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Effects Induced in Marbles by Water-Repellent Compounds: the NMR Contribution

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Abstract. The purpose of this paper is to investigate nuclear magnetic resonance (NMR) applications to porous materials widely employed in artistic and historical monuments and largely studied in the Cultural Heritage conservation field, with the aim of studying structural variations induced in the porous matrix by the application of strengthening and water-repellent agents. Carrara marble and Candoglia marble samples, both in the native state and after treatment, were studied and data from relaxation time measurements were compared. Results collected on treated samples are reported and explained in terms of the relation between spin-lattice relaxation time and the structure of the porous materials. Traditional techniques were employed in addition to NMR analysis on marble samples for the evaluation of the preservative performances of three agents generally employed in the restoration yards. Comparative images showing untreated samples with the treated ones were obtained suggesting very useful applications for the determination of treatment effectiveness.

1 Introduction

Nuclear magnetic resonance (NMR) applications on porous structures range over a wide field of systems. Among porous media our interest is devoted to some kind of important lapideous materials extensively employed in historical buildings, statues, monuments and works of art. The study was born from the ever increasing interest for the safeguard of the cultural property and represents a valid contribution in the study of methods devoted to conservation. Water is often the solvent inoculating external agents within the porous structure, thus the study of fluid ingress and diffusion inside natural stones is very important for the stone preservation. Some water vapor is naturally present in porous rocks, but excess water volumes penetrating into the stone via capillary rise or total immersion can degrade the material by changing the pore and throat geometry and distribution thus leading to dangerous effects for the structure resistance. Besides, the crystal formation from liquid phases within porous media is a well-known phenom-

enon that generates an excess of pressure, which produces high mechanical stresses within the pores. Many different chemical agents were and are still tested and applied on lapideous surfaces with the aim of preserving them from water ingress. The compounds employed are generally characterized by rapid polymerization, hydrophobic behavior, high affinity for the lapideous substrate, and chromatic neutrality since any alteration by light exposure must be avoided. Among many other properties that a good preservative should exhibit, the most important is the integration with the stone structure: the thin film formed should allow the perspiration and reproduce the same porosity characteristics of the surroundings. The former qualification is fundamental to avoid that the polymeric film entraps water which diffuses within the porous structure; thermal gradients can cause pressure gradients whose cycles with time can disaggregate the stone, causing a serious damage. Besides this, porosity value alteration is dangerous for the chromatic and bright characteristics of the work of art more than for the structure endurance. The goal of this paper is to show how NMR data can be interpreted and related to data obtained via traditional techniques [1, 2], as scanning electron microscopy (SEM) and energy dispersion X-ray (EDX) analysis, contact angle measurements and capillary rise curves. The employment of portable NMR instruments will make the technique totally nondestructive. Until now, the possibility of repeating different NMR measurements on the same sample, after coating it or artificially ageing, makes the NMR technique very useful to test water ingress and diffusion in the porous matrix. Most important, NMR imaging allows to obtain very detailed maps of the water distribution, thus suggesting the opportunity to nondestructively test the effectiveness of the agents used for treatment.

2 Materials and Methods

The NMR experimental measurements were performed with a Bruker Biospec BMT 70/15 spectrometer equipped with an Avance digital. A superconductive horizontal magnet generating a 7.05 T static field H_0 , with maximum homogeneity in a cylindrical region, 6 cm in length and diameter, was employed. A birdcage radio-frequency coil with a diameter of 15 cm and a length of 60 cm and tuned to 300 MHz for the ¹H resonance was used to irradiate samples. The sample container had a cylindrical volume with a diameter of 6 cm and a length of 6 cm.

NMR relaxation times of water protons entrapped in samples (volume, 5 by 5 by 2 cm; average weight, 130 g) of two marble varieties coming from different Italian regions, Carrara (CR) in the central and Candoglia (CD) in the northern part of Italy were studied. Water proton spin-lattice and spin-spin relaxation data were evaluated to study the effect induced on the stone surfaces by the presence of products commonly employed for restoration. Three compounds were applied: a fluorinated copolymer of vinylidene and esafluoropropene (Fluorophase, FP), a protective compound constituted by alkyl-alcoxy silanic chains (Hydrophase, HP), a strengthener composed by a copolymer of ethyl-acrylate and meta-acrylate (ParaloidB72, B72). The untreated sample will be referred to as NT. The products were applied on the stone surfaces by brush, following standard procedures reported in literature [3]. The carbonate stones examined are composed of calcium carbonate (over 99%), and SEM combined with EDX [4] analysis revealed absence of heavy metal impurities: strong interactions with paramagnetic ions can thus be neglected.

