DIRECT OBSERVATION OF CONSERVATION TREATMENTS BY SINGLE-SIDED NMR RELAXOMETRY

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Abstract

Non-destructive techniques are key to assessing the effectiveness of treatments and the state of conservation of stones. Nuclear magnetic resonance (NMR) relaxometric profiling is an innovative, non-invasive, and non-destructive candidate to address these issues directly in situ using single-sided portable devices. In this study, low-field 1H NMR relaxometry was used to investigate conservation treatments on stone samples by depth profiling up to 25 mm. Two types of stone strengthening consolidants (KSE 100 and KSE 300) and a hydrophobic agent (Funcosil SNL) were tested on four types of sandstone: Schilf sandstone, Bunter sandstone, and two types of Stuben sandstone. The evolution of conservation treatments was monitored over time, also considering the influence of sediment bed direction and stone granularity. The depth distribution and the curing of the products could be followed until 74 hours after application. NMR can localize the agent because the NMR signal of the hydrogen nuclei of the solvent is acquired as a function of depth in the stone, monitoring the product during the application and curing of the treatment directly in situ with a non-invasive technique. The hydrophobic effect of stone strengtheners shortly after treatments in limiting and slowing down water ingress has also been assessed 50 days after treatment with capillary suction tests. Additionally, NMR was used to assess water distribution within the porous structure of sandstones samples from the Hoppenlau Cemetery, Stuttgart, currently undergoing restoration. Water content was measured as a function of distance from the external surfaces, alongside NMR parameters related to the properties of the stone's porous structure. By characterizing both water content and the penetration dynamics of conservation products, this study highlights the potential of NMR as a diagnostic tool for evaluating the effectiveness of treatments and the state of conservation of historical stone materials. This information is useful for restorers in designing and implementing appropriate restoration strategies.

Keywords: NMR relaxometry, single-sided NMR, sandstone, conservation treatments.

1. Introduction

Research in the field of magnetic resonance techniques applied to cultural heritage has resulted in a large body of international scientific literature, although these applications are not yet well known outside the NMR community. Today, it is possible to carry out measurements with portable instruments (Eidmann *et al.,* 1996; Blümich *et al.,* 2008; Blümich and Anders 2021) that allow non-invasive and non-destructive studies of objects of any size and of high artistic and historical value, as well as diagnosing their state of conservation. NMR relaxation times (T_1 and T_2) of nuclear magnetization, molecular self-diffusion (D), and their correlations can be used to investigate the structural properties of hydrogenated fluid systems for a wide variety of cultural heritage materials (Capitani *et al.,* 2012). The main applications are the study of stone materials and the performance evaluation of new chemical compounds for the consolidation and protection of these porous materials (Sharma *et al.,* 2003; Brizi *et al.,* 2018; Braun and Orlowsky 2020; Orlowsky *et al.,* 2020). Advanced two-dimensional NMR relaxometry methods enable the study of correlations between two NMR parameters, further improving the understanding of the structure of the porous space and pore connectivity.

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This study presents recent applications of portable NMR technology to stone materials using NMR depth profiles. The evolution of three conservation treatments over time in four different types of sandstone is monitored directly in situ and non-invasively. The case study of the stone conservation at the cemetery of Hoppenlau, Stuttgart, is presented and discussed.

2. The NMR-MOUSE device

In recent decades, compact devices (Blümich *et al.,* 2008; Blümich and Anders 2021) have been developed for measurements of the magnetic resonance signal in the time domain (relaxometry). Only applications of low-field NMR will be presented in this work. The NMR-MOUSE (PM25, *Magritek*), a portable device for non-destructive and non-invasive measurements, was used (Figure 1). It is composed of a permanent magnet that creates a static polarizing magnetic field B_0 of about 0.327 T. A radiofrequency (RF) coil sends RF pulses to the sample and detects the signal related to the NMR relaxation phenomenon. The peculiarity of this instrument is related to the position of the sample because the object under investigation is outside the magnet, unlike most NMR measurements where the sample is placed inside. This configuration leads to the presence of a strong magnetic field gradient along the direction into the sample or object. For this reason, the resonance condition is satisfied in a small region of the sample, called sensitive volume, from which the signal is acquired. One useful measurement with the NMR-MOUSE is a depth profile, where the magnet is moved away from the sample, causing the position of the sensitive volume to pass through the sample. In this way, signal from different volume elements of the sample at different depths is acquired reaching a maximum depth of 25 mm.

