STONE CONSERVATION

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Abstract

This micro review presents a series of possible applications of neutron imaging in stone conservation and is supported by a collection of data obtained during experiments performed at *IMAGINE* beamline, located at the Laboratoire Léon Brillouin, at the Orphée Reactor in Saclay, France, with a special focus on water transport and retention. Here fore, advantages and limitations of the technique are discussed. Additional neutron scattering techniques are presented and focus on the analysis of materials used to conserve stone. This work will be completed by a short introduction to image analysis.

As a first example, the monitoring of liquid flow in sound and artificially aged natural stones is presented. Hereby, it was possible to visualise and evaluate microstructural differences. Furthermore, in respect to degradation processes, the radiographs show that gypsum crusts on stone surfaces exhibit a risk due to different densities present in the stone fabric. And finally, investigation of consolidated stone provided information on the differences in water absorption kinetics that are related to the amount of materials applied as well as the application techniques used.

Within this work, further applicants will have an overview of major facilities and workshops around Europe to enhance their knowledge in neutron techniques and therefore support research in the field of architectural heritage.

Keywords: Neutrons; Imaging; Radiography; Stone Conservation; Scattering Techniques

Introduction

Since the discovery of neutrons in 1932 by James Chadwick, this matter waves have changed our view of the atomic nuclei, established the field of nuclear physicist, radiotherapy for cancer treatments and have laid the foundation for nuclear energy, among others. In parallel, the potential of neutrons for materials science has captivated scientist worldwide across disciplines. The growing application of neutron scattering techniques in conservation- and geosciences can be seen through emerging publications in the last decades (Perfect et al., 2014).

Neutrons are highly penetrating, non-destructive and can be spin-polarized (i. e. spin alignment with a given direction). Therefore, they can be used in complex environments like magnets, pressure cells or cryostats. Neutrons interact directly with the atomic nuclei, they probe the bulk of a material, their intensity can be adjusted, the analysis is quantitative, and their theory is accurate and understood. Compared to X-rays, light elements such as hydrogen can have a high interaction; moreover, neutrons can distinguish isotopes. One weakness of neutron scattering is the requirement of large sample sizes. However, the latter is used as an advantage in geosciences, as it enables to visualize and quantify internal structures and dynamic processes on a scale relevant to the discipline, especially in the case of neutron imaging. As imaging has a pivotal role in conservation sciences in general, the present work aims to give an overview about the potential of neutron imaging in the field of stone conservation highlighting some experimental applications and further ideas of possible topics.

Principle of Neutron Imaging

Neutron imaging is based on the ability of neutron to penetrate materials and give back images of the structural arrangement of the studied matter. When a beam of neutrons passes through an object, absorption and scattering properties make it possible to obtain an image that is a map of neutron attenuation within the sample under study. Neutrons have zero net electrical charge and interact directly with the nuclei of atoms constituting the investigated material; specifically, the interaction forces are not correlated with the atomic number of the element but depend upon the particular isotope of the element. This is the reason why neutrons can detect light elements, like hydrogen, in solid matrix. This property makes neutrons suitable in soft matter sciences and, in the case of building stones, for performing dynamic studies on the behaviour of stones against water or conservation treatments.

The typical experimental set-up is composed by a neutron source, a collimator, a sample-set and a detector. The latter is usually constituted by 2D-pixels array like a CCD camera (charge-coupled device), able to convert the radiation in digital images. By moving the SSD (source-sample distance) and the SDD (sample-detector distance) it is possible to operate on magnification; in general, the closer the sample is to the source, the higher is the magnification and the spatial resolution. Noteworthy is that the spatial resolution is not only affected by the magnification but also by factors as the focal spot size of the source, the pixel size of the detector and other physical phenomena due to radiation-matter interaction. By rotating the sample, acquiring several radiographs at different angular steps and by using reconstruction algorithms, it is possible to obtain a 3D reconstruction of the objects.

The main advantage of the technique is that it is probing the inner structure of the material visualising it either in radiography (2D) or tomography (3D) mode in a non-destructive manner. The main disadvantage of this technique is the spatial resolution obtained that amounts to a lowermost ~20 µm, which is limited through the scintillating material used (Kardjilov et al., 2011). However, the time necessary to obtain a good quality image in the ~50 to ~100 µm range amounts to less than two seconds, making this technique a unique tool to investigate dynamical and real-time processes that range over a large sample volume. The application of the technique has its highest use in the aircraft and automotive industry, mainly as a quality control tool for the manufactured elements but, its use in geosciences, archaeology and heritage preservation in general is indispensable.