Silica and fluorine are elements heavy enough to allow an X-ray analysis, while carbon, hydrogen and oxygen contained in B72 are not observable with EDX. These probe elements allowed the reconstruction of the resin mapping within the matrix and the evaluation of the penetration efficiency. EDX mapping showed that the treatments are mainly superficial: penetration depths lower than 10 μ m were found as shown in Figs. 1 and 2. Such experimental evidence can be explained by the low porosity values of the marble samples and the high molecular-weight values of the employed compounds. Resins lie on the surface and form a thin film that constitutes a discontinuity at the surface level by reducing the affinity for water. Since the effectiveness and appropriateness of a good preservative agent depends on its compatibility with the substrate, porous matrix characteristics like porosity, moisture permeability and elasticity should be preserved. Thus variations induced on the stone surface by the thin layer of a preservative agent should be carefully evaluated before choosing the best fitting compound.

The amount of water absorbed by capillary rise was evaluated by time-repeated sample mass weighing procedures, during the contact with wet filter paper. Capillary rise curves are fundamental to determine the behavior of the porous system with a wet surface. Most important, this method allows testing the water repellency effectiveness of the preservative agents employed. Contact times corresponding to water volumes in contact with the hydrorepellent layer can only be evaluated from capillary rise curves.

Water proton relaxation times acquired on the untreated samples were thus compared with relaxation times obtained on samples which absorbed water to the depth of the layer of a preservative agent. This parameter is correlated with the absorption time length. Variations in sample mass, calculated from the capillary rise curves, are in fact related with water volume increase within the sample, which can be employed for determining the water penetration depth, as long as taking into account the porosity value in the sample volume evaluation. Thus, the values of absorption time lengths were chosen to obtain information on water interacting



Fig. 1. SEM-EDX mapping from silica element on CD marble sample treated with HP.





Fig. 2. SEM-EDX mapping from fluorine on CR marble sample treated with FP.

with stone surface layers where interaction occurs between water spins and resin thin film. The poor signal-to-noise ratio for the examined samples is a lower limit to the observable water signal resulting in very dispersed spin-spin relaxation data. To analyze the influence of preservative agents at the stone-water separation surface, it is necessary to compare relaxation time values from both the untreated sample and the treated one after an absorption time corresponding to the water volume contained within a sample section delimited by the thin preservative layer. By assuming the value of $\rho = 10^6$ gm⁻³ for water density and a surface area value of $S = 25 \cdot 10^{-4}$ m², the relation that correlates the mass increment Δm with the absorption time via the capillary rise curves can be assumed as depending on the sample porosity φ as follows:

$$\Delta m$$
(absorption time) $\approx (2500 \times \Delta h)/(1 - \varphi),$ (1)

where Δh indicates the level reached by water during absorption. By assuming $\Delta h \approx 10^{-5}$ m, corresponding to the preservative thin layer, as can be evaluated



Fig. 3. Capillary rise curves for CR marble samples: NT, FP-, HP-, and B72-treated.



Fig. 4. Capillary rise curves for CD marble samples: NT, FP-, HP-, and B72-treated.

from SEM pictures, and φ values in the range of 1.6–3.3%, mass variations of 25 mg are expected. Corresponding absorption times are evaluated for each sample from the capillary rise kinetics whose curves are shown in Figs. 3 and 4.

For longer absorption times corresponding to saturation levels the signal would predominantly come from regions in the sample not covered by the resin, which represent the larger part of the sample and are not representatives of the interactions at the separation surface of interest. The treatment effect was thus analyzed for each sample, as a function of the absorption time length. A good preservative solution is supposed to form a thin water-repellent film, a few micrometers thick and a few millimeters deep from the surface of application. The film formation will locally alter the porous geometry with more evident effects on smaller pores and throats. Thus a change in structure-related parameters should be expected [5], as large as the behavior variation shown by the capillary rise curves. This local structure variation induced by the application of the preservative agent can, in principle, be revealed by measuring spin-lattice relaxation times of the water absorbed by treated samples [6, 7]. Traditional techniques employed to test the stone internal geometry and total porosity give more complete information but are not indicative of surface variations eventually induced by the treatment.