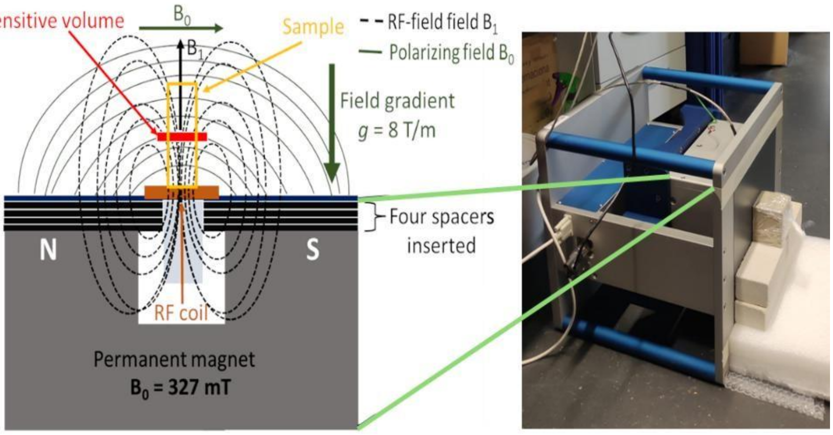

Figure 1: Right: the NMR-MOUSE PM25 instrument manufactured by Magritek consists of a magnetic probe system and a translation stage. Left: schematic representation of the probe system that supports the sample. The B_1 RF field, the static B_0 polarization field, and the sensitive volume are depicted.

3. Laboratory results: the evolution of conservation treatments over time

To study the consolidation and hydrophobization characteristics, treatments with different types of products were simulated and studied in the laboratory using NMR. A similar hydrophobic agent to the one used in the 1980s in Stuttgart for the Hoppenlau Cemetery restoration (see next section) was applied with a brush to stone samples of the same type as those used in the cemetery. Two types of stone strengthening consolidants (KSE 100 and KSE 300, Remmers GmbH, Loningen) and a hydrophobic agent (Funcosil SNL, Remmers GmbH, Loningen) were used. A total of 4 stone types were tested: Schilf sandstone (grey, porosity ~13%), Bunter sandstone (red, porosity ~8%), and two types of Stuben sandstone (yellow, porosity ~16% and white, porosity ~10%). Many samples of each stone type were used. All three products were applied to the stone samples using a brush, maintaining the amount of applied product as constant as possible across the samples. Each stone sample was treated only once with a single product. The NMR-MOUSE 10-mm-spacer configuration was used to measure at a maximum depth of 16 mm inside the samples, with echo time = 80 µs, repetition time = 200 ms and resolution = 200 µm. Three different main observations have been selected from the analyses and are presented and discussed in the following sections.

3.1 The role of sediment bed direction

The uptake and distribution of the consolidants/protectants in the hours following the treatment were monitored. Figure 2 shows the NMR profiles of Schilf sandstone after 5, 25, and 74 hours from the time of treatment. The NMR signal of the hydrogen nuclei of the solvent, acquired as a function of depth in the stone (surface = 0 mm), is shown. To obtain a reference for the background noise and the amount of moisture present in the stone, the NMR signal of the stone before treatment was measured (the continuous black line near zero).

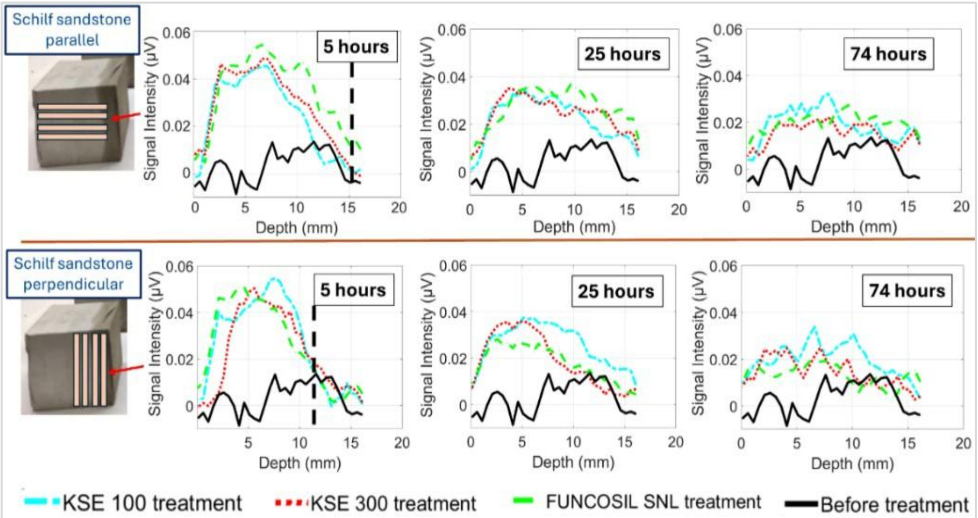

Figure 2: NMR profiles of the two consolidants (KSE 100 and KSE 300) and the hydrophobic agent (Funcosil SNL) 5 hours (first column), 25 hours (second column), and 74 hours (third column) after treatment of the Schilf sandstone parallel to the sedimentation layers (first row) and perpendicular to them (second row).