Image Analysis

Image analysis is required for quantitative interpretations of data. Raw data are usually analysed in collaboration with the beam scientists, according to in-house protocols. Image pre-processing involves corrections with dark-field images, normalization with open beam images and noise filtering (including dead camera pixels and spurious gamma events). After processing, the images are ready to be used for image analysis, e. g. extracting water absorption coefficients, amounts of liquid water in particular areas or kinetical data, among other parameters. If the adsorption of water inside of the stones structure is the goal to be studied, the first steps will include the normalisation of the water absorption images and normalise them with the steady-state dry images taken prior to absorption. In that way, the measured transmission can be directly related to the amount of water. For that purposes, the scanning of a vessel filled with water in different volumes with standardised thickness must be done, from which a calibration curve of water attenuation and resulting image grey values can be created (e. g. Dewanckele et al., 2014). Such procedures are necessary to account for deviations from the Beer–Lambert law (i. e. because of the energy dependence of the attenuation coefficient). Pre-processing and image analysis are often performed with the help of *Fiji ImageJ* (Fiji Is Just ImageJ – Image Processing and Analysis in Java, open source, general public license) (Schindelin et al., 2012) but also other programs are available (e. g. *Octopus* for reconstruction or analysis).

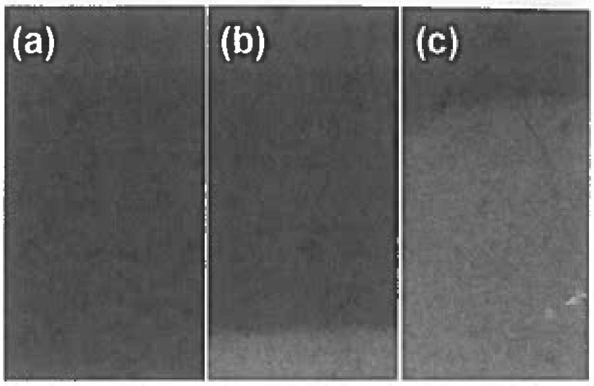

Figure 1: Water absorption of (a) freshly quarried and (b and c) thermally aged Apuan marble at different time intervals. Light grey scale values indicate the water saturated area. The scans helped analyzed the inducement of homogeneously distributed micro cracks.

Monitoring of Liquid Flow

Neutron imaging is most known for studies concerning flow of hydrogenous fluids in porous materials. It is possible to visualize and quantify the amount of liquid in function of space and time. As such, conclusions about textural differences in the material can be made (e. g. local differences in porosity).

Specifically, neutron imaging can be used to study artificially or naturally aged substrates indirectly through water absorption tests. Heat-treatment of natural stone is often employed prior to study stone consolidation, as a technique to decay the stone and mimic a microstructural defect. This is a condition aimed to be achieved before testing the efficiency and compatibility of different consolidants. Neutron imaging can provide criteria to classify this pre-requisite, necessary for mechanical studies (i. e. a homogeneously artificially aged sample used further for mechanical tests). Different degradation processes will result in varying absorption properties. Neutron imaging studies demonstrated their usefulness in visualising specific decay patterns (for examples micro cracks) throughout the stones' structure (see Fig. 1).

Moreover, a correlation with laboratory studies of water absorption and sound speed propagation is also possible (Ban et al., 2019), where the absolute values are in the order of experimental errors and come about due to the techniques used but follow the same trend.

Transport of the consolidant can be also monitored over time; if a certain decay reaches certain depths, neutron imaging can be used to study if the liquid product (i. e. protective or consolidants) reaches solely the decayed part or if it is continuing to flow into the sound bulk structure. Additionally, studies concerning drying properties can be carried out by using foils to imitate on-site conditions.

Fluid flow monitoring can be carried out on treated stone samples in order to support the evaluation of a treatment's compatibility. The latter might depend on several factors, including substrate features, application technique employed or consolidant used, among others. Recent water absorption experiments have revealed a water trapping and pore clogging in a consolidated sample. Namely, as the polycondensation reaction was not finished, parts of the stone were still hydrophobic and water trapping and anomalous capillary suction of water was visible (Fig. 2).