3 Results

Information about the microscopic structure of porous media can, in principle, be obtained from measurements of longitudinal or transverse relaxation with experiments conducted on a sample saturated with a single fluid phase. This is accomplished through the representation of the porous structure with a microscopic model and estimating the geometrical parameters through an analysis utilizing the experimental data and the mathematical model for the experimental response [9, 10]. Reported analyses were based on the representation of the porous media as being composed of noninteracting pores of arbitrary shape. The neglect of interpore coupling is however not adequate for describing relaxation in systems characteristic of reservoir rocks, and creating a model is very difficult when the range of porosities is very low as for the studied marbles. Standard inversion recovery (IR) [8] pulse sequence was employed for T_1 measurements. A 180° pulse is followed by the recovery delay the value of which is contained in an appropriate delay list and is varied over the course of the experiment. A one-dimensional (1-D) spectrum is obtained for each value of the delay, and the results are stored in a 2-D data set. The 2-D data set is used by the T_1 calculation routine, which allows determining T_1 for any number of peaks of the 1-D spectrum. Mono-exponential relaxation data were found, related to the pore size distribution and to the interactions between water layers and the confining pore walls.

In principle, transverse relaxation can provide information regarding the porous structures similar to that from longitudinal relaxation. However, the interpretation of these measurements is complicated due to the effects that diffusion through magnetic field gradients has on the observed relaxation.

Transverse magnetization relaxation times were evaluated by the standard CPMG pulse sequence. For nonmonoexponential decays the CPMG echoes envelope is described by the following function:

$$M(t) = \sum M_{2i} \exp(-t/T_{2i}),$$
 (2)

where the M_{2i} coefficients are proportional to the number of pores where water spins relax with the constants T_{2i} .

The magnetization relaxation curves exhibit, as expected, a nonmonoexponential decay, in agreement with NMR theory on porous media: inhomogeneous porous structures are in fact characterized by a wide range of pore dimensions where different water layers relax with different constants of time depending on their position with respect to the pore wall and on the presence and localization

 Table 1. Spin-spin two-component relaxation times for treated and untreated CR and CD marble samples as a function of the absorption time.

Absorption time (min)	Sample (treatment)	Treated sample		Untreated sample	
		T ₂₁ (ms)	T ₂₂ (ms)	T_{21} (ms)	T_{22} (ms)
25	CR (HP)	0.37	123	1.62	961.17
120	CR (FP)	0.21	662	0.08	0.13
480	CR (B72)	0.23	5.04	0.32	1009
36	CD (HP)	0.48	4.60	0.42	15.57
56	CD (B72)	3.27	1160	0.21	0.76
150	CD (FP)	0.19	0.83	0.43	19.21

Absorption time (min)	Sample (treatment) CR (HP)	T_1 (ms) of sample:		
		treated	untreated	
25		607	605	
120	CR (FP)	635	633	
480	CR (B72)	590	682	
36	CD (HP)	631	626	
56	CD (B72)	CD (B72) 607		
150	CD (FP)	616	600	

 Table 2. Spin-lattice relaxation times for treated and untreated CR and CD marble samples as a function of the absorption time.

of eventually present paramagnetic ions which act as enhancing relaxation sinks. Nonmonoexponential fitting curves were chosen to fit experimental data for transversal component of the magnetization.

The IR sequence employed to measure spin-lattice relaxation times with 8 signal averages and 5 s repetition time (TR) gave a monoexponential decay for the longitudinal magnetization besides reduced T_1 values, in agreement with theory and literature [11–13].

Spin-spin relaxation times were measured by application of the CPMG sequence with 8 signal averages, 5 s repetition time and 0.4 ms echo time. Very short T_2 values resulted from multiexponential fit of the curves as shown in Table 1.

Table 2 shows spin-lattice relaxation times for CD and CR marbles for different absorption times as a function of the treatments. Relaxation times of fluids confined in porous media are strictly related to the geometry and the surface composition of the structure [14–16]. The presence of relaxation sinks at the surface of pore grain and the inhomogeneity of pore dimensions even in short ranges cause nonmonoexponential decay of the magnetization and a reduction of the relaxation times. Spin-lattice relaxation behavior of fluids confined within porous media is sensitive to both the pore geometry and the size distributions [17, 18]. Thus T_1 values can be analyzed to obtain information on structure variations.