In the top row of Figure 2, the treatment was applied parallel to the rock sedimentation layers (KSE 100: 82 mg/cm^2, KSE 300: 100 mg/cm^2 and Funcosil SNL: 63 mg/cm^2), while in the bottom row the layers were perpendicular to the treatment (KSE 100: 73 mg/cm^2, KSE 300: 93 mg/cm^2 and Funcosil SNL: 47 mg/cm^2). It is interesting to compare the different absorption and diffusion behaviour of the treatment, both due to the type of consolidant/protective agent used and the orientation of the sedimentation layers. Focusing on KSE 300 and Funcosil SNL treatments, if the layers are parallel to the treatment, the stone absorbs more, and the consolidant/protective agent penetrates deeper. If they are perpendicular, absorption is hindered by the alternation of the different layers. In Figure 2, for example, 5 hours after treatment, the products reach a depth of about 11.5 mm in the perpendicular layers (perpendicular dashed line), whereas in the parallel layers Funcosil SNL and KSE 300 penetrates deeper (> 15 mm). For the KSE 100 treatment, the behaviour is different: this product does not seem to be influenced by the orientation of sedimentation layers. It should be noted that as the hours pass, the signal from the solidifier/agent decreases significantly due to the evaporation of the solvent: after 74 hours, the signal is more than halved. These results suggest how the in-situ NMR profile can help to follow the ingress of the product over time after treatment of, for example, the facade of a building, and to determine the depth reached.

3.2 The role of granularity

The analyses also focused on comparing the same treatment in different types of stones after a fixed time after treatment. Figure 3 shows the results of the two types of Stuben sandstone (yellow and white) and Schilf sandstone (with treatments applied parallel and perpendicular to the sedimentation layers). All the NMR profiles were acquired 5 hours after the treatments. Since the sample volumes were not the same for all stone types, it was necessary to convert the NMR signal intensity to the percentage of the volumetric agent content. These profiles provide insights into the distribution of the agent content along the depth into the stones.

The different granularity of the stones plays a crucial role in the ingress and distribution of the agent during the first hours after treatment. This effect is particularly evident in the case of Stuben sandstone (yellow) compared to the other samples. Since this stone has the highest porosity and larger grains, a more scattered NMR profile is observed, with distinct peaks where the volumetric agent content is higher than in the other stones.

The variation in the profile is due to the large grain size. Another direct observation from Figure 3 is that Stuben sandstone (white) appears to absorb less agent (~3-4%) compared to Schilf sandstones (~4-5%), despite the same amount of agent being used for treatment. These results highlight how NMR can detect differences in the distribution of products on various stones in terms of porosity and granularity immediately after treatment.

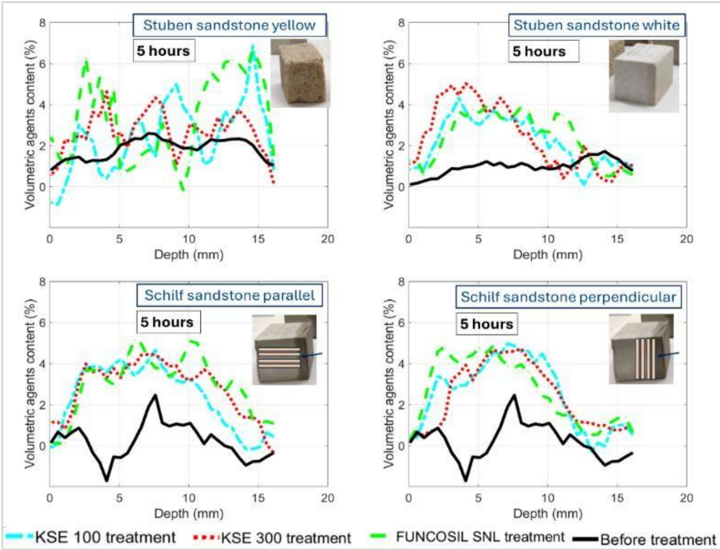

Figure 3: Volumetric content of the two consolidants (KSE 100 and KSE 300) and the hydrophobic agent (Funcosil SNL) 5 hours after treatments. Three types of stones are compared: Stuben sandstone (yellow), Stuben sandstone (white) and Schilf sandstone (with treatments applied parallel and perpendicular to the sedimentation layers).