It was noticeable that the reaction rate varies with the amount of consolidant applied. In the case of porous stone, the substrate can therefore be considered as one of the governing factors when considering reaction rates. Moreover, the wetting front visible by naked eye was not reliable.

Laboratory based water absorption tests are not

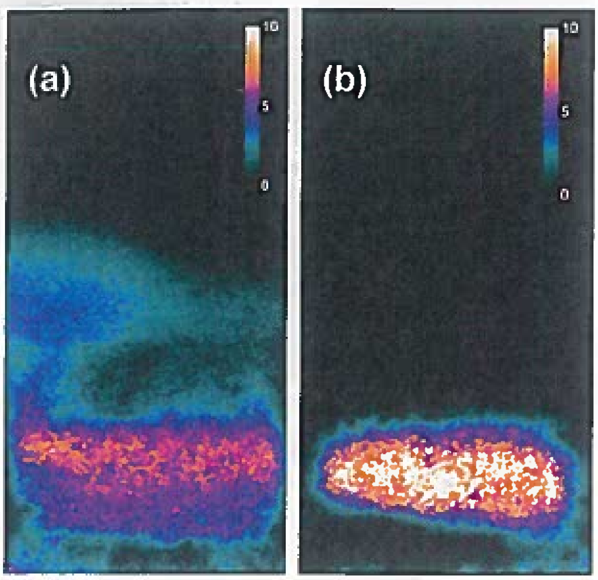

Figure 2: Polymerization degree of alkoxysilanes was indirectly observed through water trapping inside the stone. The lateral surfaces are still hydrophobic, while water could penetrate through small opening from the bottom of the stone through capillary forces, in Ban et al., 2019.

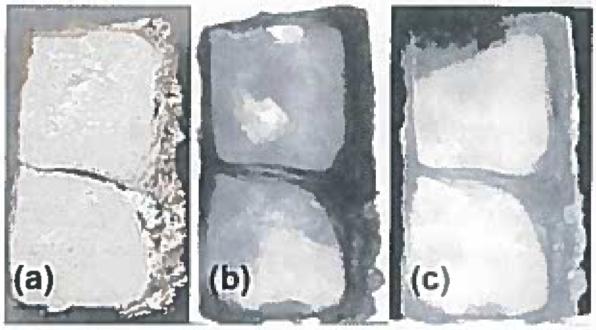

Figure 3: Presence of a gypsum crust on a porous calcareous substrate: (a) micrograph taken with an optical microscope, (b) neutron scan in dry state and (c) neutron scan after 30 min in contact with water.

able to give the same insights as neutron imaging. Only the latter allowed for an improved interpretation of a consolidation treatment and the influence of different application techniques. The radiographs further suggested that changes in wettability caused by the treatments, determine the penetration depth and distribution of water inside the stones.

Studies of Structural Changes

Textural differences are important for the study of conservation states of building materials. Because different matter will attenuate neutrons differently, structural changes can be visualised. In respect to treated stones, neutron imaging proved valuable in detecting the distribution of consolidants (Hameed et al., 2009 and Graziani et al., 2018).
Degradation phenomena, which create structural changes can also be visualised; as an example, gypsum crusts can be clearly differentiated from the stones (see Fig. 3) as they have a different crystal structure. Such differences in density can indicate where the weak zones in a material lies.
Gypsum crusts represents one of the most common degradation patterns in stone conservation for carbonate substrates. Studies surrounding changes in structure and their relation to moisture related properties are particularly useful, as they are scarce. Often, a removal of the gypsum crust is possible solely at the surface, but it also remains inside the stones structure and influences the materials interaction with the environment (e.g. water vapour properties, drying, differential expansion, etc.).

Analysis of Drying Properties

Drying properties are crucial for building stone, as water retention might cause damage. In that regard, water repellent treatments play an important role, as they are regularly used as conservation products. They are often negatively connoted with spalling processes as they can prevent the transport of moisture in capillary and vapour form. The latter phenomenon might pose a danger if water vapour diffusion is too slow, which is why the study surrounding prospective treatments is of priority in this field of studies. Moreover, the study of the interface area between water repellent and sound stone might pose a danger too, which is why studies on such topics are desirable.
As water repellent treatments hinder water penetration, flipping the samples can give reliable results on their penetration depth and homogeneity of their distribution. Moreover, mimicking a case

where water penetrates from behind is a valuable diagnostic tool for real on-site conditions, especially when the drying of such a structure is monitored.

