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In situ diagnosis of cultural heritage using NMR techniques

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Summary. — This study presents applications of portable Nuclear Magnetic Resonance (NMR) technology to stone and wood materials through NMR profiles. First, the results of consolidation and protection treatments with hydrophobic agents on sand-stones from the cemetery of Hoppenlau, Stuttgart, are presented and discussed. The second case study focuses on measurements of the Holy Thursday altarpiece in the sacristy of the Freising Cathedral, Bavaria. Portable NMR instrumentation was successfully applied, demonstrating the ability of this non-invasive and non-destructive technique to investigate the porous structure of cultural heritage materials.

1. – Introduction

Research in the field of Nuclear Magnetic Resonance (NMR) 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 [1, 2] that allow non-invasive and non-destructive studies of artistic objects, as well as diagnosing their state of conservation. NMR relaxation times (T_1 and T_2) of nuclear magnetization can be used to investigate the structural properties of hydrogenated fluid systems for a wide variety of materials from cultural heritage [3]. The main applications are the performance evaluation of new chemical compounds for the consolidation and protection of stone materials [4-6]. Recently, paintings on canvas have been studied to characterize pictorial layers and to investigate binders, allowing the optimization of painting cleaning procedures [7, 8]. This study presents recent applications of portable NMR technology to stone and wood materials using NMR depth profiles. In the first case study, the results of the consolidation and protection treatments with hydrophobic agents on sandstone samples from the Hoppenlau cemetery in Stuttgart are presented and discussed. In the second case study, measurements on the Holy Thursday altarpiece in the sacristy of the Freising Cathedral, Bavaria, are analyzed.

2. – Experimental setup: the NMR-MOUSE device

The portable low-field NMR-MOUSE instrument (PM25, Magritek, fig. 1) has been used for the measurements of the NMR signal in the time domain. This instrument is

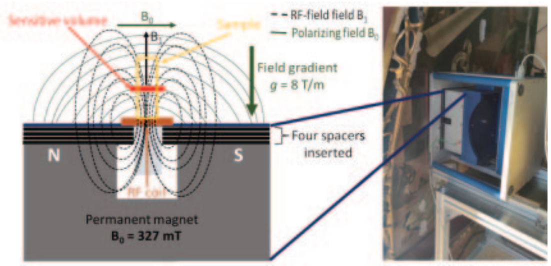

Fig. 1. – Right: the NMR-MOUSE instrument. Left: schematic representation of the probe system. The B_1 RF field, the static B_0 polarization field, and the sensitive volume are depicted.

composed of a permanent magnet that creates a static polarizing magnetic field B_0 of ~ 327 mT. There is also a radiofrequency coil that sends pulses to the sample and detects the signal related to the relaxation phenomenon. The device configuration results in the presence of a magnetic field (B_0) gradient along the direction of the sample. For this reason, the resonance condition is satisfied in a thin slice of the sample (up to 50 μm of resolution), called the sensitive volume, from which the signal is acquired. Signal intensity, T_2 and T_1 were extracted from CPMG and saturation recovery pulse sequences. One possible measurement with the NMR-MOUSE is a depth profile, along which the magnet is moved in order to acquire signal from different volumes up to a maximum depth of 25 mm inside the sample.

3. – The Hoppenlau cemetery restoration

Founded in 1626, Hoppenlau cemetery is the oldest cemetery in the city of Stuttgart. The poor restoration work carried out in 1980 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 used for restoration. It is essential to determine its behaviour, penetration depth and distribution of water within the porous stone structure.

3˙1. *Direct measure in the laboratory: the signal from the agents.* – A treatment simulation was carried out in the laboratory. Products similar to those used in the 1980s were applied to rock samples of the same type as those found in the cemetery.

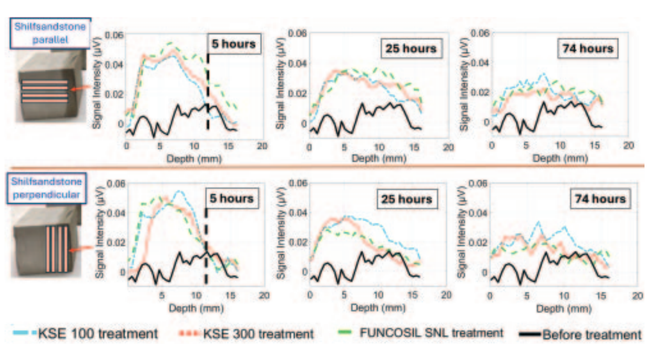

Fig. 2. – NMR profiles of the two consolidants (KSE 100 and KSE 300) and the hydrophobic agent (Funcosil SNL) 5 hours (first column), 25 hours (second column), and 74 hours (third column) after treatment of the Schilfsandstone parallel to the sedimentation layers (first row) and perpendicular to them (second row). The signal intensity is expressed in μV and the rock surface is at 0 mm.