3.3 Evaluation of treatment effectiveness

The consolidation process was evaluated 50 days after treatment. Capillary water suction tests were carried out to assess the effectiveness of treatments in limiting and slowing down water ingress. The same test was performed before treatment to compare the properties before and after. A sprayer was used for the tests. Figure 4 presents some of the results.

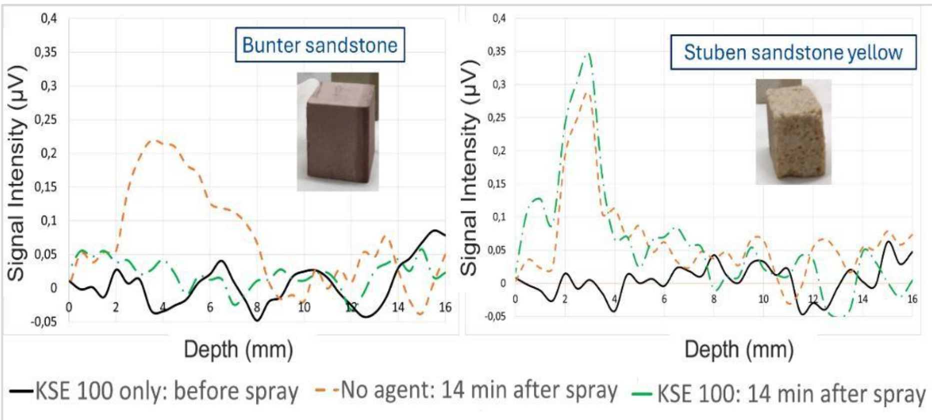

Figure 4: NMR profiles of Bunter (left) and Stuben (right) sandstones after capillary water suction tests. Tests have been carried out before treating stones with KSE 100 (dashed orange line) and 50 days after the treatment (spotted green line). The black continuous line refers to the signal of KSE 100 only (50 days after treatment) before spraying.

For comparison, the stone with the lowest porosity (Bunter sandstone, ~8%) and the stone with the highest porosity (Stuben sandstone yellow, ~16%) were selected. The water suction test involved spraying the stones ten times, with one spray every ten seconds (total water amount ~10 mL) while positioned vertically relative to the ground. Immediately after spraying the NMR profile was acquired, a process that took approximately ten minutes. This procedure was conducted both before treatment with KSE 100 (dashed orange line in Figure 4) and 50 days after the treatment (spotted green line in Figure 4). The solid black line represents the signal of KSE 100 alone (50 days after treatment) before spraying. This signal is expected to be close to zero as the solvent should have fully evaporated after such a long period. Unlike previous sections, these profiles capture only the contribution from water molecules, excluding any signal from solvent molecules.

Strengthening agents exhibit hydrophobic properties shortly after application. For subsequent treatments such as surface-flush filling, it is essential to determine the time at which the hydrophobicity wears off.

A key observation from the NMR profiles in Figure 4 is that Bunter sandstone appears to still limit water ingress, whereas Stuben sandstone does not exhibit the same behaviour. Given that the same amount of consolidant and sprayed water was applied to both stones, this difference is likely attributed to their distinct pore structures. Stuben sandstone has twice the porosity of Bunter one, which may have prevented KSE 100 from filling all pore spaces. As a result, water was still able to penetrate the rock despite the treatment. These results suggest the potential for evaluating treatment effectiveness through NMR profiles in the days and weeks following application. This approach could help to determine the filling of the pore space and the capillary suction behaviour of the treated stones over time.

4. In situ results: Hoppenlau Cemetery restoration

Founded in 1626, Hoppenlau Cemetery is the oldest preserved cemetery in the city of Stuttgart and has been a popular place for locals and tourists since it was turned into a park in the 1960s. Due to the condition of the gravestones (mostly made of various types of sandstone), restoration work was carried out at the end of the 1980s by applying a hydrophobic agent to the gravestones. Unfortunately, in the decades that followed, this intervention accelerated the deterioration and flaking of the gravestones due to the infiltration of water into the rock and its accumulation at the interface of the hydrophobic product. It is therefore essential for the actual consolidation measures to determine the depth of penetration of the hydrophobic agent, its behaviour, and the distribution of water within the porous stone structure. Some samples from the cemetery were selected. Since the rocks had been treated in the 1980s, no signal from the agent is detectable. So, an indirect measure is needed: the NMR signal of the water inside the stone was detected and studied as a function of distance from the outer surfaces. The results are shown in Figure 5, which plots the NMR signal of water as a function of depth after spraying the surface with water.