4 Discussion

Spin-lattice relaxation times depended on the absorption time: increase and decrease of T_1 values was observed for untreated CR and CD marble samples, respectively, by increasing the absorption time. Moreover, for treated samples T_1 deviations with respect to the values of untreated ones are negligible in most of the cases except for samples treated with B72 and for the FP-treated CD. This result completely agrees with data from capillary rise curves: B72, and FP for CD, are the most effective in preventing water entrance, but, as suggested by re-

Sample (treatment)	S/V (g ⁻¹ m ⁻¹)	V (%)	φ (%)	Contact angle (degree)
CD (NT)	21.57	100	2.40	69.7
CD (B72)	8.49	69.7	2.75	79.3
CD (HP)	16.20	73.5	2.85	101
CD (FP)	18.37	64.7	1.60	96.2
CR (NT)	10.28	100	3.20	61.4
CR (B72)	10.50	57.2	3.30	82.5
CR (HP)	9.61	83.8	2.95	85.2
CR (FP)	5.81	53.7	2.30	93.8

Table 3. Normalized surface-to-volume values, total absorbed water volume at saturation level, porosity values and contact angle evaluated for treated and untreated CR and CD marble samples.

laxation times, cause structure alterations not exhibited by other water-repellent resins.

Surface area per unit pore volume (S/V) normalized to the sample mass data are reported in Table 3, with percent water volumes absorbed by capillary rise (V) normalized to the untreated sample value, porosity values (φ) , and contact angle values. Surface area measurements by gas-porosimetry (N₂ adsorption), according to the BET theory [19, 20], were carried out on a surface-area analyzer Coulter SA3100.

Relaxation time results obtained for short contact times are characterized by nonequilibrium effects that cause large variations in T_2 values for both kinds of marbles. Internal magnetic field gradients cause in fact large variations in the relaxation behavior enhanced by the great inhomogeneity of the natural samples.

Images obtained with MR imaging allow nondestructive determination of water ingress and transport within the porous media. Comparative analysis of treated-sample images can thus lead to the evaluation of treatment effectiveness as shown in Figs. 5–7, where different examples are reported to show how NMR imaging can help monitoring the features of water penetration and diffusion within the sample internal volume, thus showing material inhomogeneity without the need of destroying the sample. In particular, Fig. 6 shows a comparison of the CD marble, untreated and FP-treated, where the effectiveness of the polymer to pre-



Fig. 5. Whole sample section of aged CR marble after 10 min water absorption. 500 ms TR, 6.1 ms TE, 8 signal averages. Image matrix, 256 by 256 pixels; field of view, 10.3 by 10.3 cm.

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Fig. 6. CD marble. The top sample surface was FP-treated, with evident hydrorepellent effects. The bottom sample surface was not treated. Both samples reached saturation levels of water absorption. The image was obtained with 1 s TR, 8 ms TE, 16 signal averages; image matrix, 128 by 128 pixels; field of view, 10.3 by 10.3 cm.

vent water absorption is evident, in contrast to the case shown in Fig. 7, where the CR marble sample treated with HP is compared with the corresponding untreated sample, showing, in agreement with data from capillary rise curves, a reduced polymer efficacy. Imaging methods allow nondestructive testing of the polymer efficiencies, since water is absorbed with different kinetics features due to the presence of the preservative agent. The low porosity values of the materials



Fig. 7. CR marble. The comparison of an untreated sample (bottom) with an HP-treated one (top) shows that for long absorption times the thin layer of the preservative agent is not sufficient to prevent or at least reduce water ingress and diffusion within the porous structure. The image was obtained with 1 s TR, 8 ms TE, 16 signal averages; image matrix, 128 by 128 pixels; field of view, 10.3 by 10.3 cm.

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and small pore dimensions allow only little water volume absorption, thus thinner slices of the sample cannot be obtained due to the poor signal-to-noise ratio.

5 Conclusions

Relaxation times of low-porosity materials were obtained and analyzed in the framework of the evaluation of NMR applications in the conservation field of the Cultural Heritage research.

Nonmonoexponential magnetization decay as well as reduced relaxation times were observed according to the porous media theory for the spin-spin relaxation time. Spin-lattice relaxation time variations induced by some of the treatments are attributed to porous structure variations due to the formation of a thin surface layer of resin. Images showing water distribution for short absorption times are also reported to underline feasability of MR imaging in determining water absorption rate and diffusion within the porous matrix. Moreover, images showing comparisons between treated and untreated samples suggest interesting MR imaging applications to test polymer efficacy in preventing water absorption. MR imaging can in fact be employed to nondestructively study the absorption and drying kinetics. While traditional techniques can in fact give a sample characterization in terms of physical-chemical and structural parameters, MR imaging is able to provide the map of the water distribution in the sample volume during absorption and drying processes. MR imaging represents a useful nondestructive method to test the effects induced by the presence of a polymeric resins on the material structure.

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