Studies of different interfaces are of importance in the field, between repair materials, joints and shelter coatings, among others. Little is known about the drying behaviour at such interfaces.

Neutron Scattering Techniques

Besides imaging, neutron scattering techniques have found some applications in the field of built heritage (Raneri et al., 2018). However, more insight about potential applications is offered from related disciplines. Small angle neutron scattering (SANS) can be employed in stone conservation, because it helps to interpret nano- to micro porosity changes caused by consolidation treatments (Ševčik et al., 2019). The latter technique could also be used to study structural reorganisations induced by flow or related rheological responses of soft matter used in stone conservation (Eberle and Porcar, 2012). A great potential lies in the use of neutron reflectometry to study solid-liquid interfaces, for example between a mineral material and different suspensions/dispersions used as consolidants. Moreover, localised deformation phenomena and textural changes can be studied by neutron diffraction (Schäfer, 2002). The latter could be used to study consolidated sand, mimicking stress analysis of consolidated loose surfaces.

Due to the limited space of the present work, the reader is referred to textbooks (Feigin and Svergun, 1987) in order to gain more insights about different neutron scattering techniques.

Facilities and Workshops

The community surrounding neutron science offers great help and support worldwide. During the last decades, several projects were funded by the European Union to implement knowledge and innovation in the field of neutron science and applications (e. g. *NMI3*, supported by the EU through FP5, FP6 and FP7; *SINE2020*, funded by Horizon 2020, GA No. 654000). The International Society for Neutron Radiography (ISNR) gives an overview on upcoming events and other activities in the field. Summer schools like the Oxford School on Neutron Scattering or the hands-on workshops organised by the Jülich Centre for Neutron Science (Forschungszentrum Jülich in cooperation with the RWTH Aachen University) are only some among the numerous training opportunities. Furthermore, the Hercules Schools offer an intensive program using neutrons and synchrotron radiation for science. All these workshops teach the basic techniques and evaluation programs to prepare the participants to make use of large-scale facilities. Neutronsources.org is the operating platform for sharing information, news and opportunities in the field of neutron science, where details about scientific centres and research opportunities can be found. Only in Europe, several neutron centres operating as user facilities (access under reviewed and accepted proposals) offer opportunities to perform neutron imaging experiments (e. g. Strobl et al., 2009 provides a selection of neutron imaging facilities). Unfortunately, during 2019 several reactors shut down; among relevant in the field of neutron imaging, we quote BER II reactor at HZB (Germany), with the *CONRAD* imaging beamline, the ORPHEE reactor at CEA-Saclay (France), with the *IMAGINE* beamline and the JEEP II reactor operated by NcNeutron, Institute for Energy Technology in Kjeller (Norway). The future is the new multi-disciplinary research centre based on world's most powerful neutron source, the European Spallation Source (ESS) that is still under construction in Lund, Sweden, and expected to be operating in 2023 with numerous new instrumentations, among which the new multi-purpose imaging instrument *ODIN* will operate.

Summary

The aim of the present work was to motivate emerging scientist in architectural preservation in using neutron scattering techniques and particularly neutron imaging for their research by illustrating the potential of its use. Within the present work, some examples have been presented on how to use neutron imaging in stone conservation and some ideas have been given on potential topics that are lacking in research.

We demonstrated that the effects of artificial and natural ageing can be studied by neutron imaging and provide improved interpretations. Furthermore, we evidenced that some processes, such as water trapping inside a hydrophobic sample, cannot be seen and well interpreted by simple laboratory tests like water absorption. Differences in the structure and chemistry can be distinguished with neutron imaging, which makes it possible to study interfaces between e.g. stone and gypsum or to follow the drying kinetics of a partially water repellent substrate. All the presented examples demonstrate that without neutron imaging the relevant questions in the field of stone conservation could not have been answered with this amount of precision.

Acknowledgements

University of Pisa (PRA-2018-41 Project Georisorse e Ambiente) is acknowledged for the financial support. The authors thank Frederic Ott for the continuous support during the experiments at the beamline. Heartfelt thanks to José Teixeira for the fruitfully scientific discussions and his hospitality; he taught us the basics of neutron science.

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