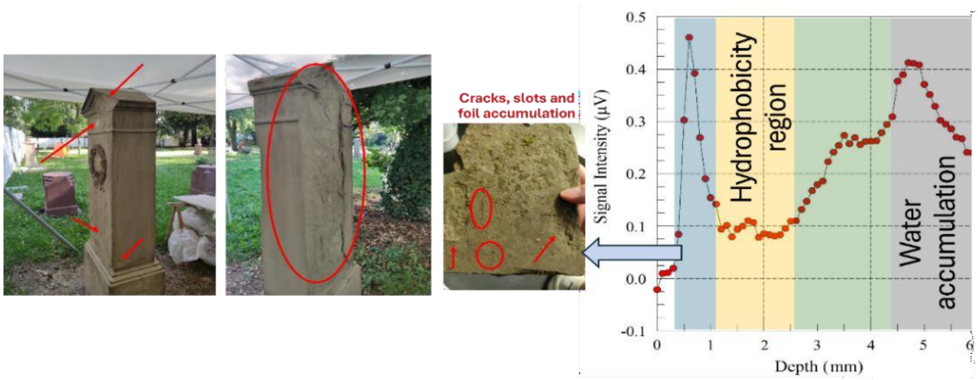

Figure 5: Left: Front and back sides of a gravestone in the Hoppenlau Cemetery, Stuttgart. Flaking and cracks caused by deterioration after inappropriate restoration treatment in the 1980s are visible. Right: NMR profile of a gravestone showing the hydrophobic and water-accumulation regions. Four regions are identified by background colour.

Interpretation of the profile in Figure 5 leads to some interesting considerations. From the left, the first peak is due to the presence of small sub-surface cracks and slots through which water can infiltrate despite the surface having being treated. The presence of these cracks is due to weathering over the past decades, and it is the reason why water infiltrates into the stone (as well as capillary rise from the ground). If this test had been carried out shortly after the treatment in the 1980s, it would have shown a water signal profile near zero, as all the water would have remained at the surface. Instead, today we see a peak (~0.47 µV) followed by a region of less intense signal (~0.1 µV) extending for about 1.5 mm. There we are in the region where the agent used in the past still has hydrophobic properties.

Beyond the hydrophobic region, water penetrates deeper. Indeed, in the third and fourth regions from the left, the NMR signal from the hydrogen nuclei of the water increases until it reaches the area of maximum accumulation at a depth of about 5 mm. In addition to the NMR signal, T_2 and T_1 relaxation times were extrapolated from CPMG and Saturation curves. They were used to determine the properties of the stone's pore structure in the hydrophobic region and compare them with those in the water accumulation region.

An interesting result is that the hydrophobic region shows shorter relaxation times ($T_1 = (111 \pm 9)$ ms and $T_2 = (39 \pm 7)$ ms) than those found in the accumulation region ($T_1 = (368 \pm 6)$ ms and $T_2 = (73 \pm 4)$ ms). In this case, the T_1 and T_2 relaxation times are an indication of the amount of water trapped in the pores of the stone matrix. In a fully water saturated porous material, the shorter the T_1 and T_2 parameters, the smaller the pore size in which the water is confined. Therefore, the presence of shorter T_1 and T_2 in the partially saturated hydrophobic region is also attributed to a reduced pore size due to the presence of the hydrophobic product being distributed on the pore surfaces along with a lower water content than in the fully saturated condition due to unsaturated larger pores. The fact that there is a region with lower water content shows the hydrophobization of the pore surfaces. Water can then only accumulate in the second phase, which is in the pore interior and reaches a maximum size (< pore diameter) at water saturation. This information can be crucial in planning and implementing an appropriate restoration strategy.

4. Conclusions

This study demonstrates the potential of NMR relaxometry as a non-invasive tool for assessing conservation treatments and the state of historical stone materials. By monitoring the depth distribution and curing of consolidants, NMR provided valuable insights into the penetration dynamics of treatments and their effectiveness in limiting water ingress. Additionally, its ability to evaluate water distribution within porous structures supported the Hoppenlau Cemetery restoration strategies. These findings highlight the relevance of portable NMR for *in situ* diagnostics, aiding restorers in optimizing treatment applications and ensuring long-term preservation of stone heritage.

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