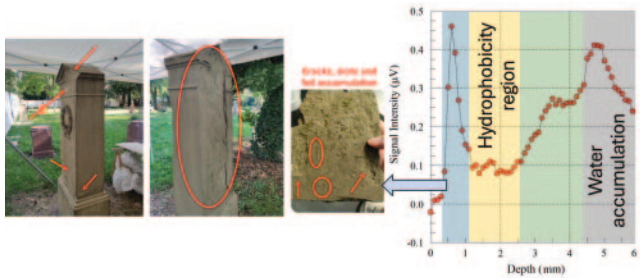

Fig. 3. – Left: two gravestones in the Hoppenlau cemetery, Stuttgart. Flaking and cracks caused by restoration work in the 1980s are visible. Right: NMR profile of a gravestone showing the hydrophobic and water-accumulation regions.

Two types of consolidation agents (KSE 100 and KSE 300, Remmers GmbH) and a hydrophobic agent (Funcosil SNL, Remmers GmbH) were used. A total of 4 rock types were tested: Schilfsandstone, Buntsandstone, and two types of Stubensandstone. The main results concern the uptake and distribution of the protectants in the hours following the application. Figure 2 shows the NMR signal from the protectants across depth at different times after Schilfsandstone treatment. The continuous black line around zero is the reference for the background noise. In the top row of fig. 2, the treatment was applied parallel to the rock sedimentation layers, while in the bottom row the layers were perpendicular to the treatment. If the layers are parallel to the treatment, the rock absorbs more, and the product penetrates deeper; if they are perpendicular, absorption is hindered by the alternation of the different layers. For example, 5 hours after treatment, the products reach a depth of 11.5 mm in the perpendicular case (perpendicular dashed line), whereas in the parallel case penetrate deeper (>15 mm for Funcosil SNL and KSE 300). After 74 hours, the signal from the agent decreases dramatically due to the evaporation of the solvent. These results suggest how the *in situ* NMR profile can help to follow the distribution of the product over time after treatment and to determine the depth reached.

3˙2. *Indirect measure in situ: the signal from the water*. – Some samples from the cemetery were selected. Figure 3 shows the NMR signal of water as a function of depth after spraying the surface with water. The first peak on the left is due to the presence of sub-surface cracks caused by weathering through which water can infiltrate despite the surface being treated. The peak is followed by a region of less intense signal, in which the agent still has hydrophobic properties. Beyond the hydrophobic region, water penetrates deeper. An interesting result is that in the hydrophobic region shows much shorter relaxation times (T_1 and T_2 times) than those found in the accumulation region. In this case, T_1 and T_2 are an indication of the amount of water trapped in the pores of the stone matrix. The presence of shorter T_1 and T_2 in the hydrophobic area can be interpreted by a reduced pore size in which the water is confined due to the presence of the hydrophobic product. This information can be crucial in planning an appropriate restoration strategy.

4. – The Holy Thursday altarpiece restoration

In the sacristy of Freising Cathedral is the Holy Thursday altarpiece (1495, fig. 4(left)). In recent decades, the painting has deteriorated (*e.g.*, shrinkage) due to the unsuitable temperature and humidity conditions. One of the main problems faced by the restorers is to understand the flow and volumetric concentration of humidity in the different layers

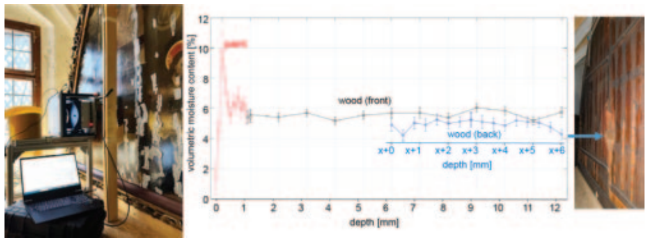

Fig. 4. – Left: NMR-MOUSE used in the investigation of the painting. Centre: NMR depth profile showing volumetric profile of moisture content in the wooden board. Right: back of the altarpiece.

of the painting in order to plan appropriate conservation measures. Figure 4 shows the trend of the volumetric percentage of moisture content as a function of depth in the painting measured without wetting the surface with water. The secondary plot on the right refers to measurements made on the wood at the back of the altarpiece (x represents the distance to the front of the painting and it is approximately 14 mm). The highest peak is due to both high moisture content and the presence of paint material that could contribute to the NMR signal. In addition, the wood measured at the back has a lower moisture content (within the measurement error) than the wood near the painted front. This could be due to two factors: the moisture in the wood close to the facade cannot as readily evaporate because of the layer of paint; and the fact that the wood on the back has been treated during the restoration to preserve it.

5. – Conclusions

In this work, applications of portable Nuclear Magnetic Resonance instrumentation demonstrate the capabilities of such non-invasive and non-destructive technique to investigate the porous structure of materials. The moisture content of stone and wood materials and the penetration of conservation products have been used to assess the effectiveness of treatments, the state of conservation and to aid the implementation of restoration interventions. The NMR relaxometric profiling technique is a powerful tool that remains underexploited for *in situ* diagnosis and monitoring of cultural heritage, particularly during restoration interventions.

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